Food Packaging

Principles and Practice

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CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
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CRC Press
Taylor & Francis Group
6000 Broken Sound Parkway NW, Suite 300
Boca Raton, FL 33487-2742

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Version Date: 2012924

International Standard Book Number-13: 978-1-4398-6242-1 (eBook - PDF)

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Preface to the Third Edition

Although it is only seven years since the second edition was completed, there have been significant developments in food packaging that warrant a third edition. This edition has been substantially rewritten, updated and extended to include the many developments in food packaging that have taken place since the second edition was published.

Having used the second edition as the course notes for workshops attended by nearly 600 people around the world, I have gained a good appreciation of which areas work well and which are in need of greater clarification and/or amplification. All the worked examples have been changed and new examples added where appropriate. As well, all the references have been updated and now number more than 1000, of which almost two-thirds have been published since 2005. There is also a 64% increase in the number of figures.

Biobased packaging has moved to center stage since the second edition was written. Therefore, Chapter 3 has been expanded to reflect this, becoming the longest chapter in the book; it includes a new section on bionanocomposites. The chapters on optical and mechanical properties of plastics, which appeared in the first edition, have, by popular request, been combined with permeability properties to form a new Chapter 4. In Chapter 5, the section on metallization has been expanded to include details of new coating methods to improve the barrier properties of plastic and paper packaging, including atomic layer deposition, which has recently been commercialized. As well, a major new section on the application of nanoclays to improve the barrier properties of plastic packaging has been added. The section in Chapter 5 on heat sealing, together with the section on closures for glass from Chapter 8, has been moved to a new Chapter 10 which also includes fresh sections on closures for plastic and composite containers in addition to recent research on openability and consumer strength and dexterity.

Other changes include a new section on the packaging of vegetable oils (in particular olive oil) and an update on legislative and safety aspects of food packaging in an attempt to do justice to the increasing regulatory and public interest in food contact materials such as BPA and phthalates and the associated issues of estrogenicity and risk assessment. The section on migration from the first edition has been added in abbreviated form to this chapter. The final chapter has been expanded in two key areas to reflect the huge increase in interest and published research in this area since the second edition was written: life cycle assessment (including carbon footprinting) and sustainability.

It would not have been possible to complete this book without assistance, encouragement and helpful advice from a number of people. I would especially like to thank the following: David Clark, Ian Darby, Bruce Gunn, Gary Hodgson, Dr. Robert V. Holland, Professor John M. Krochta, Professor Dong Sun Lee, Dr. Roger D. MacBean, Dr. Pornchai Rachtanapun, Per O. Risman, Elina Rusko, Dr. Kevin C. Spencer, Professor Tetsuya Suzuki, Dr. Noemi Zaritzky and Dr. David A. Zumbrunnen.

Once again, it is a real pleasure to acknowledge the tremendous assistance of my wife, Soozie, who has improved the look of the book by preparing all the artwork and assisting in numerous other ways: thank you so much.

In the expectation that this edition will be as popular as its predecessors, the possibility of a fourth edition is very real. Therefore, expressions of interest are invited from suitably qualified individuals who would like to be considered as coauthors for a fourth edition.

Finally, I would like to thank all those who provided feedback, constructive comments and suggestions for improvements on the second edition. I welcome further comments on this edition (including any errors which may have crept in), which I will be happy to consider in a fourth edition.

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1 Introduction to Food Packaging

1.1 INTRODUCTION

In today's society, packaging is pervasive and essential. It surrounds, enhances and protects the goods we buy, from processing and manufacturing, through handling and storage, to the final consumer. Without packaging, materials handling would be a messy, inefficient and costly exercise and modern consumer marketing would be virtually impossible. The packaging sector represents about 2% of the gross national product (GNP) in developed countries, and about half of all packaging is used to package food.

The historical development of packaging has been well documented elsewhere and will not be described in depth here. However, an appreciation of the origins of packaging materials and knowledge of the early efforts in package development can be both instructive and inspirational and for this reason they are discussed briefly in the appropriate chapters. Suffice it to say that the highly sophisticated packaging industries that characterize modern society today are far removed from the simple packaging activities of earlier times.

Very few books can lay claim to be the first to expound or develop a particular area, and the present work is no exception. An increasing number of books have appeared over the past few years with the words "food" and "packaging" in their titles, and several are listed at the end of this chapter. The whole field of food science and technology has undergone tremendous development over the last 30 years, and this has been reflected in a plethora of books, many of which address quite specific subject areas (Robertson 2009a, b). In addition, there has also been a significant increase in the number of papers dealing with food and packaging published in the scientific literature, and many of them are referenced at the end of the appropriate chapters.

Food packaging lies at the very heart of the modern food industry, and successful food packaging technologists must bring to their professional duties a wide-ranging background drawn from a multitude of disciplines. The interdisciplinary nature of food packaging is evident from the chapter headings in this book. Sufficient material has been included in the text for it to stand alone as a textbook for undergraduate and graduate students who are taking a two-semester course in food packaging. The earlier editions of this book were also widely used in industry, often by those with no formal education in food science and technology. Therefore, brief descriptions of the basic composition and manufacturing processes used for a wide range of foods are included, with an emphasis on those aspects that influence package choice and performance. Key references are given at the end of each chapter so that those who wish to pursue particular aspects in more depth will have some guidance to start them on their way.

1.2 DEFINITIONS

Despite the important and key role that packaging plays, it is often regarded as a necessary evil or an unnecessary cost. Furthermore, in the view of many consumers, packaging is, at best, somewhat superfluous, and, at worst, a serious waste of resources and an environmental menace. Such views arise because the functions that packaging has to perform are either unknown or not considered in full. By the time most consumers come into contact with a package, its job, in many cases, is almost over, and it is perhaps understandable that the view that excessive packaging has been used has gained some credence.

Packaging has been defined as a socio-scientific discipline that operates in society to ensure the delivery of goods to the ultimate consumer of those goods in the best condition intended for their use (Lockhart, 1997). The now-defunct Packaging Institute International (*Glossary of Packaging Terms*, 1988) defined packaging as the enclosure of products, items or packages in a wrapped pouch, bag, box, cup, tray, can, tube, bottle or other container form to perform one or more of the following functions: containment, protection, preservation, communication, utility and performance. If the device or container performed one or more of these functions, it was considered a package.

Other definitions of packaging include a coordinated system of preparing goods for transport, distribution, storage, retailing and end use, a means of ensuring safe delivery to the ultimate consumer in sound condition at optimum cost and a techno-commercial function aimed at optimizing the costs of delivery while maximizing sales (and, hence, profits) (Coles and Kirwan, 2011).

It is important to distinguish between the words “package,” “packaging” and “packing.” The package is the physical entity that contains the product. Packaging was defined in the previous paragraphs and, in addition, it is also a discipline as in “Packaging Technologist.” The verb “packing” can be defined as the enclosing of an individual item (or several items) in a package or container.

A distinction is usually made between the various “levels” of packaging. A primary package is one that is in direct contact with the contained product. It provides the initial, and usually the major, protective barrier. Examples of primary packages include metal cans, paperboard cartons, glass bottles and plastic pouches. It is frequently only the primary package that the consumer purchases at retail outlets. This book will confine itself to a consideration of the primary package.

A secondary package, for example, a corrugated case or box, contains a number of primary packages. It is the physical distribution carrier and is increasingly designed so that it can be used in retail outlets for the display of primary packages, in which case it is referred to as shelf ready. A tertiary package is made up of a number of secondary packages, with the most common example being a stretch-wrapped pallet of corrugated cases. In interstate and international trade, a quaternary package is frequently used to facilitate the handling of tertiary packages. This is generally a metal container up to 40 m in length that can hold many pallets and is intermodal in nature, that is, it can be transferred to or from ships, trains and flatbed trucks by giant cranes. Certain containers are also able to have their temperature, humidity and gas atmosphere controlled; this is necessary in particular situations such as the transportation of frozen foods, chilled meats and fresh fruits and vegetables.

Although the aforementioned definitions cover the basic role and form of packaging, it is necessary to discuss in more detail the functions of packaging and the environments where the package must perform those functions.

1.3 FUNCTIONS OF PACKAGING

Packaging performs a series of disparate tasks: it protects its contents from contamination and spoilage, makes it easier to transport and store goods and provides uniform measuring of contents (Hine, 1995). By allowing brands to be created and standardized, it makes advertising meaningful and large-scale distribution possible. Special kinds of packages with dispensing caps, sprays and other convenience features make products easier to use. Packages serve as symbols of their contents and a way of life and, just as they can very powerfully communicate the satisfaction a product offers, they are equally potent symbols of wastefulness once the product is gone.

Four primary functions of packaging have been identified: containment, protection, convenience and communication. These four functions are interconnected and all must be assessed and considered simultaneously in the package development process.

1.3.1 Containment

This function of packaging is so obvious as to be overlooked by many, but, with the exception of large, discrete products, all other products must be contained before they can be moved from one place to another. The “package,” whether it is a bottle of cola or a bulk cement rail wagon, must contain the product to function successfully. Without containment, product loss and pollution would be widespread.

The containment function of packaging makes a huge contribution to protecting the environment from the myriad of products that are moved from one place to another on numerous occasions each day in any modern society. Faulty packaging (or under-packaging) could result in major pollution of the environment. Even today, the containment function of packaging is not always addressed satisfactorily, as evidenced by the number of packaged foods that leak their contents, especially around the closures and seals.

1.3.2 Protection

This is often regarded as the primary function of the package: to protect its contents from outside environmental influences such as water, water vapor, gases, odors, microorganisms, dust, shocks, vibrations and compressive forces.

For the majority of foods, the protection afforded by the package is an essential part of the preservation process. For example, aseptically packaged milk and fruit juices in paperboard cartons only remain aseptic for as long as the package provides protection. Likewise, vacuum-packaged meat will not achieve its desired shelf life if the package permits O_2 to enter. In general, once the integrity of the package is breached, the product is no longer preserved.

Packaging also protects or conserves much of the energy expended during the production and processing of the product. For example, to produce, transport, sell and store 1 kg of bread requires 15.8 MJ (megajoules) of energy. This energy is required in the form of transport fuel, heat, power and refrigeration in farming and milling the wheat, baking and retailing the bread, and in distributing both the raw materials and the finished product. To manufacture the low density polyethylene (LDPE) bag to package a 1 kg loaf of bread requires 1.4 MJ of energy. This means that each unit of energy in the packaging protects 11 units of energy in the product. While eliminating the packaging might save 1.4 MJ of energy, it would also lead to spoilage of the bread and a consequent waste of 15.8 MJ of energy.

1.3.3 Convenience

Modern industrialized societies have brought about tremendous changes in lifestyles and the packaging industry has had to respond to those changes. Now an ever-increasing number of households are single person, many couples either delay having children or opt not to at all and a greater percentage of women are in the workforce than ever before.

All these changes, as well as other factors such as the trend toward "grazing" (i.e., eating snack-type meals frequently and on the run rather than regular meals), the demand for a wide variety of food and drink at outdoor functions such as sports events, and increased leisure time, have created a demand for greater convenience in household products. Products designed to increase convenience include foods that are preprepared and can be cooked or reheated in a very short time, preferably without removing them from their primary package, and sauces, dressings and condiments that can be applied simply through aerosol or pump-action packages that minimize mess. Thus, packaging plays an important role in meeting the demands of consumers for convenience. Convenient packages promote sales.

Two other aspects of convenience are important in package design. One of these can best be described as the apportionment function of packaging. In this context, the package functions by reducing the output from industrial production to a manageable, desirable "consumer" size. Thus, a vat of wine is "apportioned" into 750 mL bottles; a churn of butter is "apportioned" by packing into 25 g minipats and a batch of ice cream is "apportioned" by filling into 2 L plastic tubs.

Put simply, the large-scale production of products that characterizes modern society could not succeed without the apportionment function of packaging. The relative cheapness of consumer products is largely because of their production on an enormous scale and the resultant savings. But, as the scale of production has increased, so too has the need for effective methods of apportioning the product into consumer-sized dimensions.

For a product that is not entirely consumed when the package is first opened, the package should be resealable and retain the quality of the product until completely used. Furthermore, the package should contain a portion size that is convenient for the intended consumers; a package that contains so much product that it would deteriorate before being completely consumed clearly contains too large a portion.

An associated aspect is the shape (relative proportions) of the primary package with regard to consumer convenience (e.g., easy to hold, open and pour as appropriate) and efficiency in building into secondary and tertiary packages. In the movement of packaged goods in interstate and international trade, it is clearly inefficient to handle each primary package individually. Here, packaging plays another very important role in permitting primary packages to be unitized into secondary packages (e.g., placed inside a corrugated case) and secondary packages to be unitized into a tertiary package (e.g., a stretch-wrapped pallet). This unitizing activity can be carried a stage further to produce a quaternary package (e.g., a container that is loaded with several pallets). If the dimensions of the primary and secondary packages are optimal, then the maximum space available on the pallet can be used. As a consequence of this unitizing function, materials handling is optimized since only a minimal number of discrete packages or loads need to be handled.

1.3.4 COMMUNICATION

There is an old saying that "a package must protect what it sells and sell what it protects." It may be old, but it is still true; a package functions as a "silent salesman" (Judd et al., 1989). The modern methods of consumer marketing would fail were it not for the messages communicated by the package. The ability of consumers to instantly recognize products through distinctive shapes, branding and labeling enables supermarkets to function on a self-service basis. Without this communication function (i.e., if there were only plain packs and standard package sizes), shopping in a supermarket would be a lengthy, frustrating nightmare as consumers attempted to make purchasing decisions without the numerous visual clues provided by the graphics and the distinctive shapes of the packaging.

Other communication functions of the package are equally important. Today, the widespread use of modern scanning equipment at retail checkouts relies on all packages displaying a universal product code (UPC) that can be read accurately and rapidly. Nutritional information on the outside of food packages has become mandatory in many countries. Smart labels that can be read by camera phones are also appearing on packages and these are discussed in Chapter 9.

But it is not only in the supermarket that the communication function of packaging is important. Warehouses and distribution centers would (and sometimes do) become chaotic if secondary and tertiary packages lack labels or carry incomplete details.

When international trade is involved and different languages are spoken, the use of unambiguous, readily understood symbols on the package is imperative. UPCs are also frequently used in warehouses where handheld barcode readers linked to a computer make stocktaking quick and efficient. Today, the use of RFID tags attached to secondary and tertiary packages is revolutionizing the supply chain.

1.4 PACKAGE ENVIRONMENTS

The packaging has to perform its functions in three different environments (Lockhart, 1997). Failure to consider all three environments during package development will result in poorly designed packages, increased costs, consumer complaints and even avoidance or rejection of the product by the customer.

1.4.1 PHYSICAL ENVIRONMENT

This is the environment in which physical damage can be caused to the product. It includes shocks from drops, falls and bumps, damage from vibrations arising from transportation modes including road, rail, sea and air and compression and crushing damage arising from stacking during transportation or storage in warehouses, retail outlets and the home.

1.4.2 AMBIENT ENVIRONMENT

This is the environment that surrounds the package. Damage to the product can be caused as a result of gases (particularly O_2), water and water vapor, light (particularly UV radiation) and temperature, as well as microorganisms (bacteria, fungi, molds, yeasts and viruses) and macro-organisms (rodents, insects, mites and birds) that are ubiquitous in many warehouses and retail outlets. Contaminants in the ambient environment such as exhaust fumes from automobiles and dust and dirt can also find their way into the product unless the package acts as an effective barrier.

1.4.3 HUMAN ENVIRONMENT

This is the environment in which the package interacts with people, and designing packages for this environment requires knowledge of the variability of consumers' capabilities including vision, strength, weakness, dexterity, memory and cognitive behavior. It includes knowledge of the results of human activity such as liability, litigation, legislation and regulation. Because one of the functions of the package is to communicate, it is important that the messages are clearly received by consumers. In addition, the package must contain information required by law such as nutritional content and net weight.

1.5 FUNCTIONS/ENVIRONMENT GRID

The functions of packaging and the environments where the package has to perform can be laid out in a two-way matrix or grid as shown in Figure 1.1 (Lockhart, 1997). Anything that is done in packaging can be classified and located in one or more of the 12 function/environment cells. The grid provides a methodical yet simple way of evaluating the suitability of a particular package design before it is actually adopted and put into use. As well, the grid serves as a useful aid when evaluating existing packaging.

Separate grids can be laid out for distribution packaging analysis, corrugated packaging analysis, legal/regulatory impact or for any mix of package-related concepts that are of interest. In a further refinement of the grid, a third dimension has been suggested to represent the intensity of the interactions in each cell.

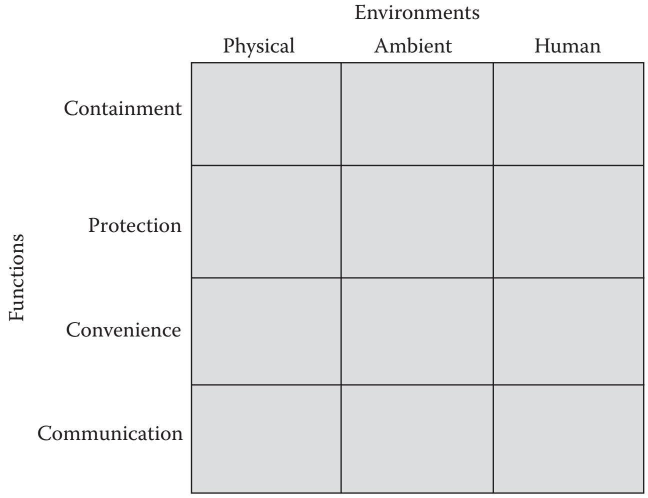

FIGURE 1.1 Functions/environments grid for evaluating package performance. (From Lockhart, H.E., *Packag. Technol. Sci.*, 10, 237, 1997.)

Missing from the grid is an opportunity to evaluate the environmental impacts of the package. This aspect has now become such an important element in package design that it should be considered fully in its own right and in addition to the evaluation carried out using the grid shown in Figure 1.1; it is the subject of the last chapter in this book as part of the broader topic of sustainability.

Knowledge of the functions of packaging and the environments where it has to perform will lead to the optimization of package design and the development of real, cost-effective packaging. Despite the several functions that a package must perform, this book focuses almost exclusively on the protective and containment functions of the primary package and possible food and package interactions in relation to the ambient environment. Package performance in the physical environment is usually considered under the heading of packaging engineering (Hanlon et al., 1998). The communication function of package performance in the human environment is properly the major concern of those with a primary interest in marketing and advertising. For those focusing on the convenience-in-use aspects of packaging, books in the area of consumer ergonomics are the best source of information.

The standard ISO 11156 provides a framework for design and evaluation of packages so that more people, including persons from different cultural and linguistic backgrounds, older persons and persons whose sensory, physical and cognitive functions have been weakened or have allergies, can appropriately identify, handle and use the contents. It considers varying aspects of the packaged product life cycle from identification of the product, through purchase and use of the product to the separation and disposal of the package. However, ISO 11156 does not apply to dimensions, materials, manufacturing methods or evaluation methods of individual packages.

In recent years, greater attention has been given to the difficulties faced by an ageing population in accessing packaging. The openability of packaging is of increasing concern, with a survey of consumers aged over 60 finding that more than 50% of respondents had problems very often or frequently in opening peelable induction seals, lug closures and continuous thread closures (Duizer et al., 2009). If products and their packaging are designed with the weakest target consumer in mind, then the entire target population will be able to physically access the package and product. Yoxall et al. (2010) showed that larger-diameter jars (85 mm) required much higher opening forces than smaller ones (75 mm and below). Smaller jars required lower opening torques, although the force required to open many jars was still higher than many elderly people are able to generate. The authors noted that further work is required to more accurately determine the strength of consumers and the forces required to open common items of food packaging. This topic is discussed further in Chapter 10.

The term “biomechanical data” is used to describe quantities relating to motion, position and force, that is, the movements of a person when interacting with a product and the forces acting on the product during such an interaction. A survey of packaging design professionals revealed that biomechanical data were rarely used and inclusive (or universal) design principles were not routinely incorporated into company procedures (Carse et al., 2010). Although there are some standards and methods provided as a guideline for universal design (UD), it does not reflect packaging requirements for consumers. Yiangkamolsing et al. (2010) identified the five principles relevant to UD as (1) convenient, intuitive, simple and safe use; (2) perceptible information; (3) structure and graphic design; (4) easy opening; and (5) equitable use. For each group of UD performance measures, a minimal but relevant set of consumer requirements were identified for flexible packaging that ensures that the flexible packaging designer conforms to UD principles.

1.6 PACKAGING INNOVATION

Innovation has been defined as invention plus exploitation (Roberts, 2007). The invention process covers all efforts aimed at creating new ideas, concepts, devices or processes and getting them to work. The exploitation process includes all stages of commercial development, application and transfer, including the focusing of ideas or inventions toward specific objectives, evaluating those objectives, downstream transfer of research and/or development results and the eventual broad-based utilization, dissemination and diffusion of the technology-based outcomes. Whereas invention is marked by discovery or a state of new existence (usually in the laboratory or at the bench), innovation is marked by first use in manufacturing or in a market.

The patent literature is full of packaging inventions but fewer than 10% will ever be exploited and, thus, qualify as innovations. The process of technological innovation can take as long as 20–30 years according to some studies, but for most industrial product innovations, the duration from initial idea to market is more likely to be 3–8 years (Roberts, 2007). Awareness of customer needs plays a powerful role in invention and innovation, leading to what is known as "market pull" in contrast to "technological push," which is less likely to be successful. Mostly, innovation is all about small changes that build on inherent flexibility in existing products or systems. Occasionally, something big happens, and a completely new idea is born that can best be described as a mutation rather than an adaptation.

There are several drivers for packaging innovations. One is the fast-changing social trends and the increasing consumer demand for convenience and safety. Another is growing environmental awareness, while profitability and differentiation are also important for food companies seeking to attract consumer attention. Sustainability will receive increasing attention and a plethora of labels such as carbon footprint and paper from sustainably managed forests will indicate how companies are performing in this area. Because consumers want innovation and value novelty, the packaging industry must continue to innovate or risk stagnation.

An interesting way to view innovations is provided by the Gartner hype cycle (Morris, 2011), introduced in 1995 by technology consulting firm Gartner Research. It characterizes the typical progression of an innovation from overenthusiasm through a period of disillusionment to an eventual understanding of the technology's relevance and role in a market (see Figure 1.2). The first part of the hype curve begins with an innovation trigger from a potential technology breakthrough or invention. Early proof-of-concept stories and media interest trigger significant publicity, although often no usable products exist and commercial viability is unproven. This positive hype (mainly by the media and especially the trade press in the case of packaging innovations) speculates on the technology's prospects and is followed by negative hype when the innovation fails to immediately deliver as promised. The message to companies at this stage is not to invest in or adopt a technology just because it is being hyped, nor ignore a technology just because it is not living up to early overexpectations. After a period of disillusionment, an eventual understanding of the technology's relevance and role in a market or domain emerges, driven primarily by performance gains and adoption growth and the release of second- and third-generation products (Fenn and Raskino, 2008). By understanding the hype cycle, it can be ridden more skillfully and investment decisions timed so that the innovations adopted stand the best chance of succeeding in the long term.

However, there have been numerous criticisms of the hype cycle, prominent among which are that it is not a cycle, that the outcome does not depend on the nature of the technology itself, that it is not scientific in nature and that it does not reflect changes over time in the speed at which technology develops. Another is that the cycle has no real benefits to the development or marketing of new technologies and merely comments on preexisting trends. Despite these criticisms, it has remained a popular and useful way for companies to evaluate innovations.

In the area of food packaging, smart packaging is still subject to positive hype, together with biobased polymers such as bioPET and bioHDPE. Antimicrobial packaging is also at this early stage but is unlikely to ever reach the plateau of productivity. Biobased polymers such as PLA and PHA are now experiencing negative hype as more companies trial them. Time–temperature indicators, after more than 40 years, have moved up the slope of enlightenment but are unlikely to ever become more than a niche market. The retort pouch is approaching the plateau of productivity. It is important to remember that the big innovations in food packaging such as MAP and aseptic packaging took 20–30 years before they reached the plateau of productivity.

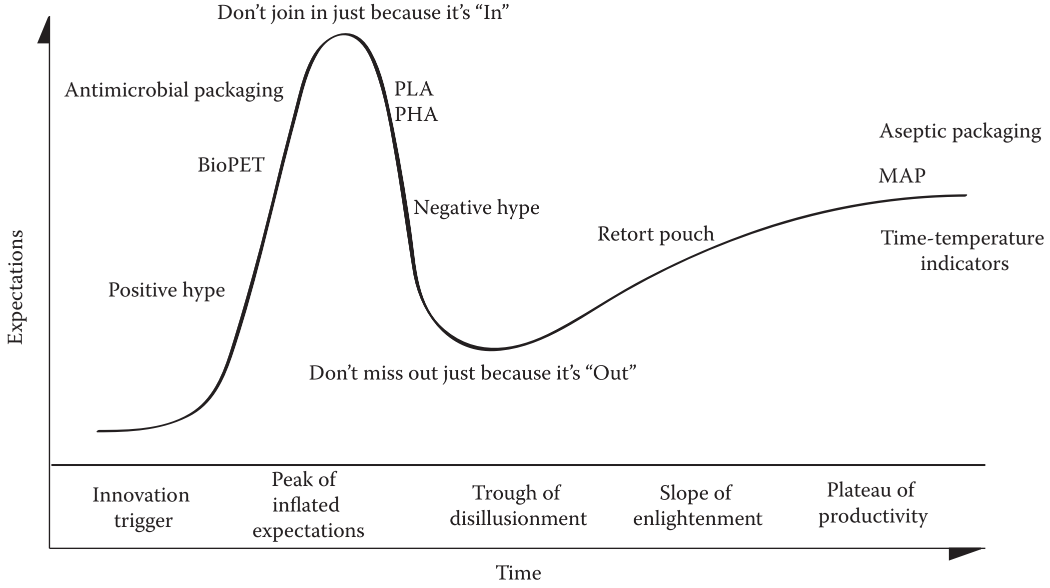

FIGURE 1.2 Gartner hype cycle characterizing the typical progression of an innovation from overenthusiasm through a period of disillusionment to an eventual understanding of the technology's relevance and role in a market or domain. (Adapted from Gartner Inc. Used with permission.)

1.7 FINDING INFORMATION

It has never been simpler to keep up-to-date or find the latest information, provided one has an Internet connection. Although there are various approaches that one can adopt, Google Scholar (www.scholar.google.com) is free and provides a simple way to broadly search for scholarly literature. From one place, you can search across many disciplines and sources: articles, books, theses and abstracts from academic publishers, professional societies, online repositories, universities and other websites. With Google Scholar, you can find relevant work across the world of scholarly research, including where it was published, who it was written by, as well as how often and how recently it has been cited in other scholarly literature.

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2 Structure and Related Properties of Plastic Polymers

2.1 INTRODUCTION

The adjective *plastic* is derived from the Greek *plastikos*, meaning easily shaped or deformed. It was first introduced into the English language in the nineteenth century to describe the behavior of the recently discovered cellulose nitrate that behaved like clay when mixed with solvents. The noun "plastics" is often defined in dictionaries as a group of synthetic resinous or other substances that can be molded into any form. From a technical viewpoint, *plastics* is a generic term for macromolecular organic compounds obtained from molecules with a lower molecular weight (MW) or by chemical alteration of natural macromolecular compounds. At some stage of their manufacture, they can be formed to shape by flow, aided in many cases by heat and pressure. The term plastics can be used as a noun, singular or plural, and as an adjective.

The standard terms used for plastics are defined in ASTM D833. Commonly, the word "plastic" is used to describe the easily deformable state of the material, and the word "plastics" to describe the vast range of materials based on macromolecular organic compounds. This chapter will describe plastics relevant to food packaging, with particular emphasis on their structure and related properties.

The utility of flexible sheet materials depends on the properties of a special kind of molecular structure: long, flexible molecules interlocked into a strong and nonbrittle lattice. These structures are built up by the repeated joining of small basic building blocks called *monomers*, the resulting compound being called a *polymer*, derived from the Greek roots *meros* meaning parts, and *poly* meaning many. Differences in the chemical constitution of the monomers, in the structure of the polymer chains and in the interrelationship of the chains determine the different properties of the various polymeric materials.

2.2 HISTORY

Although the chemical nature of polymers (and the fact that they consist of enormous molecules) was not understood until well into the mid-twentieth century, the materials themselves, and the industry based on them, existed long before that (Andrady and Neal, 2009).

Since plastics include compounds obtained by chemical alteration of natural macromolecular compounds, then the earliest example of a plastics material would have to be hard rubber. In 1839 Charles Goodyear, an American inventor, found that rubber heated with sulfur retained its elasticity over a wider temperature range than the raw material and that it had greater resistance to solvents. The rubber–sulfur reaction was termed "vulcanization." The significance of the discovery of hard rubber lies in the fact that it was the first thermosetting (defined in Section 2.3.1.1) plastics material to be prepared and also the first plastics material that involved a distinct chemical modification of a natural material.

It is generally considered that the development of the plastics industry began in the 1860s. At the International Exhibition of 1862 in London, Alexander Parkes, an English chemist and metallurgist, displayed a new material (which he later modestly called "Parkesine") that he had made by treating cotton waste with a mixture of nitric and sulfuric acids. This was already a well-known process used for making the explosive called guncotton, but Parkes found that by altering the proportions and then mixing the resulting material with castor oil and camphor, the compound could be molded into decorative and useful articles. Unfortunately, the Parkesine Company, which he formed in 1866 to commercialize his process, went bankrupt in less than 2 years. In 1869, a collaborator of Parkes, Daniel Spill, formed the Xylonite Company to process materials similar to Parkesine. Once again, economic failure resulted and the company was wound up in 1874. Undaunted, Spill moved to a new site, established the Daniel Spill Company and continued production of Xylonite and Ivoride.

In the 1860s, Phelan and Collander, a U.S. firm manufacturing ivory billiard balls, offered a prize of $10,000 for a satisfactory substitute for ivory because the decimation of elephant herds had resulted in an enormous increase in the price of ivory. In an attempt to win this prize, the U.S. inventor John Wesley Hyatt solved the technical problems that beset Parkes by using camphor in place of castor oil. Although Hyatt did not win the prize, his product, which he patented with his brother in 1870 under the trademark "Celluloid," was used in the manufacture of objects ranging from dental plates to shirt collars. Despite its flammability and liability to deterioration under the action of light, Celluloid achieved notable commercial success.

Other plastics were gradually introduced over the next few decades. Among them were the first totally synthetic plastics, the family of phenol–formaldehyde resins developed by the Belgian–American chemist Leo Hendrik Baekeland and sold under the trademark "Bakelite." The first of his 119 patents on phenol–formaldehyde plastics was taken out in 1907. Other plastics introduced during this period include modified natural polymers such as rayon, made from cellulose products.

The first hypothesis of the existence of macromolecules was advanced by Kekule in 1877 when he proposed that many natural organic substances consist of very long chains of molecules from which they derive their special properties. The step from the idea of macromolecules to the reality of producing them took the genius of the German chemist Hermann Staudinger, who in 1924 proposed linear structures for polystyrene (PS) and natural rubber. In 1920 he had hypothesized that plastics were truly giant molecules or, as he called them, "macromolecules." His subsequent efforts to prove this claim initiated an outburst of scientific investigation that resulted in major breakthroughs in the chemistry of plastics and the introduction of large numbers of new products such as cellulose acetate and poly(vinyl chloride) (PVC) in 1927 and urea–formaldehyde resins in 1929. Staudinger was awarded the Nobel Prize for chemistry in 1953 for his efforts in establishing the new polymer science.

Further developments occurred in the 1920s, but the years 1930–1940 were probably the most important decade in the history of plastics as today's major thermoplastics (PS, PVC and the polyolefins) were developed. Further developments continue, with special purpose rather than general purpose materials having been discovered in recent years.

Although the possibility of discovering dramatically new polymers is remote, the plastics industry continues to grow, despite a serious check to growth following the oil crisis of the 1970s. Current global annual consumption of plastics is about 250 million tonnes, which requires about 8% of world oil production; ~30% of these plastics are used for packaging. With modern society so dependent on plastics, and the food industry a major user of plastics packaging materials, continued research and development will provide new combinations of established plastics materials to perform specific functions in more efficient and cost-effective ways. In order to become more sustainable, some plastics are now being manufactured from biobased materials, for example, biopolyethylene from sugar cane. This is discussed further in Sections 3.3.6.2 and 3.3.6.3.

2.3 FACTORS INFLUENCING POLYMER STRUCTURES AND RELATED PROPERTIES

The properties of plastics are determined by the chemical and physical nature of the polymers used in their manufacture; the properties of polymers are determined by their molecular structure, MW, degree of crystallinity and chemical composition. These factors in turn affect the density of the polymers and the temperatures at which they undergo physical transitions. The discussion that follows is necessarily brief, and readers are referred to such standard textbooks on polymer chemistry as Sperling (2006), Cowie (2007), van Krevelen and te Nijenhuis (2009) and Carraher (2010) for more detailed treatments.

2.3.1 MOLECULAR STRUCTURE

2.3.1.1 Classification of Polymers

Polymers are molecular materials with the unique characteristic that each molecule is either a long chain or a network of repeating units. This can best be understood by considering polyethylene (commonly referred to as polythene), which is one of the simplest polymers and most common food packaging film. A polyethylene (PE) molecule is built up by joining together many molecules of the monomer ethylene (C_2H_4), as indicated in Figure 2.1.

In terms of chemical composition, there are two broad types of polymers—homopolymers and heteropolymers. The former have the same repeating building-block unit throughout their molecules; the latter are polymers with two or more different building-block units regularly or irregularly distributed throughout their length. Heteropolymers are referred to as copolymers when two different monomers are polymerized together and terpolymers when three monomers are used.

Polymers such as the PE used as an example in Figure 2.1 are called linear polymers and consist of a backbone of carbon atoms and a number of side groups that differ from polymer to polymer. An alternative way of describing a linear polymer is shown in Figure 2.2a, in which it is pictured as a covalently bonded chain of monomer units. Linear copolymers may exhibit any of three combinational forms (Figure 2.2b through d). One is the form of a regular copolymer, in which two different repeating units occur alternately along the chain. It is actually equivalent to a homopolymer in terms of regularity. Another form is that of the random copolymer, in which, during polymerization, the units have taken up a statistically random placement along the length of the chain. The third type of structure is, in a sense, a combination of the previous two: it is the block copolymer, which is composed of alternating lengths of homopolymer along the molecular chains. Figure 2.2 shows two types of backbone units in the structure, although in practice there may be more than two.

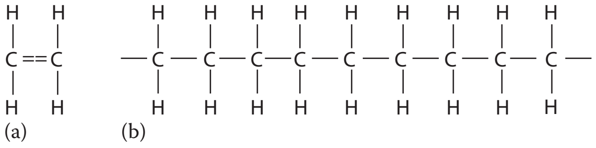


FIGURE 2.1 (a) The monomer ethylene and (b) the polymer PE.

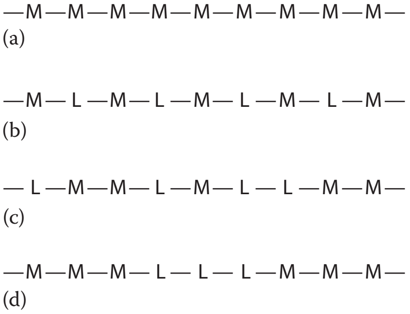


FIGURE 2.2 Copolymers made with different structures. L and M are any monomers. (a) Linear polymer, (b) alternating copolymer, (c) random copolymer and (d) block copolymer.

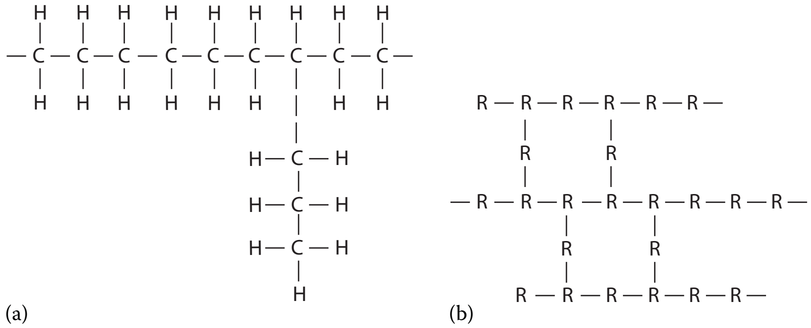


FIGURE 2.3 (a) Branched PE and (b) cross-linked polymer.

Branched PE is shown in Figure 2.3a, while Figure 2.3b shows a cross-linked polymer in which the long chains are connected together, often by relatively short cross-links.

Thus, plastic polymers can be divided into two broad categories: those polymers that extend in one dimension (i.e., they consist of linear chains), and those polymers that have links between the chains, so that the material is really one giant molecule.

The first group is the linear polymers and they are thermoplastic; that is, they gradually soften with increasing temperature and finally melt because the molecular chains can move independently. They are characterized by extremely long molecules with saturated carbon–carbon backbones. Such polymers may be readily molded or extruded because of the absence of cross-links. If their temperature is raised, they become very flexible and can be molded into shape, even at temperatures below their melting point. Not surprisingly, their mechanical properties are rather temperature sensitive. Thermoplastics are the most important class of plastics material available commercially, and account for more than two-thirds of all polymers used in the world today.

The second group is the cross-linked polymers and they are thermosetting. As the name suggests, these polymers become set into a given network when manufactured and cannot be subsequently remolded to a new shape. If the temperature is raised to the point where the cross-links are broken, then irreversible chemical processes also occur that destroy the useful properties of the plastic. This is called degradation. At normal temperatures, the cross-links make the solid quite rigid. Thermosetting polymers do not melt on heating but finally blister (due to the release of gases) and char. Examples of thermosetting plastics are epoxy resins and unsaturated polyesters.

The aforementioned categorization of polymers is convenient since polymers in the two groups differ in their structure, their properties and the chemical processes used in their manufacture. The importance of thermosetting polymers in food packaging is minimal except for epoxy resins that find use as enamels (lacquers) for metal cans.

2.3.1.2 Polymerization Processes

Thermoplastics can be made by joining together a sequence of monomers. Under suitable conditions of temperature and pressure, and in the presence of a catalyst called an initiator, the molecular chains grow by the addition of monomer molecules one by one to the ends of the chains. Branching can occur but cross-links are nearly absent.

The formation of thermoplastics by a process that involves the joining together of monomers to form polymers that have the same atoms as the monomers in their repeating units is called *addition polymerization*. A simple, low MW molecule (which must possess a double bond) is induced to break the double bond and the resulting free valences are able to join up to other similar molecules. This reaction occurs in the form of a chain addition process with initiation, propagation and termination steps.

Under normal conditions with the usual catalysts, the spatial arrangements of the branches of the polymers are random; such polymers are called *atactic*. Some processes give products in which the branches are arranged in an orderly manner; these are called *isotactic* polymers. In the case of PE, this form of polymerization has the advantage of reducing the number of branches that are formed. Thus, the molecules in linear isotactic PE can line up with one another very easily, yielding a tough, high density compound. Atactic PE is less dense, more flexible than, and not nearly as tough as, the linear polymer, because the molecules are further apart.

Plastic polymers are also prepared by the process of *condensation polymerization* that involves two active sites joining together to form a chemical bond, a small molecule being ejected in the process. In this case, the starting monomers are not identical to those of which the chains are to be composed; the superfluous groups of atoms must be ejected when the monomer is added to the end of the chain. If there are enough groups of such superfluous atoms on each monomer molecule, some of them may be temporarily retained on the side of the chain as it grows. This promotes easy branching and leads rather rapidly to a highly cross-linked structure.

It follows that if monomers with few superfluous groups are used, cross-linking does not occur so that thermoplastic materials may also be made by the process of condensation. Polyesters and polyamides (PAs) (see Sections 2.3.6.4 and 2.3.6.6) are examples of thermoplastic polymers made by the condensation process. However, it should be noted in passing that a thermoset polyester can be made if one (or both) of the reactant molecules has a double bond and a third compound is added; under these circumstances cross-linking occurs. Epoxy resins (basically condensation products of a dihydroxyphenol and a compound containing an epoxy group) are examples of thermosetting plastics formed by condensation.

To summarize, thermoplastic polymers can be formed either by addition or condensation polymerization, whereas thermosetting plastics are formed only by condensation polymerization. The degree of cross-linking in a polymer may vary over a very wide range, thus blurring the boundary between thermosetting and thermoplastic materials.

2.3.2 MOLECULAR WEIGHT

The average number of repeating units in a single molecule of a polymer is known as the *degree of polymerization* or DP. At DP values of about 10–20, the substance formed is a light oil (paraffin if formed from ethylene). As the DP increases, the substance becomes greasy, then waxy and, finally, at a DP of about 1000 it becomes a solid and is then a true polymer. The DP is almost unlimited and may increase to around 100,000 or so. Typical properties and applications of straight chain hydrocarbons are presented in Table 2.1 where it can be seen that as the number of carbon atoms in the chain increases, the materials go from gas to liquid to solid.

TABLE 2.1
Typical Properties and Applications of the Alkane/PE Series

Average Number of Carbon Atoms in Chain	Physical State at Room Temperature	Typical Uses
1–4	Gas	Bottle gas for cooking and heating
5–10	Liquid	Gasoline
11–12	Liquid	Kerosene
13–17	Medium-viscosity liquid	Diesel fuel
18–25	High-viscosity liquid	Oil and grease
26–50	Crystalline solid	Paraffin wax candles
50–1000	Semicrystalline waxy solid	Wax coating of paperboard
1000–5000	Tough plastic solid	Films and bottles
$3–6 \times 10^5$	Fibers	Surgical gloves; bullet-proof vests

Source: Adapted from Carraher, C.E., *Introduction to Polymer Chemistry,* 2nd edn., CRC Press, Boca Raton, FL, p. 24, 2010.

From knowledge of the atomic mass of the repeating unit and the DP, the MW of the polymer molecule can be calculated; it is equal to the DP multiplied by the MW of the monomer. Thus, PE with a DP of 10,000 would have a MW of 280,000 since the MW of the repeating unit [$–CH_2CH_2$] is 28. In the case of copolymers, it is necessary to know not only the MW but also the relative proportions and arrangement of the two structural units in the chain.

In practically all industrial polymerization processes, the molecular chains that are produced vary considerably in dimensions. For this reason, the MW of a polymer is actually a distribution of MWs. Hence, a polymer system has to be characterized in terms of average MW and broadness or molecular weight distribution (MWD).

Two average MWs are commonly employed: the number-average MW (M_n) and the weight-average MW (M_w). If the polymer molecules are averaged in terms of number fractions of various lengths, the M_n is obtained. Most thermodynamic properties are related to the number of particles present and are, thus, dependent on M_n. M_n values are independent of molecular size and are highly sensitive to small molecules present in the mixture. However, many bulk properties such as viscosity and toughness depend as much on the size of the molecules as on their number. In this case, the appropriate function is the M_w, which is more dependent on the number of heavier molecules than M_n.

As the MWD becomes increasingly broad, the weight average assumes numerically larger values than the number average, so that the ratio M_w:M_n (known as the *dispersity index* [DI]) is taken as a measure of the spread of molecular chain lengths. For most commercial polymers, DI falls between 2 and 8.

2.3.3 DENSITY

Density is a function of chemical composition, being dependent on the weight of individual molecules and the way they pack together. The hydrocarbon polymers do not possess heavy atoms, and, therefore, the mass of the molecule per unit volume is rather low. Oxygen, chlorine, fluorine and bromine increase the density of polymers. For example, amorphous hydrocarbon polymers generally have densities of 0.86–1.05 g cm^{-3}, while polymers containing chlorine have densities of 1.4 in the case of PVC and 1.7 for PVdC (poly(vinylidene chloride)).

2.3.4 CRYSTALLINITY

When a low MW material such as a metal crystallizes from the molten state, nucleation occurs at various points, from each of which a crystal or grain grows. Likewise, when a molten crystallizable polymer is cooled, crystallization spreads out from individual nuclei. However, instead of individual grains, a considerably more complex structure develops from each nucleus.

The degree of crystallinity is an important factor affecting polymer properties. The great length of polymer chains means that a certain amount of entanglement normally occurs and this prevents complete crystallization on cooling as in the case of metals. This phenomenon is due to the difficulty of aligning every portion of each chain of the polymer. Thus, crystallinity in plastics consists of thousands of small “islands” of *crystalline* regions surrounded by unordered or *amorphous* (without structure) material, as shown in Figure 2.4.

Figure 2.4 depicts in diagrammatic form the amorphous and crystalline regions of a semicrystalline polymer. The crystalline region has an orderly arrangement of molecules as the chains are parallel and closely packed, whereas in the amorphous region, the molecular chains are disordered and without structure. The crystalline areas are known as *crystallites*. Unlike crystals of small molecules, crystallites are not composed of whole molecules or molecules of uniform size. High MW, narrow MWD and linearity in the polymer backbone can yield high crystallinity. The crystallization rate is enhanced by the presence of impurities such as catalysts, fillers and pigments.

In crystalline polymers, the degree of crystallinity is normally limited and the crystallites are separated by amorphous supercooled regions. Thus, PE, which crystallizes readily because of its

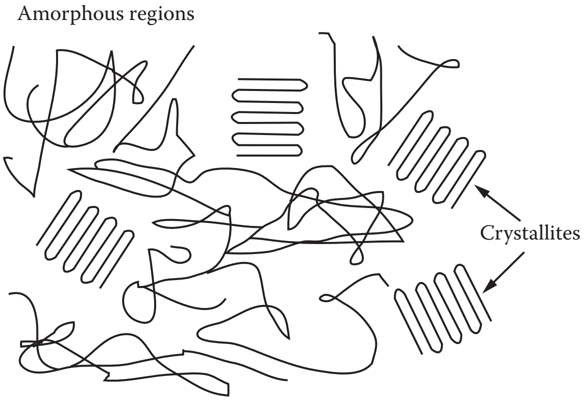


FIGURE 2.4 Schematic diagram of the amorphous (unordered) and crystalline (ordered) regions of a semicrystalline polymer.

rather simple molecular structure, is tough and flexible rather than brittle because of the presence of the amorphous fraction. Of course, the ultimate strength depends as much on the weaker, amorphous part of the solid as on the strength of the crystallites. PVC, on the other hand, does not crystallize so readily and is more of a supercooled liquid.

The presence of chain branching will tend to reduce the possibility of an ordered arrangement and so reduce the crystallinity. For example, the crystallinity of LDPE (low density polyethylene) usually varies between 55% and 70%, compared with 75%–90% for HDPE (high density polyethylene).

Stretching a film orients the crystallites and realigns other molecules or segments of molecules, causing the total crystallinity of the film to increase. Such oriented films are generally tougher than either amorphous or unoriented crystalline materials. Orientation (see Section 5.7.1) and crystallinity are related in that only polymers that are capable of crystallization can be oriented. During orientation, crystallites become aligned and the total amount of crystalline material increases. The crystallites disappear when the polymer is heated, and the temperature at which crystalline regions vanish is called the crystalline melting point. Noncrystalline, amorphous polymers have no melting point. They simply soften when heated, in much the same way as glass. To summarize, high shear during processing and rapid cooling inhibit crystallinity; annealing and orientation enhance it.

Transparency of unfilled plastics is a function of crystallinity, with noncrystalline polymers such as PS and PC (polycarbonate) having excellent transparency. Other polymers range from cloudy to opaque, depending on the degree of crystallinity, the size of spherulites or other forms of crystal aggregates and the ratio of the density between the crystalline phase and the amorphous phase. Thus, relatively thick films of PE are translucent because of the presence of crystals. Long-chain, highly branched LDPE has low crystallinity and a broad melting point and LDPE blown films have very low haze and high gloss; HDPE chains are largely devoid of branching and so can be crystallized to a greater extent, resulting in translucent films.

2.3.5 Physical Transitions in Polymers

Simple molecules such as water can exist in any one of the three fundamental physical states; that is, solid, liquid and gas, according to the ambient conditions. The change from one state to another (transition) occurs at a specific, sharply defined temperature depending on the atmospheric pressure. In polymers, changes of state are less well defined. There is no transition from the liquid to the gaseous state because the temperature required to completely separate the molecules from one another is far too high; decomposition occurs instead. To date, there is no universally accepted scheme for classifying transitions in polymers, partly due to the diversity of experimental methods used for the study of these phenomena and partly to their complex nature.

Noncrystalline (amorphous) polymers are characterized by a glass transition at a temperature called the *glass transition temperature* (T_g); crystalline polymers are characterized by a melting transition at a temperature called the *crystalline melting temperature* (T_m). T_m and T_g are important parameters that define the upper and lower temperature limits for numerous applications, especially for semicrystalline polymers.

At a sufficiently high temperature, a thermoplastic polymer is a liquid. In this state, it consists of an amorphous mass of wriggling molecular chains. As it is cooled, the thermal agitation decreases, and, at the T_m, the polymer may crystallize. In the crystalline state, the molecules are all aligned and are packed together in a regular fashion. However, this state is not easily achieved because the molecular chains are normally entangled with each other. Therefore, many polymers will crystallize so slowly that supercooling is readily achieved. (Supercooling occurs when a material remains liquid below the temperature at which the crystalline solid melts.) These supercooled polymers remain viscous until a still lower temperature is reached at which the material vitrifies; that is, it becomes a glassy and relatively brittle solid. The temperature at which this occurs is the T_g. In the glassy state, a polymer has physical properties similar to a crystalline solid but has the molecular disorder of a liquid. T_g describes the approximate temperature below which segmental rigidity (i.e., loss of rotational and translational motion) sets in. Although a single value is often cited, in reality, a polymer undergoes the transition over a range of temperatures.

T_g is the main transition temperature found in amorphous polymers. The underlying molecular process is that frozen backbone sequences begin to move at the T_g. Therefore, T_g is determined not only by the main chain architecture but also by its immediate surroundings. Chain ends and low-MW plasticizers lower the T_g of a polymer; a sufficiently large number of cross-links will increase T_g. Above T_g, a few of the carbon atoms in each chain can still move with relative freedom, but below T_g, nearly all the carbon atoms become fixed, and only side groups or very short chain sections can change position.

In linear amorphous polymers such as PS, two transition temperatures are observed: a rigid solid-rubber transition known as the T_g and a very indefinite rubber-liquid transition referred to as the flow temperature, the term melting point being reserved strictly for crystalline polymers. The term *softening point* is associated with T_g for amorphous polymers and with T_m for highly crystalline polymers. In addition, there are many polymers that soften progressively between T_g and T_m, and the value determined for the softening point depends very considerably on the test method used. While melting is something that happens to a crystalline polymer, the glass transition happens only to polymers in the amorphous state. However, a given polymer will often have both amorphous and crystalline domains within it, so the same sample can show a T_m and a T_g, but the chains that melt are not the chains that undergo the glass transition.

The structure of crystalline polymers such as PE and isotactic PP is sufficiently regular so that they are capable of some degree of crystallization. The presence of crystalline regions in a polymer has large effects on such properties as density, stiffness and clarity. In a highly crystalline polymer, there is little difference in properties immediately above and below the glass transition. In fact, finding T_g can prove difficult with some highly crystalline polymers. This is largely because there is little scope for segmented motion as most segments are involved in a lattice formation in which they have low mobility.

For crystalline polymers, an approximate relationship between T_g and T_m is

$$T_g \approx \frac{2}{3} T_m \quad \text{(for unsymmetrical chains)} \tag{2.1}$$

and

$$T_g \approx \frac{1}{2} T_m \quad \text{(for symmetrical chains)} \tag{2.2}$$

when both temperatures are expressed in Kelvin. An important exception to this occurs with copolymers. Copolymerization also tends to broaden the temperature range over which T_g occurs, due to differences in chemical composition among the copolymer chains in the same sample. Generally, the crystalline copolymer is expected to have a lower melting temperature than the corresponding homopolymer. Ordered copolymers exhibit different transition behavior from random copolymers, generally showing a single, characteristic T_g and, if crystallizable, a single, sharp melting temperature.

The physical properties of a thermoplastic polymer depend on the values of T_m and T_g relative to room temperature. If both T_m and T_g lie below room temperature, the polymer is a liquid. If room temperature lies between T_m and T_g, the polymer is either a very viscous supercooled liquid or a crystalline solid. If both T_m and T_g are above room temperature, an amorphous polymer is glassy in nature, tending to be brittle. Other properties such as stiffness (modulus), refractive index, dielectric properties, gas permeability and heat capacity all change at T_g (Carraher, 2010).

The glass transition temperatures of the majority of the commercially important crystallizable polymers lie below 25°C as shown in Table 2.2, which also lists values for T_m and T_m/T_g. The T_g values are low for flexible, linear polymers such as the PEs, and relatively high for stiff chain polymers such as PET (poly(ethylene terephthalate)) and PC, which require higher temperatures for the onset of molecular motions necessary for the glass transitions.

Bulky side groups decrease the mobility of the chain and, thus, raise T_g. For instance, substitution of alternate hydrogens in the PE with methyl groups to give PP, or with phenyl groups to give PS, increases T_g from −110°C to −18°C and +100°C, respectively. Molecular symmetry tends to lower T_g. For instance, PVC has a T_g of 87°C, whereas for PVdC the T_g is −17°C.

Because bulky side groups tend to restrict molecular rotation, they also raise T_m. For example, the CH_3 side groups on PP are larger than the H atoms found on LDPE, and, therefore, the T_ms are 176°C and 115°C, respectively. The presence of polar side groups such as Cl, OH and CN,

TABLE 2.2
Glass Transition and Melting Temperatures of Some Polymers

Polymer	T_g (°C)	T_m (°C)	T_m/T_g[a]
Polyethylene			
Low density	−110	115	2.38
High density	−90	137	2.24
Polypropylene	−18	176	1.76
Poly(ethylene terephthalate)	69	265	1.57
Poly(ethylene naphthalate)	120	265	1.37
Polystyrene (isotactic)	100	240	1.38
Poly(vinyl chloride)	87	212	1.34
Poly(vinylidene chloride)	−17	202	1.86
Polyacrylonitrile	104	317	1.56
Poly(11-aminoundecanoic acid) (nylon-11)	51	185	1.41
Poly(caprolactam) (nylon-6)	47	220	1.54
Poly(hexamethylene adipamide) (nylon-6,6)	57	265	1.49
Poly(hexamethylene sebacamide) (nylon-6,10)	40	277	1.59
Poly(tetrafluoroethylene)	126	327	1.50
Poly(ethylene-co-vinyl alcohol) 29%	62	188	1.38
Poly(ethylene-co-vinyl alcohol) 44%	55	164	1.33
Polycarbonate	150	265	1.16

[a] Ratio calculated from T_m and T_g temperatures in Kelvin.

even though not excessively large, leads to significant intermolecular bonding forces and relatively high T_ms. For instance, the T_m for PVC is 212°C and for PAN (poly(acrylonitrile)) 317°C.

The temperatures T_m and T_g are governed by the strength of the intermolecular forces (just as in inorganic materials) and by the degree of flexibility and length of the chains. Thus, polar side groups such as chloride and hydroxyl groups favor higher melting and glass transition temperatures because they enhance the strength of the intermolecular bonds.

In some cases, the T_g can be lowered by as much as 100° by the efficient use of plasticizers. For example, pure PVC has a T_g of 87°C and is quite brittle at room temperature. The addition of only 15% plasticizer lowers this to 60°C, and with the addition of further plasticizer, PVC becomes tough and flexible at room temperature.

2.3.6 CHEMICAL STRUCTURE

Polymer chains can and do align themselves in ordered structures, and the thermodynamics of this ordered state determines such properties as the melting point, the glass transition temperature, other transition temperatures and the mechanical and electrical properties. However, it is the chemical nature of the polymer that determines its stability to temperature, light, water and solvents.

In the published literature, it is rare to find many details about a particular plastic packaging material apart from its name, sometimes the resin supplier and maybe if it has been oriented. This makes it virtually impossible to replicate the experimental conditions described in the literature since the range of polymers available is vast. For example, the website www.ides.com contains data sheets on over 77,000 commercial polymers from 694 resin manufacturers. Of course, many of these polymers are not approved or suitable for use in food packaging.

2.3.6.1 Polyolefins

Olefin means oil-forming and was originally the name given to ethylene. Today polyolefin is a common term in the plastics industry and refers to the family of plastics based on ethylene and propylene. The term *alkene* is used for hydrocarbons containing a carbon–carbon double bond, for example, ethylene, propylene and octene. The formula, MW, density and boiling point of the alkenes important in food packaging are given in Table 2.3. Polyolefins form an important class of thermoplastics and include low, very low, linear, medium and high density PEs and polypropylene (PP). Industry commonly divides PEs into the following broad categories based on density: HDPE 940–975 kg m^{-3}, MDPE 926–940 kg m^{-3}, LDPE 915–940 kg m^{-3}, LLDPE 915–925 kg m^{-3}, VLDPE 880–915 kg m^{-3}.

2.3.6.1.1 Low Density Polyethylene

This is the largest volume single polymer used in food packaging in both the film and blow molded form. It is a polymer of ethylene, a hydrocarbon gas available in large quantities as a by product of petroleum refining and other processes. Increasing quantities are now also being produced by the catalytic dehydration of ethanol produced by the fermentation of biobased materials, especially sugarcane (Morschbacker, 2009). PE was first produced by Imperial Chemical Industries (ICI) in 1933

TABLE 2.3
Molecular Details and Some Physical Properties of Common Hydrocarbon Monomers

Name	Molecular Formula	Molecular Weight	Density at 15°C (kg m^{-3})	Boiling Point (°C)
Ethylene	C_2H_4	28.05	1.180	−103.7
Propylene	C_3H_6	42.08	1.810	−47.6
Butene-1	C_4H_8	56.11	2.370	−6.3
Hexene-1	C_6H_{12}	84.16	0.678	63
Octene-1	C_8H_{16}	112.24	0.715	121

during a research program devoted to the effects of extremely high pressures on chain reactions, and the basic patent relating to polymerization of ethylene was granted in 1937. It was produced on a pilot plant scale that same year with full commercial-scale production commencing in 1939. For the first few years of its production, it was used in the electrical industry, particularly as an insulating material for underwater cables.

The polymerization of ethylene can occur over a wide range of temperatures and pressures but most commercial high pressure processes utilize pressures between 1000 and 3000 atm and temperatures between 100°C and 350°C (higher temperatures cause degradation of the PE).

The simplest structure for PE is a completely unbranched structure of $-CH_2-$ units as shown in Figure 2.1b. However, the vigorous nature of the high pressure process leads to a great deal of chain branching, with both short and long chains being formed. From Figure 2.3a, it can be seen that the branch contains a terminal methyl ($-CH_3$) group. A convenient way of characterizing branching is by the number of methyl groups per 1000 carbon atoms. Figure 2.5 is a schematic representation of linear and branched polymers of which HDPE short chain branches (SCB) and LDPE with long-chain branches (LCB) are good examples.

The branch chains prevent close packing of the main polymer chains, resulting in the production of PEs of relatively low density (typically 910–940 kg m^{-3}). MWs also tend to be relatively low. The great length of the polymer chains results in a certain amount of entanglement that prevents complete crystallization on cooling. When the polymer melt is cooled slowly, the crystallites may form *spherulites*.

The crystallinity of LDPE usually varies between 55% and 70%. The softening point is also affected by chain branching. The attractive forces between the chains are reduced because they are unable to approach each other closely, and, therefore, less energy (in the form of heat) is necessary to cause them to move relative to each other and thus flow. The softening point of LDPE is just below 100°C, thus precluding the use of steam to sterilize it in certain food packaging applications.

LDPE is a tough, slightly translucent material that can be blow extruded into tubular film, or extruded through a slit die and chill-roll cast, the latter process giving a clearer film. It has good tensile strength, burst strength, impact resistance and tear strength, retaining its strength down to −60°C. While it is an excellent barrier to water and water vapor, it is not a good barrier to gases. One of the great attributes of LDPE is its ability to be fusion welded to itself to give good, tough, liquid-tight seals. It cannot be sealed by high-frequency methods. It has excellent chemical resistance, particularly to acids, alkalis and inorganic solutions, but is sensitive to hydrocarbons, halogenated hydrocarbons, oils and greases. These latter compounds are absorbed by the LDPE, which then swells.

When a polymer is stressed in air to just below its yield point, stress cracking can occur after a certain period of time. However, when simultaneously exposed to both stress and a chemical medium, there is a dramatic reduction in the time to failure. This latter type of failure is termed

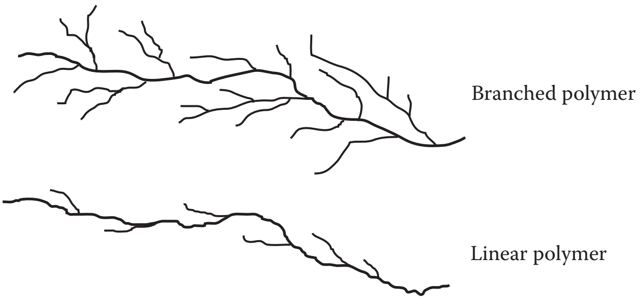


FIGURE 2.5 Schematic representation of branched and linear polymers showing the larger volume swept out by the branched structure, resulting in its lower density. Branches of the main backbone are indicated by narrower lines; they have no direct proportional relationship to cross-sectional dimensions. (From Brown, W.E., *Plastics in Food Packaging: Properties, Design and Fabrication*, Marcel Dekker, New York, p. 106, 1992.)

environmental stress cracking (ESC) and generally manifests itself as surface-initiated cracks or brittle failure (Scheirs, 2000). The stress may be internal (e.g., due to inbuilt molding stress) or external (such as mechanically applied stress). For example, ESC can occur when filled plastic containers are stacked on pallets in a warehouse or during transportation. Although ESC results from the interaction of the polymer with certain chemicals, it is a purely physical mechanism and not a chemical reaction (i.e., not a degradation in the true sense). Interactions between the fluid, the stress and the polymer include local yielding, fluid absorption, plasticization, craze initiation, crack growth and fracture without irreversible chemical change (i.e., without change in MW). The fluid only accelerates the mechanism. ESC is strongly related to the crystallinity of the polymer: the higher the crystallinity, the lower is the ESCR (environmental stress crack resistance). To reduce the crystallinity in polyolefins, comonomers such as butene, hexene, or octene can be used at less than 2%.

Essential oils (a common component of flavorings) and vegetable oils are capable of causing ESC in PEs and PS, and whenever a new flavor is introduced for an existing product, adequate testing must be carried out to ensure that ESC does not result. ASTM D2561 details test methods to measure the ESCR of containers, which is the summation of the influence of container design, resin, blow-molding conditions, posttreatment or other factors that can influence ESC. Three procedures are provided and procedure A can be useful for determining the effect of container design on the ESCR of a blow-molded HDPE package containing a liquid food product. However, any tests have to be correlated with actual field performance to be of practical use. The inability to measure the extent of ESC under controlled laboratory conditions makes it very difficult to understand the role of any one variable, the interaction between variables and the mechanisms of ESC.

PE is one of the most inert polymers and constitutes no hazard in normal handling.

Besides films, LDPE also finds use as a rigid packaging material as it can be easily blow molded into bottles where its flexibility enables the contents to be squeezed out. It is also widely used in the form of snap-on caps, collapsible tubes and a variety of spouts and other dispensers. The surface of PE containers can be treated with fluorine after blow molding to form a very thin, polar, cross-linked surface that decreases the permeability of the PE to nonpolar penetrants. It also eliminates the need for treating the surface by corona-arc discharge or flame techniques (see Section 5.3.1.2) to improve printability properties. The process has been cleared by the U.S. Food and Drug Administration (FDA) for use with food containers.

At the present time, there are many hundreds of grades of LDPE available, most of which differ in their properties in one way or another. Differences arise from the following variables:

1. Variation in the degree of short chain branching in the polymer
2. Variation in the degree of long chain branching
3. Variation in the average MW
4. Variation in the MWD (which may in part depend on the long-chain branching)
5. Presence of small amounts of comonomer residues
6. Presence of impurities or polymerization residues, some of which may be combined with the polymer

2.3.6.1.2 Linear Low Density Polyethylene

The first production of LLDPE was made in a solution process in 1960. Attempts in the 1970s to produce LDPE, either by low pressure gas-phase polymerization or by liquid-phase processes similar to those used for producing HDPE, led to the development of LLDPE and its commercialization in 1977. The term *linear* in LLDPE is used to imply the absence of LCBs. LLDPE has a similar molecular structure to HDPE and although virtually free of LCBs, it does contain numerous short side chains. These arise as a result of copolymerizing ethylene with a small amount of a higher alkene (α-olefin) such as butene. An α-olefin has the chemical formula C_xH_{2x} and a double bond at the primary or alpha (α) position. The general formula for ethylene copolymers with α-olefins is $–CH_2–CHR–$, where R is C_2H_5 in ethylene-1-butene copolymers, n-C_4H_9 in ethylene-1-hexene copolymers and n-C_6H_{13} in ethylene-1-octene copolymers (Kissin, 2005). An increase in α-olefin content results in a decrease in crystallinity and density and a significant reduction of the polymer mechanical modulus (stiffness). Industry convention is not to indicate the presence of a copolymer such as octene in PE if its concentration is less than 10%.

Due to the linearity of its molecules, LLDPE is more crystalline and, therefore, stiffer but less transparent than LDPE, resulting in an increase of 10°C–15°C in the melting point of LLDPE compared to LDPE. The linearity provides strength, while the branching provides toughness. LLDPEs made with hexene and octene have better puncture resistance, impact strength and tear strength, but are more costly relative to LLDPE made with butene comonomer. The crystallinity and, consequently, the density of PE are controlled by the amount and type of α-olefin incorporated into the backbone. Decreasing α-olefin content leads to higher densities. The concentration of α-olefin in a copolymer varies from 1 mol% in MDPE to 2.5–3.5 mol% in LLDPE and 10–15 mol% in VLDPE (Kissin, 2005).

LLDPE combines the main features of both LDPE and HDPE, a major feature being that its MWD is narrower than that of LDPE. Generally, the advantages of LLDPE over LDPE are improved chemical resistance, improved performance at low and high temperatures, higher surface gloss, higher strength at a given density, better heat sealing properties and a greater resistance to ESC. In film form, LLDPE has higher tensile strength, puncture resistance, tear properties and elongation than LDPE. High-clarity film produced with LLDPE manufactured with metallocene catalysts is widely used for food packaging films and blow molding of bottles. The superior properties of LLDPE have led to its use in new applications for PE as well as the replacement of LDPE and HDPE in some areas; LLDPE is also often blended with LDPE.

2.3.6.1.3 Very Low Density Polyethylene

VLDPE (sometimes referred to as ultralow density polyethylene or ULDPE) is a subclass of LLDPE with a density $<915\,\text{kg m}^{-3}$. It has an α-olefin content (normally octene) of >4 mol% and a crystallinity of <25% (Kissin, 2005). In stretch film applications, VLDPE exhibits excellent stretchability as well as good physical and cling properties. VLDPE can also be utilized for the production of blown film requiring a combination of excellent optical properties, outstanding tear and impact strength and very good sealability. VLDPE copolymer is also used as a skin layer in cast film and has excellent low temperature hot tack properties combined with outstanding tear and impact strength. VLDPE can be blended with other PE and PP-based resins to enhance clarity, sealability and toughness of the materials and can be used as a sealant in multilayer film structures. VLDPE also offers greater low temperature flexibility and flex crack resistance. VLDPE is mostly used for the packaging of fresh produce, milk, meat and cheese, as well as for the manufacture of multilayer coextruded film.

2.3.6.1.4 High Density Polyethylene

Prior to 1950, the only commercial polymer of ethylene was the highly branched polymer LDPE. The technique for making a linear polymer was discovered by Nobel laureate Karl Ziegler of Germany in the early 1950s. Ziegler prepared HDPE by polymerizing ethylene at low pressure and ambient temperatures using mixtures of triethylaluminum and titanium tetrachloride. Another Nobel laureate, Giulio Natta of Italy (he shared the Nobel Prize for chemistry with Ziegler in 1963), used these complex coordination catalysts to produce crystalline PP; these are now known as Ziegler–Natta (Z–N) catalysts. However, the credit for first producing stereospecific olefin polymers and HDPE belongs to J. Paul Hogan and Robert Banks of Phillips Petroleum Company, who did so in 1952 using chromium trioxide supported on a silica-alumina catalyst (Carraher, 2010).

HDPE is a nonpolar, linear thermoplastic that possesses a much more linear structure than LDPE. It has up to 90% crystallinity, whereas LDPE exhibits crystallinities as low as 50%. Although some branch chains are formed, these are short and few in number. HDPE film is stiffer and harder than LDPE and densities range from 940 to $975\,\text{kg m}^{-3}$. Because HDPE contains a crystalline phase and an amorphous phase, the measured density directly reflects the percentage of each. Typical homopolymer is normally 70% crystalline and has a density of 960–965 kg m^{-3}. Higher densities can be achieved by low MW and slow cooling. The MW of typical commercial HDPE grades can vary from 20,000 to >3,000,000, depending on the application. Its softening point is about 121°C, and its low temperature resistance is about the same as LDPE. Tensile and bursting strengths are higher but impact and tear strengths are both lower than LDPE. Of interest is the fact that due to the linear nature of the HDPE molecules, they tend to align themselves in the direction of flow and, thus, the tear strength of the film is much lower in the machine direction (MD) than the transverse direction (TD). This difference can be accentuated by orientation to give a built-in tear tape effect.

The chemical resistance of HDPE is also superior to that of LDPE and, in particular, it has better resistance to oils and greases. The film offers excellent moisture protection, a much decreased gas permeability compared with LDPE film, but is much more opaque. Heat sealing is considerably more difficult compared to LDPE film. The melting point is a function of both MW and branch content. A decrease in MW from ~1,000,000 to 40,000 is accompanied by a decrease in melting point from 137°C to 128°C.

HDPE film has a white, translucent appearance and, therefore, tends to compete more with paper than transparent films. To be competitive with paper on a price-per-unit-area basis, it must be thin, and, consequently, much of the HDPE film used is only 10–12 µm thick.

HDPE is blow molded into bottles for a variety of food packaging applications, although its uses in this area have tended to be taken up by PET bottles that generally have better barrier properties than HDPE.

The basic properties of various PE films are shown in Table 2.4. The melting point of PEs is primarily a function of their densities, the melting point increasing with density, as does the softening temperature.

2.3.6.1.5 Irradiated Polyethylene

Irradiated PE is produced by passing ordinary LDPE film continuously under an electron beam accelerator that produces high-energy ß rays. This converts it to an infusible film, which causes cross-linking between the chains and gives it exceptional strength from the point of view of stretch resistance and shrink tension. Other effects include the evolution of H_2 and a reduction in crystallinity. The process slightly reduces gas and water vapor transmission rates but increases the heat sealing range to make a practical shrink film from PE. The film has good clarity. It is sealed by welding the overlaps together on a hot plate and shrunk by passing through a hot air tunnel at 220°C.

2.3.6.1.6 Polypropylene

Early attempts to polymerize propylene using the high pressure process used to make LDPE gave only oily liquids or rubbery solids of no commercial value. Work by Natta in Italy using Ziegler-type catalysts led to the development in 1954 of a stereospecific catalyst that controlled the position of each monomer unit as it was added to the growing chain, thus giving a polymer of regular structure. Today, typical processes take place at about 100 atm and 60°C. A significant innovation in PP

TABLE 2.4
Basic Properties of Various PE Films

Type of Polyethylene	Water Vapor Transmission	Gas Transmission O_2	Gas Transmission CO_2	Tensile Strength (MPa)	Softening Point (°C)	CH_3 Groups per 1000 C's
Low density (920 kg m^{-3})	1.4	500	1350	9–15	120–180	20–33
Medium density (940 kg m^{-3})	0.6	225	500	21	120–180	5–7
High density (960 kg m^{-3})	0.3	125	350	28	135–180	<1.5

production has been the Spherizone process technology, which is based on a multizone circulating reactor (MZCR). In comparison to traditional multistep technologies, the MZCR provides a step change in the polymer homogeneity of the final product by continuously circulating the growing polymeric granules between two interrelated zones where different gas phase compositions are realized (Mei et al., 2009). The Spherizone process can produce all conventional PP grades as well as new and improved products including highly modified random copolymers. In addition to traditional Z–N catalysts, metallocene catalysts are also being introduced in PP manufacture (see next section).

PP is a linear polymer containing little or no unsaturation. Depending on the type of catalyst and polymerization conditions, the molecular structure of the resulting polymer consists of the three different types of stereo configurations: *isotactic*, *syndiotactic* and *atactic*, as shown in Figure 2.6. Industrial processes are designed to minimize the production of atactic PP (where the methyl groups are randomly distributed on either side of the chain), which results when polymerization occurs in the absence of stereospecific catalysts. This noncrystalline material has a density of about 850 kg m^{-3} and is soft, tacky and soluble in many solvents. It is a lower-value product and finds use mainly in hot-melt adhesives.

The most regular crystalline polymer produced by stereospecific catalysts is known as the isotactic form, the name stemming from the original idea that the methyl groups were always above or below the horizontal plane. Isotactic PP, the most common commercial form of PP homopolymer, is never perfectly stereoregular, the degree of isotacticity varying from 88% to 97%. It is a highly crystalline material with good chemical and heat resistance but poor transparency. Two other forms are syndiotactic, where the methyl groups alternate above and below the horizontal plane, and stereoblock, where blocks of methyl groups are alternately above and below the horizontal plane. The regular helices of the isotactic form can pack closely together, whereas the atactic molecules have a more random arrangement.

While atactic PP is an amorphous, rubbery material of little value, isotactic PP is stiff, highly crystalline and has a high melting point. In commercial polymers, the greater the amount of isotactic material, the greater is the crystallinity and, thus, the greater the softening point, tensile strength and hardness, all other structural features being equal (Carraher, 2010). Impact-resistant PP is a mixture of isotactic PP and amorphous ethylene–propylene copolymer.

PP has a lower density (900 kg m^{-3}) and a higher softening point (140°C–150°C) than the PEs, low water vapor transmission, medium gas permeability, good resistance to greases and chemicals, good abrasion resistance, high temperature stability, good gloss and high clarity, with the latter two factors making it ideal for reverse printing.

PP can be blow molded and injection molded, the latter process being widely used to produce closures for HDPE, PET and glass bottles, as well as thin-walled pots and crates. The T_g of PP is placed between 10°C and −20°C with the result that the polymer can become brittle as subzero

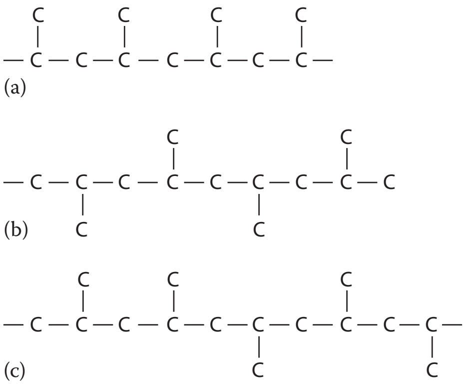


FIGURE 2.6 Types of PP: (a) isotactic, (b) syndiotactic and (c) atactic.

temperatures are approached. The T_m is in the range of 160°C–178°C, enabling foods inside PP containers to be sterilized by heat or reheated in microwave ovens. Copolymerization with 4%–15% ethylene improves the strength and clarity, reduces stiffness, increases impact resistance and lowers the T_m and T_g. For example, homopolymer PP with 3%–4% atactic fraction has a T_m of ~165°C, while a random copolymer with 2% ethylene has a T_m of about 150°C. Such copolymers are often preferred to the homopolymer in injection molding and bottle blowing applications and also find use in shrink wrapping where the lower melting point is an advantage.

Although free from ESC problems, PP is more susceptible to oxidative degradation at elevated temperatures, necessitating the inclusion of antioxidants in all commercial PP compounds. Whereas PE cross-links on oxidation, PP degrades to form lower MW products. A similar effect is observed when PP is irradiated.

Nonoriented PP film is often referred to as cast PP film because it is generally made by the chill-roll cast process, although other methods can be used. PP film is a very versatile material, being used as a thermoformable sheet, in cast form for film and bags, and as thin, strong biaxially oriented films for many applications. Cast and oriented PP are sufficiently different that they do not compete for the same end uses, the cost of cast PP being much lower than that of oriented PP. The cast form has PE-type uses while the oriented form has regenerated cellulose film (RCF)-type uses and has largely replaced RCF in food packaging applications. Cast PP use in food packaging is limited owing to its brittleness at below freezing temperatures, and it is generally not recommended for use with heavy, sharp or dense products unless laminated to stronger, more puncture-resistant materials. The relatively high temperature resistance of PP permits its use as the seal layer in retortable pouches, hot-filled bottles and microwavable packaging.

In recent years there has been a large increase in the use of oriented polypropylene (OPP) for food packaging. Wide variations are possible in the extent of orientation in two directions, leading to a wide range of properties. However, biaxially oriented polypropylene (BOPP) film has a high clarity because layering of the crystalline structures reduces the variations in refractive index across the thickness of the film and this in turn reduces the amount of light scattering. OPP can be produced by the blown tubular or high expansion bubble process, or the tenter frame process.

BOPP film has a tensile strength in each direction roughly equal to four times that of cast PP film. Although tear initiation is difficult, tear resistance after initiation is low. Biaxial orientation also improves the moisture barrier properties of PP film and its low-temperature impact strength. OPP film is not considered to be a gas barrier film but this deficiency can be overcome by coating with PVdC copolymer. OPP films often have a stiff feel and tend to audibly crinkle.

If heating sealing is required, PP is normally coated with a lower melting point polymer because shrinkage tends to occur when highly stretched film is heated. LDPE, PVdC copolymer and acrylic polymers are used as fusible coatings for OPP film. LDPE is cheaper, but PVdC copolymer confers far better resistance to water vapor and O_2 permeability; acrylic polymer adds no barrier properties to OPP film.

Another addition to the family of OPP films is white opaque film, generally made by the tenter frame process and known as cavitated or pearlized film because the diffusion of light gives the film the visual effect of pearlescence. Homopolymer resin is evenly mixed with a small amount of foreign particulate matter such as starch or titanium dioxide. In one product, when the thick filled sheet is oriented, the PP pulls away from each particle creating an air-filled void or closed cell. After heat stabilization, the OPP film is similar to a micropore foamed product. In the second product, the material produced is a filled film without voids, the opacity being a direct result of the amount of particulate material included in the film. The primary opacification is caused by light rays bouncing off the PP cell walls and the air within each cell. White opaque OPP film is widely used for cold seals and finds application in snack food packaging, candy-bar overwraps, ice cream novelties, beverage bottle labels, soup wrappers and other applications that have traditionally used specialty paper-based packaging materials (Mount, 2009).

Another new technology exploits the unique combination of properties, including melt strength, of PP grades for use in foam applications. For example, foamed PP food packaging trays are used for meat, fish, poultry, fruits and cheese where the material overcomes the typical expanded polystyrene (EPS) limitations, that is, aromatics release and susceptibility to cracking (Mei et al., 2009).

2.3.6.1.7 Metallocenes

Metallocenes are a relatively old class of organometallic complexes first discovered in 1951. They are based on a metal atom such as titanium, zirconium or hafnium. As early as 1957 Natta reported the (unsuccessful) polymerization of ethylene with a titanocene catalyst. The current interest in metallocenes originated with a discovery by Kaminsky at the University of Hamburg in the mid-1970s. While studying a homogenous polymerization system, water was accidentally introduced into the reactor, leading to an extremely active ethylene polymerization system. Subsequent studies revealed that the high activity was due to the hydrolysis of the cocatalyst trimethyl aluminum. Because of the discovery of this new cocatalyst, metallocenes are sometimes called “Kaminsky” catalysts (Scheirs and Kaminsky, 2000).

Metallocene-based catalyst technology has revolutionized the polyolefin industry, particularly in the PE and PP markets. Metallocenes have been deemed the single-most important development in catalyst technology since the discovery of Z–N catalysts. Compared to conventional Z–N technology, metallocenes offer some significant process advantages and produce polymers with very favorable properties. The development of metallocene polymers has brought forth the concept of single-site catalysis of which metallocenes are just one example, albeit the first commercial success.

Metallocene catalysts allow the production of consistent, controllable molecular polymer structures that can be designed to improve toughness, provide excellent impact resistance, reduced haze and better clarity (Janiak, 2002). Since 1991, various polyolefins have been produced with the aid of single-site metallocene catalysts. By altering the metallocene structure, the types of polymers produced can be controlled. This characteristic of metallocenes is very important when producing polymers that can have different side branches such as isotactic and syndiotactic PP. These new polymers have features such as lower melting points, better optical characteristics, better heat stability, increased impact strength and toughness, better melt characteristics and improved clarity as films. These advantages are obtained through the control of polymer MW, MWD (elimination of both high- and low-MW fractions), comonomer distribution and content and tacticity.

Metallocenes are important in the production of PE in that they allow the control of side branching due to the single activity site found at the metal center. Traditional Z–N catalysts are hard to control because they have several active sites and polymers are produced by adding monomers to the end of the chain.

Using traditional catalysts, PP is produced as a mixture of the three forms consisting of 95% isotactic, some undesirable atactic and even less of the syndiotactic PP. With metallocene technology, the amount of each type of PP can be controlled through changes in the catalysts’ stereochemistry. Isotactic PP made with classical Z–N catalysts still has some atactic fractions. The presence of atactic PP fractions reduces stiffness, heat distortion temperature and cleanliness. The absence of atactic PP in metallocene isotactic PP means higher stiffness, higher use temperature and lower extractable content (Janiak, 2002). New isotactic PP resins can be produced with improved stereoregularity and controlled comonomer content resulting in higher stiffness, clarity and melt strength. Comonomers employed to produce these enhanced PP resins include ethylene, butene and octene. To differentiate polymers produced with metallocenes from polymers manufactured using older, conventional catalysts, a lower case m is placed in front of the polymer abbreviation, for example, mLDPE.

Metallocene-catalyzed resins have expanded beyond PEs and PPs to polystyrenes, ethylene–styrene copolymers and cyclic olefin copolymers, and polymers made using metallocene catalysts have achieved significant market penetration in a wide array of applications including food packaging films and stretch/shrink films.

2.3.6.2 Copolymers of Ethylene

For copolymers of ethylene, the other comonomer can be an alkene such as propene, butene, hexene or octene, or a compound having a polar functional group such as vinyl acetate (VA), acrylic acid (AA), ethyl acetate (EA), methyl acrylate (MA) or vinyl alcohol (VOH). The polymer can be classified as either a copolymer or homopolymer if the molar percent of the comonomer is less than 10%. LLDPE and LDPE-PP copolymers discussed earlier can rightly be considered as copolymers of ethylene. In addition, there are four further copolymers of ethylene of particular importance in food packaging.

2.3.6.2.1 Ethylene–Vinyl Acetate

Ethylene–vinyl acetate (EVA) is a random copolymer of ethylene and VA whose properties depend on the VA content and MW. EVA with a VA content of 3%–12% is similar in flexibility to plasticized PVC and has good low-temperature flexibility and toughness. The impact strength increases with VA content and MW. As the VA content increases, EVA becomes less crystalline and more elastic; as the crystallinity decreases, the permeability to gases, moisture, fats and oils increases and the clarity improves. EVA is totally amorphous (transparent) when the VA content reaches 50%. As the MW increases, the viscosity, toughness, heat seal strength, hot tack and flexibility all increase. The absence of leachable plasticizer provides a clear advantage over plasticized PVC in some food applications. The addition of antiblocking and slip additives reduces sparkle and clarity and increases haze.

EVA copolymers are not competitive with normal film because of their high surface tack and friction that make them difficult to handle on conventional processing machinery. However, they do have three advantages over LDPE: the heat sealing temperature is lower, the barrier properties are better and they have excellent stretch properties, the first 50% of extension at room temperature being elastic. Thus, they find use as a stretch film for food packaging (particularly fresh meat) and cling-wrap purposes and have replaced PVC for many stretch-wrapping applications. Some EVA is used in coextrusion processes for the manufacture of laminated material. As a heat sealing layer, EVA is used in the extrusion coating of PET and BOPP films.

2.3.6.2.2 Ethylene–Vinyl Alcohol

EVOH copolymers were commercialized in Japan by the Kuraray Company in 1972 and in the United States and Europe in the early 1980s. EVOH copolymer is produced by transforming the VA group into VOH in a controlled hydrolysis of EVA copolymer; there is no VOH involved in the copolymerization (Marten, 2002). Ethylene and vinyl acetate are copolymerized in a solvent system to produce EVA and then saponified (hydrolyzed) with NaOH in a methanol mixture to produce EVOH, followed by coagulation and washing to become purified EVOH copolymer (Ozeki and Kim, 1996). The vinyl alcohol base has exceptionally high gas barrier properties but is water soluble and difficult to process.

EVOH copolymers offer not only excellent processability, but also superior barriers to gases, odors, aromas and solvents. It is these characteristics that have allowed plastic containers containing EVOH barrier layers to replace many glass and metal containers for packaging food.

EVOH copolymers are highly crystalline in nature and their properties are very dependent on the relative concentration of the comonomers. Generally, as the ethylene content increases, the gas barrier properties decrease, the moisture barrier properties improve and the resins process more easily. For example, EVOH of 27 mol% ethylene offers a barrier to dry O_2 10 times as great as one of 42 mol% ethylene, while providing a poorer barrier to moisture vapor (Brown, 1992). When the VOH content ranges from 50% to 70%, the EVOH copolymers combine the processability and water resistance of LDPE with the gas and odor barrier properties of polyvinyl alcohol (PVOH).

The most outstanding characteristic of EVOH is its ability to provide a barrier to gases and odors. Its use in a packaging structure enhances flavor and quality retention by preventing O_2

from penetrating the package. In those applications where gas-fill packaging techniques such as MAP are used, EVOH effectively retains the CO_2 or N_2 used to blanket the product. EVOH also provides a very high resistance to oils and organic vapors, but this resistance decreases as the polarity of the penetrant increases. For example, the resistance to linear and aromatic hydrocarbons is outstanding, yet for ethanol and methanol it is low, with EVOH absorbing up to 12% of ethanol (Hernandez, 1997).

Due to the presence of hydroxyl groups in their molecular structures, EVOH resins are hydrophilic and will absorb moisture. As moisture is absorbed, the gas barrier properties are affected. However, through the use of multilayer technology to surround the EVOH layer with high moisture barrier resins such as polyolefins, the moisture content of the barrier layer can be controlled.

EVOH resins have high mechanical strength, elasticity and surface hardness, very high gloss, low haze, excellent abrasion resistance, very high resistance to oils and organic solvents and provide an excellent barrier to odors. When used as the core of a multilayer material, they provide excellent performance. EVOH copolymers are the most thermally stable of all the high barrier resins. This stability allows the regrinding and reuse of scrap generated during processing back into the package being produced. Many of the rigid packaging containers being produced today have regrind layers containing up to 15% EVOH.

Rigid and semirigid containers such as bottles, trays, bowls and tubes, flexible films and paperboard beverage cartons containing EVOH as the functional barrier layer are commercially available. Most multilayer structures have five or six layers, with seven- and nine-layer structures being produced for special applications, the EVOH always being surrounded by polymers such as polyolefins that provide a good barrier to water vapor. When using EVOH in multilayer structures, it is necessary to use an adhesive or tie layer to gain adequate bonding strength to the other polymers (Foster, 2009).

Coextruded films containing EVOH together with LDPE, LLDPE, HDPE and EVA are used for milk powder and wine in bag-in-box packs. Coextruded, blow-molded bottles containing EVOH with PP, PET and HDPE are used for a wide range of foods including ketchup, mayonnaise, fruit juices, carbonated beverages and beer. EVOH is also used in coextruded cups and trays and thermoformed with HDPE and PP for a wide range of foods.

For multilayer packages that will be retorted after filling, the structures outlined previously may not provide a sufficient barrier to water vapor to prevent unacceptable quantities of O_2 permeating into the product. Recently, Mokwena et al. (2011) measured oxygen transmission rates (OTRs) of two multilayer films containing EVOH after water absorption at 121°C to simulate retorting conditions. The films were PET/EVOH/PP and PET/PP/PA-6/EVOH/PA-6/PP, respectively. OTR increased with water absorption for both films, the OTR of the first film going from 0.034 to 3 mL m^{-2} day^{-1} after 60 min, while the second film went from 0.021 to 5.25 mL m^{-2} day^{-1}; water absorbed by the films after 60 min was 7.3% and 5.3%, respectively.

2.3.6.2.3 Ethylene–Acrylic Acid

By copolymerizing ethylene with acrylic acid, a copolymer containing carboxyl groups along the main and side chains of the molecule is obtained. EAA copolymers are flexible thermoplastics possessing chemical resistance and barrier properties similar to LDPE. However, EAA is superior to LDPE in strength, toughness, hot tack and adhesion. Crystallinity decreases, clarity increases, adhesion strength increases and heat seal strength decreases with increasing AA content.

A related copolymer is ethylene–methacrylic acid (EMA) produced by free radical copolymerization of ethylene with methacrylic acid. EAA and EMA copolymers have excellent adhesion to metals such as aluminum and are used in adhesive lamination as an extrusion-coating tie layer between aluminum foil and other polymers. EAA and EMA are also used as precursors to ionomers (Malpass, 2010). EAA films are used for the packaging of foods such as meat, cheese and snack foods, and in skin and blister packaging.

2.3.6.2.4 Ionomers

Ionomeric polymers with unique properties result when olefinic polymers are prepared in the presence of metallic salts of organic monomers,. The term ionomers was coined by researchers at DuPont in the 1960s to describe polymers having both ionic and covalent linkages and marketed under the trade name Surlyn® (Morris, 2009). They are prepared by copolymerizing ethylene with a small amount (1%–10% in the basic patent but today it ranges from 7% to 30%) of an unsaturated carboxylic acid such as acrylic acid or methacrylic acid using the high-pressure process. Such copolymers are then neutralized to varying degrees (15%–80%) with the derivative of a metal such as sodium or zinc salts, lithium methoxide or lithium acetate, causing the carboxylic acid to ionize. This leads to the formation of ionic cross-links that confer enhanced stiffness, transparency and toughness on the material at ambient temperatures (the puncture resistance of ionomer film is equal to LDPE film of twice the gauge) as well as higher melt strength. There are more than 50 commercial grades of ionomer resin with a wide range of properties. A recent development has been a potassium-based ionomer that can be blended with polyolefins to reduce static buildup (Morris, 2009).

In comparison with LDPE, ionomers have excellent oil and grease resistance, excellent resistance to ESC, greater clarity, lower haze, greater abrasion resistance and higher water vapor permeability due to lower crystallinity. Ionomers containing unneutralized acid groups have found wide utility as the seal layer in extrusion-coated aluminum foil structures (the acid groups provide adhesion to the foil) and are particularly useful in composite structures with films and paperboard to provide an inner layer with good heat sealability. Ionomers have the ability, shared with certain other polymers, of bonding by heat sealing through particles of food that may be trapped between package layers during the filling process. Ionomers also have excellent hot tack—the ability of a newly formed (still molten) heat seal bond to resist an opening force (Morris, 2009). Laminated or coextruded films with PAs or polyesters are widely used for packaging meat and cheese where formability, toughness and visual appearance are important (Brown, 1992). Their exceptional impact and puncture resistance (even at low temperatures) makes them ideal for skin packaging of sharp objects such as meat cuts containing bone. Another advantage is their high infrared absorption that leads to fast heating during the shrink process. Their disadvantages include their poorer slip and block characteristics and relatively poor barrier to O_2.

2.3.6.2.5 Cyclic Olefin Copolymer

COC is based on the polymerization of ethylene and norbornene (2,2,1 bicyclohept-2-ene) using metallocene catalysts. Norbornene (C_7H_{10}) consists of a cyclohexene ring bridged with a methylene group in the *para* position; it carries a double bond that induces significant ring strain and reactivity. COC copolymers can have a T_g ranging from 33°C to 180°C, depending on the comonomer ratio, and a density from 1020 to 1080 kg m^{-3}. As an amorphous polymer, COC does not have a T_m and instead starts to soften above the T_g, becoming increasingly fluid as temperatures are increased. This colorless, crystal-clear material offers strong compatibility with conventional PEs but is most compatible with highly linear PEs such as LLDPE. Those most commonly used for olefin blends have T_gs ranging from 33°C to 78°C; higher T_g grades are sometimes used to enhance the heat resistance of films. On a molar basis, COC typically contains 40%–70% ethylene. However, because of the relatively high MW of the comonomer, this corresponds to only 15%–35% ethylene on a weight basis. COC are specialty resins produced in very small quantities (Malpass, 2010).

COC is also being increasingly used in polyolefin blends to produce barrier films for packaging because it has one of the highest moisture barriers of any polymer (four to five times better than LDPE). COC is not considered to have a high gas barrier but it is still significantly better than LDPE and is a much better barrier to aromas. When incorporated into the heat seal layer of bags or stand-up pouches, COC can improve hot tack and ultimate seal strength without altering the seal initiation temperature.

COC is most commonly used as a blend component to enhance modulus and allow thickness reduction of monolayer films. As little as 10% of COC added to LLDPE will double or triple its modulus while maintaining low haze. As part of a coextruded structure, a LLDPE/COC blend often allows a thinner film to provide the same performance at a reduced cost per m^2 of film. However, addition of COC to LLDPE significantly reduces tear strength, especially in the machine direction, although it does improve the puncture resistance of the film. Typical uses for COC blends include fresh-cut produce bags and pouches for drinks, cereals, candies, soups and pet foods. Monolayer COC films have good twist-wrap behavior and can be easily metallized.

2.3.6.3 Substituted Olefins

The simplest substituted olefins are those in which each ethylene group has a single substituent; these monomers are called *vinyl* compounds. Disubstituted monomers with two substituents on the one carbon are called *vinylidene*. Structures of some common monomers based on the ethylene chain are shown in Figure 2.7.

2.3.6.3.1 Polystyrene

If ethylene and benzene are reacted together with a suitable catalyst, ethylbenzene is formed and, by a process of catalytic dehydrogenation, styrene (commonly known as vinyl benzene) is produced. PS is made by the addition polymerization of styrene and typically consists of ~1000 styrene units. The polymer is normally atactic and is thus completely amorphous because the bulky nature of the benzene rings prevents a close approach of the chains. With the use of special catalysts and polymerization techniques, isotactic PS has been prepared but it reverts to the atactic form on melting.

PS was the first of the moldable clear rigid plastics to reach the commercial market in large volumes in the late 1940s. It could be rapidly molded into finished shapes because of its ease of flow in the melt and its fast-setting nature from the melt. However, an increase in monomer content from 0% to 5% can cause a 30°C reduction in softening point.

2.3.6.3.1.1 General-Purpose Polystyrene In this form, it is commonly referred to as crystal-grade PS and is the unmodified homopolymer of styrene. At temperatures in the range at which food packages are stored it is glassy and noncrystalline since its T_g is in the range 90°C–100°C because of the stiffening effect of the benzene ring. This results in a material that is stiff and brittle at room temperature with no melting temperature but excellent optical properties.

PS makes a distinctly metallic sound when dropped onto a hard surface. It has a high refractive index (1.592), which gives it a particularly high brilliance. Although acids and alkalis have no effect on it, it is soluble in higher alcohols, ketones, esters, aromatic and chlorinated hydrocarbons and some oils. Even if it is not soluble in the material, ESC and even chemical decomposition of PS

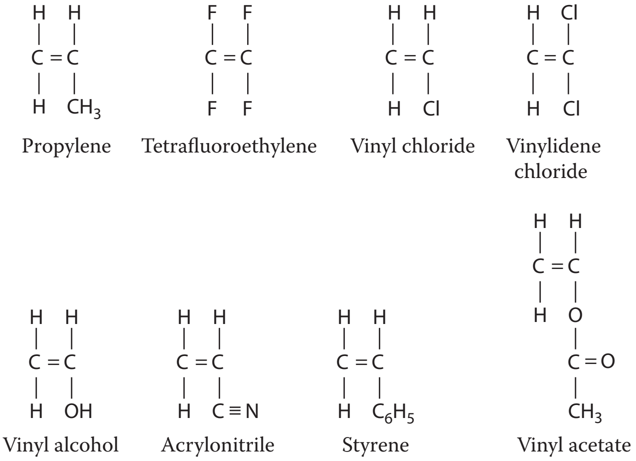


FIGURE 2.7 Structure of some common monomers based on ethylene.

may occur. The extent of the decomposition depends on the grade of PS, the time and temperature of exposure and the concentration of the reagent. In addition, many materials that do not attack PS individually do so in combination, so shelf life studies before marketing a food in PS are essential to test for any synergistic effect. PS is a poor barrier to water vapor and gases.

Crystal-grade PS can be made into film but it is brittle unless the film is biaxially oriented. The oriented film can be thermoformed into a variety of shapes, although special techniques have to be used because orientation gives it a tendency to shrink on heating. Oriented PS film, in addition to being heat shrinkable, offers a high degree of optical clarity, high surface gloss, and excellent dimensional stability, particularly with regard to relative humidity. One of its largest uses is for packaging fresh produce because it is highly permeable to O_2 and water vapor.

New applications of PS involve coextrusion with barrier resins such as EVOH and PVdC copolymer to produce thermoformed, wide-mouthed containers for shelf-stable food products and multilayer blow-molded bottles.

2.3.6.3.1.2 High Impact Polystyrene To overcome the brittleness of PS, synthetic rubbers (typically 1,3-butadiene isomer $CH_2{=}CH{-}CH{=}CH_2$) can be added during polymerization at levels generally not exceeding 25% w/w for rigid plastics. The rubbers act by restricting the propagation of microcracks formed during impact loading. At the start of the process, polybutadiene is dissolved in the styrene monomer. As the polymerization proceeds, two phases are formed: a polybutadiene-rich phase and a PS-rich phase with grafted polybutadiene. The grafting arises when some of the styrene-free radicals react with the polybutadiene. Controlling the sizes of the homopolymer blocks formed by each of the monomers determines the properties of the resulting copolymer. Blocks of PS in SB (styrene–butadiene) copolymers confer typical styrenic properties of stiffness, glossiness and ease of processing, while blocks of polybutadiene contribute great flexibility and extensibility. SB copolymer is sometimes referred to as K resin. Although copolymerization increases impact strength and flexibility, the transparency, tensile strength and thermal resistance is much reduced. The chemical properties of this toughened or high impact polystyrene (HIPS) are much the same as those for unmodified polystyrene.

HIPS is an excellent material for thermoforming. Because it is transparent, the use of radiant heat for thermoforming is inefficient and pigmented sheet is often used. It is injection molded into tubs that find wide use in food packaging, despite their being opaque. Transparent unit packs are made from untoughened PS.

2.3.6.3.1.3 Expandable Polystyrene Sheet The properties of PS that make it useful for many applications as a solid polymer also make it very desirable as a foam. PS foam has a high tensile strength, good water resistance, low moisture transmission, ease of fabrication and low cost. Closed-cell foams have excellent thermal insulating capability, low weight and good cushioning characteristics. The combination of those properties provides a wide spectrum of products.

Extruded PS foam sheet is a closed cell, 0.13–6.4 mm thick sheet with densities ranging from 32 to 160 kg m^{-3}. It can be made by a variety of extrusion processes but is most commonly made using a tandem extrusion process. A large percentage of foam sheet is thermoformed using matched metal molds. CO_2 is commonly used as a blowing agent, which results in improved organoleptic properties that have opened up new applications in food packaging. Most PS foam sheet is used for disposable packages such as meat and produce trays, egg cartons, disposable dinnerware and containers for take-away or carry-out meals.

2.3.6.3.2 Poly(Vinyl Chloride)

Ethylene dichloride is formed by an addition reaction of chlorine with ethylene, and the dichloride is then dehydrochlorinated or “cracked” to give vinyl chloride monomer (VCM). Addition polymerization of VCM produces PVC with a DP ranging from 500 to 3500. From the structure of VCM, it can be seen that addition of molecules to the growing chain can take place either head to head, head to tail or in a completely random manner. PVC polymerizing in either of the first two forms would be expected to be crystalline, while the random arrangement would be amorphous. Generally, PVC polymerizes in the atactic form and, thus, is largely an amorphous polymer.

In 1974, there was widespread publicity resulting from the announcement that a rare and invariably fatal form of liver cancer had been diagnosed among workers in VC polymerization plants in Britain and the United States. Food and drug administrators around the world became particularly interested in the VCM content of PVC material used for food packaging and the likelihood of it migrating into the food. This topic is discussed further in Chapter 22 but suffice it to say that the levels of VCM in PVC packaging material are currently extremely low.

Vinyl polymers and copolymers make up one of the most important and diversified groups of linear polymers. This is because PVC can be compounded to produce a wide spectrum of physical properties. This is reflected in the variety of uses to which it is put: from exterior guttering and water pipes to very thin, flexible surgical gloves. It is the second-most widely used synthetic polymer after PE and is commonly referred to simply as "vinyl."

A range of PVC films with widely varying properties can be obtained from the basic polymer. The two main variables are changes in formulation (principally plasticizer content) and orientation. The former can give films ranging from rigid, crisp films to limp, tacky and stretchable films. The degree of orientation can also be varied from completely uniaxial to balanced biaxial.

Unplasticized PVC tends to degrade and discolor at temperatures close to those used in its processing, so suitable stabilizers have to be included in the formulation. The stabilizers used are generally the salts of tin, lead, cadmium, barium, calcium or zinc along with epoxides and organic phosphites, and these must be carefully selected for nontoxic applications. The use of lead and cadmium compounds as stabilizers is not generally allowed in food contact materials. Approval by the U.S. FDA of certain octyltin compounds for use in stabilizing PVC during blow molding of containers expanded the use of this polymer for food packaging.

Extremely clear and glossy films can be produced having a high tensile strength and stiffness. The density is high at around 1400 kg m^{-3}. The water vapor permeability is higher than that of the polyolefins but the gas permeability is lower. Unplasticized PVC has excellent resistance to oils, fats and greases and is also resistant to acids and alkalis.

To a large extent, the properties of plasticized PVC depend on the type of plasticizer used, as well as the quantity. For these reasons, it is difficult to be very specific about the physical properties of PVC due to the wide range of plasticization possible. Rigid PVC has a T_g of 82°C, with plasticizers decreasing T_g and the processing temperature.

The plasticizers used (about 80% of all plasticizers are used with PVC) are organic liquids of low volatility that facilitate internal movement of the molecular chains. Combinations of different compounds are used, the esters of phthalic acid being the most common. The amount can vary up to 50% of the total weight of the final material. Because plasticizers are not bound chemically, they tend to migrate to the surface where they are lost by abrasion, solution or slow evaporation, leaving a more brittle, stiffer material behind. Internal plasticization may be brought about by copolymerization of VC with monomers such as vinyl acetate, ethylene or methylacrylate.

Films with excellent gloss and transparency can be obtained provided that the correct stabilizer and plasticizer are used. Both plasticized and unplasticized films can be sealed by high-frequency welding techniques. PVC is inert in its chemical behavior and self-extinguishing when exposed to a flame. Thin, plasticized PVC film is widely used for the stretch wrapping of trays containing fresh red meat and produce. The relatively high water vapor transmission rate (WVTR) of PVC prevents condensation on the inside of the film. Oriented films are used for shrink wrapping of produce and fresh meat but LLDPE films have increasingly replaced them in many applications.

Unplasticized PVC as a rigid sheet material is thermoformed to produce a wide range of inserts from chocolate boxes to biscuit trays. Unplasticized PVC bottles have better clarity, oil resistance and barrier properties than those made from HDPE. However, they are softened by certain solvents, notably ketones and chlorinated hydrocarbons. Although they made extensive penetration into the market for a wide range of foods including fruit juices and edible oils, in recent years they have been increasingly replaced by PET.

2.3.6.3.3 Poly(Vinylidene Chloride)

PVdC homopolymer has a melting temperature only a few degrees below the temperature at which it decomposes and yields a rather stiff film, which is unsuitable for packaging purposes. Therefore, copolymers were synthesized in an effort to overcome these properties. Acrylates were found to be among the most useful comonomers, along with VC and AN (Brown, 1992).

A soft, tough and relatively impermeable film results when PVdC is copolymerized with 5%–50% (but typically 20%) of VC. These copolymers were first marketed by Dow in 1939 under the trade name Saran™ but are also produced by other companies under various trade names, for example, Ixan® and Diofan®. Although the films are copolymers of VdC and either VC or AN, they are usually referred to simply as PVdC copolymer and such a convention is followed in this book. The specific properties of PVdC copolymer vary according to the degree of polymerization and the properties and relative proportions of the copolymers present.

The properties of PVdC copolymer film include a unique combination of low permeability to water vapor, gases, odors, greases and alcohols, and good ESCR to a wide variety of agents. The good barrier properties of PVdC copolymers are a consequence of crystallinity and low free volume in the amorphous phase. The symmetrical nature of the VdC unit in the polymer leads to nested packing that is adequate for crystallization and leaves very little dead volume in the amorphous phase. Although highly transparent, it has a yellowish tinge. Food packaging applications for PVdC copolymer monolayer films include packaging of processed meats, cheese and other dairy products, and bakery goods. It is an important component of many laminates and is the best coating for RCF. PVdC copolymers can be sealed to themselves and to other materials. By itself, the copolymer is frequently used as a shrink film because orientation improves tensile strength, flexibility, clarity, transparency and impact strength. As well, gas and moisture permeabilities are lowered and tear initiation becomes difficult. The shrink film can be heat sealed using impulse sealing with Teflon®-coated heating bars.

Rigid containers for food packaging can be made from coextruded sheet that contains a layer of PVdC copolymer as a barrier; PVdC has the ability to withstand hot filling and retorting. A simple example is a sheet with five layers that has a total thickness of ~1.3 mm. The outermost layers might be PP, HDPE, PS, HIPS or other nonbarrier polymers having good mechanical properties. The innermost barrier layer is ~125 μm of PVdC copolymer. Adhesive layers connect the outer layers and the barrier layer. This coextruded sheet can be formed into containers by any of several techniques, and the final container has a total wall thickness of ~500 μm and a barrier layer that is ~50 μm thick.

2.3.6.3.4 Poly(Tetrafluoroethylene)

The high thermal stability of the carbon–fluorine bond has led to considerable interest in fluorine-containing polymers as heat resistant plastics and rubbers. Chemically, the fluorine-containing polymers are set apart from other vinyl polymers because their monomers are the only ones that need not bear any hydrogen on the ethylenic carbons in order to be polymerizable. Physically, they are further set apart by their outstanding stability. Poly(tetrafluoroethylene) (PTFE) was a chance discovery by Roy Plunkett while working for DuPont in 1938. He had a cylinder of TFE gas, which, although apparently empty, had not yielded the theoretical amount of gas. When the cylinder was cut open, it was partly filled with a waxy white powder that was identified as a polymer. First marketed in 1945, today it accounts for about 80% of the fluorinated polymers produced and is commonly referred to by the trade name Teflon®.

The monomer TFE is made by reacting hydrofluoric acid with chloroform. Hydrogen chloride is displaced, forming $CHClF_2$, which can be pyrolyzed to TFE. PTFE is a linear polymer free from any significant amount of branching, with an MW that can exceed 30 million atomic mass units, making it one of the largest molecules known. Because the C–C and C–F bond strengths are very high, PTFE has very high heat stability, even when heated above its T_m of 327°C. Its chemical inertness, nonadhesive properties and excellent heat resistance and low coefficient of friction make PTFE ideal for certain specific applications.

In food packaging, PTFE finds wide use as a nonstick separating surface between thermoplastic films and the jaws of heat sealers. It is common to use a band of PTFE (often reinforced with glass fibers) on continuous heat sealers. The main disadvantages of PTFE are its very high cost and unsuitability for the processing techniques conventionally applied to plastics, poor scratch resistance and mechanical properties.

2.3.6.4 Polyesters

The polymers that have been discussed so far are all based on carbon-to-carbon links and are generally formed commercially by addition polymerization. In contrast, polyesters are based on carbon–oxygen–carbon links where one of the carbons is part of a carbonyl group, and are formed by the process of condensation polymerization. In this process, two molecules are joined together through the elimination of a smaller molecule (typically H_2O) whose atoms derive from both the parent molecules. Simple polyesters are derived from the condensation of a polyhydric alcohol and a polyfunctional acid and are sometimes described as *alkyds* (from *al*cohol and aci*d*). Each component needs a functionality (i.e., number of reactive groups such as –OH, –COOH, $-NH_2$ per molecule) of two to form a linear chain, while if one (or both) monomer has a functionality of at least 3, cross-linkage can occur resulting in a much more rigid three-dimensional lattice structure.

Fiber-forming polyesters have been the subject of extensive investigations ever since the American chemist Wallace Carothers, who worked for DuPont, began his classical research that led to the development of PAs. However, while Carothers largely confined his research to aliphatic polyesters, John Whinfield and James Dickson, working for the Calico Printers Association in England, investigated aromatic materials. This led to the discovery in 1940 and subsequent successful exploitation of poly(ethylene terephthalate) (PET) by ICI with DuPont licensed by ICI to manufacture PET in the United States (McIntyre, 2003).

2.3.6.4.1 Poly(Ethylene Terephthalate)

PET can be produced in an esterification reaction where ethylene glycol (EG) reacts with terephthalic acid (TPA). Alternatively, a *trans*-esterification reaction where the dimethyl ester of TPA (dimethyl terephthalate or DMT) reacts with EG is preferred as it is a more controllable reaction. Water is a by-product of the first reaction and methanol of the second; it can be recovered for further use. The output of both these processes is bis(hydroxyethyl) terephthalate (BHET). A pre-polymerization step follows in which BHET is polymerized to a DP of up to 30 after which a polycondensation process increases the DP further to 100. After polymerization in the melt phase, the MW is further increased by solid-state polymerization (SSP) to a DP of 150 (Awaja and Pavel, 2005). The overall scheme of the reaction is shown in Figure 2.8. The product has a carboxyl group at one end and a hydroxyl group at the other, so it can condense with another molecule of alcohol and acid. The PET repeating unit has an MW of 176, resulting in a final MW of up to 27,000. EG is obtained from ethylene, mostly by the direct hydration of ethylene oxide. DMT is prepared by the catalytic partial oxidation of *p*-xylene, itself a by-product of the petroleum industry; *p*-xylene can also be converted into TPA.

PET is a linear, transparent thermoplastic polymer with a T_m of 267°C and a T_g between 67°C and 80°C. It has the capacity to crystallize under certain controlled conditions. PET is strong, stiff, ductile and tough while in the glassy state (i.e., at temperatures below T_g where side motion is restrained) and can be oriented by stretching during molding and extrusion, which increases its strength and stiffness still further. PET bottles and films are largely amorphous (APET) with small crystallites and excellent transparency. However, crystalline PET (CPET) containers have a higher degree of crystallinity, larger crystallites and are an opaque white (see Section 5.12 for further discussion of APET and CPET).

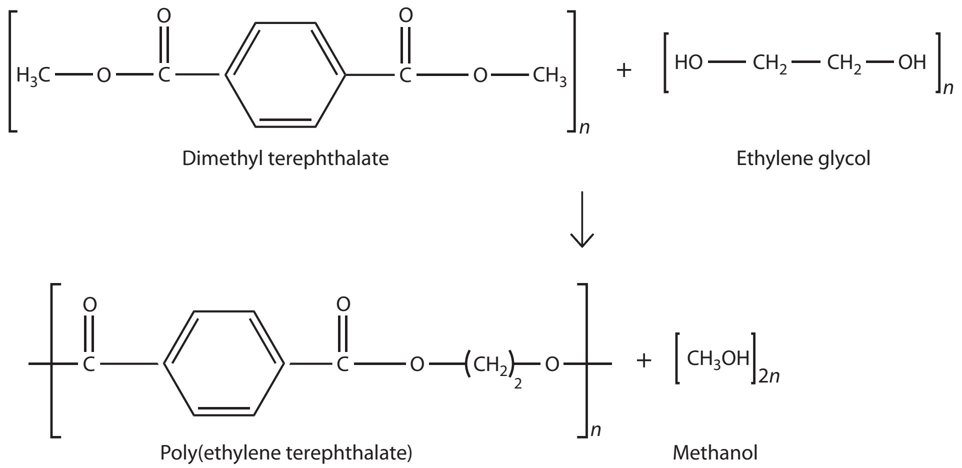


FIGURE 2.8 Reaction scheme for formation of poly(ethylene terephthalate) (PET).

PET films are most widely used in the biaxially oriented, heat stabilized form. There are virtually no applications for the material in its unoriented form because, if crystalline, it is extremely brittle and opaque, and if amorphous, it is clear but not tough. In a two-stage process, machine direction stretching induces 10%–14% crystallinity and this is raised to 20%–25% by transverse orientation. In order to stabilize the biaxially oriented film, it is annealed (or heat set) under restraint at 180°C–210°C, which increases the crystallinity to around 40% without appreciably affecting the orientation and reduces the tendency to shrink on heating. Subsequent coatings are applied to obtain special barrier properties, slip characteristics or heat sealability.

PET film's outstanding properties as a food packaging material are its great tensile strength, excellent chemical resistance, light weight, elasticity and stability over a wide range of temperatures (−60°C to 220°C). This latter property has led to the use of PET for "boil-in-the-bag" products that are frozen before use (the PET is usually laminated to or extrusion coated with LDPE and is typically the outside and primary support film of such laminations), and as oven bags where they are able to withstand high temperatures without decomposing.

APET has nearly the same thermoforming characteristics as PS and has attracted some interest as a replacement for PVC. The properties of unoriented APET are similar to those of semicrystalline oriented PET with the exceptions of strength and stiffness that are enhanced by orientation (Brown, 1992).

To improve the barrier properties of PET, coatings of LDPE, PVdC copolymer or PVdC-co-AN have been used. PET film extrusion coated with LDPE is very easy to seal and very tough. It can be sealed through powders and some liquids, and the integral seal will withstand sterilization by UV. Two-side, PVdC copolymer-coated grades provide a high barrier; a major special application was the single-slice cheese wrap.

Although many films can be metallized, PET is the most common. Metallization (see Section 5.5) results in a considerable improvement in barrier properties. Reductions in WVTRs by a factor of 40 and O_2 permeabilities by over 300 are obtainable. Coextruded, heat sealable films are frequently metallized and used as the inner ply of snack food packages. Rigid grades of metallized PET can be used in thermoformable applications.

PET is also used to make "ovenable" trays for frozen food and prepared meals, where they are preferable to foil trays because of their ability to be microwaved without the necessity for an outer paperboard carton. These trays are thermoformed from cast PET film and crystallized, the crystallization heat setting the tray and preventing deformation during cooking and serving. The properties of the various physical states of PET are summarized in Table 2.5.

TABLE 2.5
Properties of PET

Physical State	Property	Application
Amorphous	0%–5% crystallinity, heat stable to 67°C, clear	Blister packs
Oriented amorphous	5%–20% crystallinity, heat stable to 73°C, clear	Bottles
Crystalline	25%–35% crystallinity, heat stable to 127°C, opaque	Food trays
Oriented crystalline	35%–45% crystallinity, heat stable to 140°C–160°C, clear	Hot-fill containers, films

In the 1970s, the benefits of biaxial orientation of PET were extended from sheet film to bottle manufacture. Nathaniel Wyeth (brother of artist Andrew) and Ronald Roseveare were issued a series of patents (assigned to DuPont) in 1973 (filed in 1970) for a stretch blow molded, biaxially oriented bottle prepared from PET. DuPont chose not to embark on bottle production itself but instead to license the product to others (McIntyre, 2003). The first PET test market was held in New York State during 1975/1976 and the first commercial production appeared on the market in 1977. As a result, important new markets developed, particularly for carbonated beverages.

The bottles are stretch blow molded, the stretching or biaxial orientation being necessary to get maximum tensile strength and gas barrier, which in turn enables bottle weights to be low enough to be economical. The presence of moisture during the extrusion of PET reverses the condensation reaction and produces some depolymerization. Therefore, before extrusion, PET must be dried to a moisture content of less than 0.005% to minimize hydrolytic breakdown and loss of properties.

The major significant volatile compound in PET is acetaldehyde (AA), which is present as a thermal degradation product formed during the melt condensation reaction and melt processing of PET. AA itself is also unstable and readily oxidizes and polymerizes when exposed to air. AA possesses a distinct odor and taste, generally described as sweet, plastic-like and fruity, with a low sensory detection threshold. Present manufacturing techniques have dramatically reduced residual AA levels in PET packaging. The first generation of resins typically had residual AA levels of 2–3 ppm, but today these are <1 ppm. However, AA increases when the pellets are remelted and converted into preforms.

PET bottles used for packaging carbonated beverages are also susceptible to ESC (Morrison et al., 2010). A large crack forms in the base portion of the bottle through which all of the liquid contents can be lost. These cracks initiate on the outside bottle wall and progress inward, consistent with chemical attack as a first step. Thus, in PET stress cracking, the chemical environment on the outside of the bottle must be considered; the contents of the bottle are irrelevant. In the past, attempts have been made to relate ESC of PET bottles with water alkalinity but Morrison et al. (2010) found it was not possible to correlate ESC to water alkalinity without also accounting for water hardness. The metric for water that is relevant to PET stress cracking is excess alkalinity. Most often, naturally occurring water has hardness equal to or greater than alkalinity, that is, it has no excess alkalinity. Ion exchange softening of water removes all hardness and leaves in all alkalinity, in which case all alkalinity originally present becomes excess alkalinity. For this reason, it is important to prevent contact of filled, carbonated PET bottles with water softened by ion exchange as it removes all the hardness but none of the alkalinity.

In 2009, PTI developed the first lightweight foamed PET bottle/jar blow molding process. It is based on microcellular foam injection molding technology to mold preforms, which can then be blow molded on conventional equipment. The package has significant light barrier characteristics with up to 95% reduction in transmitted light. One early application has been for single serve beer. In addition to PET, the foam bottle technology is applicable to other resins such as poly(lactic acid) (PLA) and poly(ethylene napthalate) (PEN).

2.3.6.4.2 Poly(Ethylene Naphthalate)

In the late 1980s, a high-barrier polyester called PEN was developed. The precursor for PEN is 2,6-dimethylnaphthalene (DMN), which can be oxidized and esterified to give 2,6-dimethylnaphthalene dicarboxylate (NDC). This monomer undergoes polycondensation with EG to form PEN (poly(ethylenenaphthalene-2,6-dicarboxylate)), a semicrystalline polymer similar to PET but with a double ring structure that makes it more rigid and improves its barrier and mechanical properties.

PEN provides approximately five times more barrier to CO_2, O_2 and water vapor than PET, giving it obvious advantages as a flexible film, or as a rigid container for beer and carbonated beverages. It has a T_g of 120°C (51° higher than for PET) and is stronger and stiffer (but more expensive) than PET. The FDA gave final approval for food use of PEN homopolymers in April 1996 (the petition was filed in 1988), and for PET–PEN copolymers in March 2000.

Because the PEN homopolymer is priced at a significant premium to PET (PEN resin is about four times the cost of PET), attractive applications for PEN are those where its physical advantages outweigh its cost disadvantage. PEN extrusion blow molded containers exhibit excellent properties in hot-fill food (baby food, ketchup) and drink applications, reusable packaging, and packaging of O_2 sensitive foods such as beer. PEN, like PET, has good clarity. The advantages of PEN over PET are its 35°C–55°C higher use temperature, 50% greater tensile strength, and fivefold better barrier performance. Additional markets for PEN encompass laminates, copolymers and blends. However, if PEN homopolymer is to penetrate large-volume applications such as beer and single-serve carbonated beverage bottles, then the cost of making 2,6-DMN will need to be reduced. Like PET, PEN film can be vacuum metallized or coated with aluminum or silica oxides.

2.3.6.4.3 Copolyesters

The term copolyester is applied to those polyesters whose synthesis uses more than one glycol and/or more than one dibasic acid. The copolyester chain is less regular than the monopolyester chain and, therefore, has a reduced tendency to crystallize. As a result, some of the copolyesters are amorphous, some are crystalline and some can be made to be either crystalline or amorphous, depending on processing conditions.

An important cycloaliphatic diol used in a variety of commercial copolyesters is 1,4-cyclohexanedimethanol (CHDM), which is produced by the catalytic hydrogenation of DMT; it can exist as the *cis* or *trans* isomer, and the isomer ratio plays an important role in determining the final properties of the copolyester. The polyester of CHDM with TPA is poly(1,4-cyclohexylenedimethylene terephthalate) (PCT), which melts at 300°C. When this structure is modified with an acid such as IPA, the abbreviation PCTA (acid-modified PCT) is used. PCT polyesters with glycol modification of up to 50 mol% EG are abbreviated as PCTGs. Likewise, PET polyesters with up to 50% CHDM content are called PETGs. The abbreviations of PETG, PCTG, and PCTA are generally reserved for compositions that contain enough of the comonomer to render the backbone slow to crystallize or amorphous (Turner et al., 2003).

A well-established application for extruded unreinforced PCTA is in the preparation of crystallized, thermoformed trays for foods. Crystallized PET is widely used for this application, but where higher temperature performance is needed, PCTA may be chosen. Such trays are formed from extruded sheet, using a hot mold to promote crystallization (Turner et al., 2003).

In recent years, PET manufacturers have tended to produce copolymers of PET containing minor amounts (<5 mol%) of such comonomers as IPA or CHDM to reduce the polymer melting point by ~4°C–12°C. This improves the molding characteristics of PET and assists in imparting enhanced clarity to stretch blow molded bottles by modifying the crystallization characteristics of the PET backbone. Other performance benefits of PCT versus PET include improved toughness, hydrolysis resistance and color.

PETG copolyester is a clear, amorphous polymer with a T_g of 81°C. It can be readily molded or extrusion blow molded and normally remains amorphous, clear and virtually colorless even in very heavy thicknesses. It has high stiffness and hardness and good toughness, retaining an acceptable degree of toughness even at low temperatures. However, it is a poorer barrier than PET.

PET–PEN copolymers, which are made up primarily of PET with DMN as a comonomer at 10%–25%, meet market hot-fill requirements up to 95°C at a much more economical cost than PEN homopolymer, which has a maximum hot-fill temperature of 85°C. PET and PEN can also be blended together. PEN homopolymers, copolymers and blends have not yet been used for any major, high-volume, food packaging application.

2.3.6.5 Polycarbonates

PCs are polyesters of unstable carbonic acid and have carbonate (–O–(C=O)–O–) linkages. They were originally produced by the reaction of phosgene (also known as carbonyl chloride [$COCl_2$]) with bisphenol A (BPA) and, hence, have the name poly(bisphenol-A carbonate). While BPA is still the most commonly used phenol, diphenyl carbonate has replaced phosgene. PCs have an outstanding combination of high temperature resistance, high impact strength and clarity, retaining their properties well with increasing temperature. Chemically they are resistant to dilute acids but strongly attacked by alkalis and bases such as amines. Permeability to both water vapor and gases is high, and if appreciable barrier properties are required, they must be coated. While PCs can be oriented, there is no decrease in permeability, although tensile strength increases. PCs are not suitable as shrink films since the rate of shrinkage above their heat distortion point is extremely slow.

Because PCs are amorphous, they soften over a wide temperature range; the T_m of bisphenol A PCs is 220°C–265°C and the T_g 150°C. The melting point of PCs is decreased from 225°C to 195°C when the methyl pendant groups are replaced by propyl groups. Thermoforming of PC film is readily carried out and deep draws with good mold detail are obtainable.

PCs are used to a very limited extent in food packaging as components of multilayer coextrusions and co-injection moldings to provide transparency and high strength to containers that undergo hot filling or hot processing after filling (Brown, 1992). PC can be laminated or coextruded to PP, PE, PET, PVC and PVdC copolymer; coextrusions with EVOH or PAs are carried out with the help of adhesives. Multilayered bottles typically contain a central EVOH layer to reduce O_2 ingress, with the PC layers on either side providing strength. However, the relatively high cost of PC limits its use in these applications.

Another application for PCs is ovenable trays for frozen foods and prepared meals where low-temperature impact strength adds durability and toughness; they are commonly coextruded with PET. The film has been used for boil-in-bag packs and, when coated with LDPE, skin packaging. Uses as a retort pouch and for microwave oven cookware are possible because of good stability at high temperatures. Vacuum metallizing gives good results because of PCs transparency, with the finished product having a high gloss.

Although the film is biaxially oriented for electrical applications, it is not used in this form in food packaging. However, blow and injection molded PC is used for reusable bottles (particularly bottles for babies), which take advantage of PC's toughness and clarity. As well, PC has high resistance to staining by tea, coffee, fruit juices, tomato sauces, lipstick, ink, soaps and detergents.

2.3.6.6 Polyamides

PAs are condensation, generally linear, thermoplastics made from monomers with amine and carboxylic acid functional groups resulting in amide (–(C=O)–NH–) linkages in the main polymer chain that provide mechanical strength and barrier properties. Their development was not fortuitous but the result of a long search for a family of polymers that would resemble silk, the most highly valued of all natural textile fibers.

The early development of the nylons (originally the DuPont brand name for the family of synthetic polyamides) is largely due to the work of Carothers and his colleagues at DuPont between 1928 and 1937. They first synthesized nylon-6,6 in 1935 after extensive research into condensation polymerization. Commercial production of this polymer for subsequent conversion into fibers was commenced by DuPont in 1939. There is no evidence for the popular belief that nylon is a contraction of the names of the cities, *N*ew *Y*ork and *Lon*don. In 1940, John W. Eckelberry of DuPont stated that the letters "nyl" were arbitrary and the "on" was copied from the names of other fibers such as cotton and rayon. A later publication by DuPont explained that the name was originally intended to be "No-Run" (run in this context meaning unravel as an early application was for stockings) but was then modified to avoid making such an unjustified claim and to make it sound better. The word nylon was never trademarked.

In an attempt to circumvent the DuPont patents, German chemists investigated a wide range of synthetic fiber-forming polymers in the late 1930s. This work resulted in the successful introduction of nylon-6 (where a six-carbon molecule contained an acid group at one end and an amine group at the other) and between them nylons-6 and -6,6 account for nearly all of the PAs produced for fiber application.

Today, two different types of PA films are available based on their resin manufacture. One type is made by the condensation of mixtures of diamines and dibasic acids. These are identified by the number of carbon atoms in the diamine, followed by the number of carbon atoms in the diacid. The other type is formed by the condensation of single, hetero-functional amino acids, known as omega or ω-amino acids since the amino and carboxyl groups are at opposite ends of the polyamides. Identification is made by a single number signifying the total number of carbon atoms in the amino acid. Water is released as a by-product of the condensation reaction. The average DP is ~200 for a typical nylon-6 and about 100 for nylon-6,6.

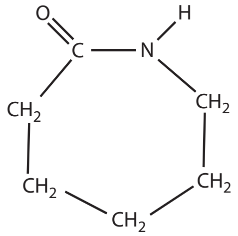
Although a large number of likely combinations have been tried on a laboratory scale, commercial production has been limited to those where the starting materials can be produced most cheaply. PAs did not become a commercial reality for packaging film applications until the late 1950s. Although considered a specialty film, many presently available food packages would not be possible without PAs:

- Nylon-6 refers to PA made from the monomer ε-caprolactam that already contains an amide link and contains six carbon atoms (Figure 2.9). During polymerization, the ring opens and the molecules join up in a continuous chain.
- Nylon-11 refers to PA made from the monomer ω-undecanolactam that contains 11 carbon atoms.
- Nylon-6,6 (sometimes written nylon-66) is formed by reacting hexamethylenediamine with adipic acid. Both materials each contain six carbon atoms.
- Nylon-6,10 (nylon 610) is made by reacting hexamethylenediamine with sebacic acid ($HOOC–(CH_2)_8–COOH$). The diamine has six carbon atoms and is numerically first, followed by the acid that contains 10 carbon atoms.

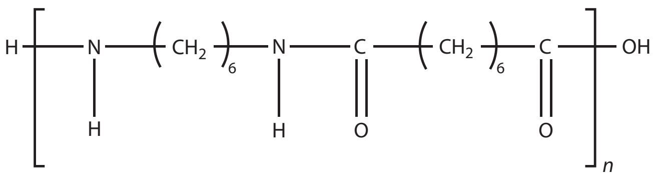
Most PA packaging films in the United States are produced from nylon-6 while European films are usually nylon-11, due to lower raw material costs. Films from nylon-6 have higher temperature, grease and oil resistance than nylon-11 films. The structures of three common PAs are depicted in Figure 2.9.

PAs produced with greater than six-carbon chains result in films with a lower melting point and an increased resistance to water vapor. Again, the key to successful commercialization is to find cheap sources of the monomers.

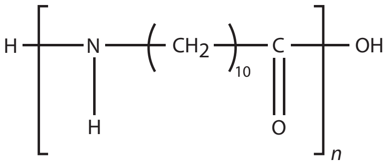
In addition to the homopolymers discussed earlier, copolymerization is used to introduce many additional varieties. Nylon-6,6 and -6,10 can be copolymerized to yield a film with a lower melting point than either of the homopolymers. Fillers, plasticizers, antioxidants and stabilizers can also be used with any or all of the many types of PA films. Over 100 different formulations are



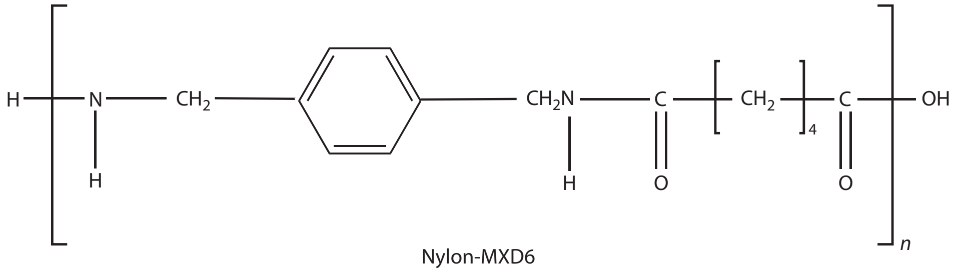
Caprolactam



Nylon-6, 6



Nylon-11



Nylon-MXD6

FIGURE 2.9 Structures of the monomer ε-caprolactam (used to make nylon-6) and three other common polyamides.

available in the production of PA film, but most of those used in food packaging applications consist of nylons-6,6, -6 and -11.

The distance between the repeating polar amide (–CONH–) group can considerably affect the properties of PAs. As the length of the aliphatic segment (i.e., the number of methylene groups between amide groups in the chain) increases, there is a reduction in melting point, tensile strength and water absorption, and an increase in elongation and impact strength. Thus, nylon-11 (where the distance is approximately twice that of nylon-6) has a lower interchain attraction, has a lower melting point, has a lower water absorption and is softer. Nylon-11 may be considered to be intermediate in structure and properties between nylon-6 and LDPE. The T_gs of PAs are in the range of 40°C–60°C, while the T_ms are as follows: nylon-6 = 215°C, nylon-6,6 = 255°C, nylon-6,10 = 220°C and nylon-11 = 190°C. The high T_ms of PAs such as nylon-6,6 is a function of both the strong hydrogen bonding between the chains and the crystal structure. This also allows the materials to retain significant stiffness above the T_g and almost up to the melting point.

As might be expected, copolymerization tends to inhibit crystallization by breaking up the regular polymer chain structure and, consequently, results in lower T_ms than the corresponding homopolymer. The properties of PAs are considerably affected by the amount of crystallization. Although each variety of PA film has its own characteristic properties, certain similarities exist. PA films are characterized by excellent thermal stability, that is, they are capable of withstanding steam at temperatures up to 140°C and dry heat to even higher temperatures; low temperature flexibility is excellent and they are resistant to alkalis and dilute acids. Strong acids and oxidizing agents react with PAs.

In general, PAs are highly permeable to water vapor since the amide group is polar. The absorbed water has a plasticizing effect, which causes a reduction in tensile strength and an increase in impact strength. Their permeability to O_2 and other gases is quite low when the films are dry. PVdC copolymer-coated PAs offer improved O_2, water vapor, grease and UV light barrier properties. Odor retention is excellent and the films are odorless and nontoxic. Other important attributes of PAs are their excellent thermoformability, flex-crack resistance, abrasion resistance and mechanical strength up to 200°C.

For most applications, PAs are combined with other materials such as LDPE, ionomer and EVA to add moisture barrier and heat sealability. Multilayer films containing a PA layer are used principally in the vacuum packing of processed meats and cheeses.

Biaxial orientation of PA films provides improved flex-crack resistance, mechanical strength and barrier properties. These films have applications in packaging foods such as processed and natural cheese, fresh and processed meats and frozen foods. They are used in pouches and bag-in-box structures. In some applications the PAs compete with biaxially oriented PET; although oriented PAs offer better gas barrier, softness and puncture resistance, oriented PET offers better rigidity and moisture barrier.

In the 1980s, a new polymer, nylon-MXD6, was introduced by the Mitsubishi Gas Chemical Company in Japan. It is made from meta-xylylenediamine (MXD) and adipic acid and is technically referred to as poly(meta-xylylene adipamide); the 6 indicates the number of carbon atoms in the acid. It has a T_g of 64°C and a T_m of 243°C (between those of nylon-6 and PET). Nylon-MXD6 has better gas barrier properties than nylon-6 and PET at all humidities and is better than EVOH at 100% RH, due to the existence of the benzene ring in the MXD6 polymer chain (see Figure 2.9). For example, nylon-6 is 5 times as permeable as MXD6 at 0% RH and 12 times as permeable at 75% RH (Brown, 1992). Biaxially oriented film produced from nylon-MXD6 is used in several packaging applications as it has significantly higher gas and moisture barrier properties and greater strength and stiffness than other PAs. When nylon-MXD6 is blended at up to 50% with nylon-6 or nylon-6,6, it can dramatically improve thermoformability by lowering the thermoforming temperature and, thus, shortening the preheat time; the gas barrier performance is also enhanced.

Together with its high clarity and good processability, the aforementioned properties make nylon-MXD6 film suitable as a base substrate for laminated film structures for use in lidding and pouches, especially when the film is exposed to retort conditions. As the T_g and T_m of nylon-MXD6 are similar to those of PET, blending or coextruding nylon-MXD6 and PET at any ratio give films with good processability. Nylon-MXD6/PET multilayered bottles, made by co-injection molding and stretch blow molding, improve on the gas barrier properties and are used for beer and wine.

In the early 1990s, amorphous polyamides (APAs) appeared in food packages as gas barriers intermediate to the higher barrier EVOH and PVdC copolymer and the lower barrier PET and PVC. Their manufacture involves introducing a ring into the linear nylon chain that prevents crystallization (Brown, 1992). Consequently, they remain in the amorphous state and are, therefore, transparent. An unusual property is the fact that their gas barrier properties improve with increasing absorption of moisture in contrast to "normal" PAs because of their high T_gs (125°C).

2.3.6.7 Acrylonitriles

The ready availability of acrylic acid derivatives from propylene has led to their use in numerous industrial polymer products. AN (sometimes referred to by its synonym vinyl cyanide, especially by those who seek to raise fears about the safety of the polymer as a food contact material since the monomer is carcinogenic), b.p. 70°C, is produced mainly by the ammoxidation of propylene and contains a carbon–nitrogen triple bond.

2.3.6.7.1 Polyacrylonitrile

Polyacrylonitrile (PAN) is produced in quantity as a fiber being commonly referred to simply as "acrylic" and often containing small quantities of other monomers, typically methyl acrylate, methyl methacrylate and vinyl acetate.

The pure nitrile polymer PAN is 49% nitrile and is an amorphous, transparent polymer. It has a relatively low T_g (87°C) and provides an outstanding barrier to gas permeation and exceptional resistance to a wide range of chemicals. However, it is of no commercial value in packaging, due largely to its inability to be melt processed since it degrades at 220°C. It is, therefore, copolymerized with other monomers that impart melt processability, thus making its desirable properties available in a packaging form.

AN can be copolymerized with styrene in a ratio of about 1:3 by weight to yield styrene–acrylonitrile copolymer (SAN), an amorphous and transparent material with a poor gas barrier because of its relatively low AN content. When grafted onto a polybutadiene backbone, the graft copolymer acrylonitrile–butadiene–styrene (ABS) can be produced. However, SAN and ABS find limited use in food packaging apart from the thermoforming of some ABS sheet into trays and tubs for fat-based spreads since it has better ESCR than PS.

2.3.6.7.2 High-Nitrile Resins

2.3.6.7.2.1 Acrylonitrile–Styrene Acrylonitrile–Styrene (ANS) copolymers are produced by combining AN and styrene in a 70:30 ratio. The backbone of ANS copolymers is characterized by a high degree of chain-to-chain attraction as a result of polarity, resulting in chain stiffness and immobility, high T_g and chemical inertness; most of these properties are attributed to the high nitrile content of the copolymer.

The realization of the excellent gas and moisture barriers of these high-percentage AN copolymers, coupled with new and improved molding techniques, led to their development for carbonated beverage packaging in the 1970s but toxicological problems with AN monomer surfaced. The FDA withdrew its sanction for the use of high-nitrile resins in beverage packaging in September 1977 because of concern about potential AN migration from the bottle into the beverage, but amended its position in 1984 to limit the residual AN content of the finished container to 0.1 ppm. This limit can be met with modern processing methods. However, by this time PET had been successfully commercialized for carbonated beverages, gaining a commanding lead that proved impossible to overcome (Brown, 1992).

2.3.6.7.2.2 Rubber-Modified Acrylonitrile–Methyl Acrylate Acrylonitrile–methyl acrylate (ANMA) copolymers have high barrier properties and are made by copolymerizing AN and methyl acrylate (MA) in a 75:25 ratio onto a nitrile rubber backbone (Lund and McCaul, 2009). It was originally developed as a bottle blowing material for carbonated beverages, having good clarity, excellent gas barrier properties and a high resistance to creep. In addition, it has good impact strength and is insoluble in most organic solvents.

ANMA is also produced in film and sheet form and, when laminated with other materials such as LDPE, it is suitable for thermoforming into containers for products such as cheese and meat.

ANS and ANMA copolymers have similar barrier properties, their gas barrier properties being surpassed only by EVOH and PVdC copolymer. However, high-nitrile resins show an affinity for water because of the polarity that the nitrile group imparts to the molecule. Thus, their moisture barrier is lower than that of the nonpolar polyolefins but their polarity does mean that they are resistant to many solvents. ANMA is tougher than ANS because of the rubber content. Furthermore, ANMA can be blown into bottles using conventional bottle-blowing methods, whereas ANS requires stretching to improve toughness.

2.3.7 ADDITIVES IN PLASTICS

Early in the development of the plastics industry it was realized that to obtain better products, additives needed to be added to the base polymer. Within the context of thermoplastics materials technology, the term additive is used to denote an auxiliary ingredient that enhances the properties of the parent polymer without appreciably altering its chemical structure.

In food packaging, all additives should have received clearance by the appropriate food regulatory authority. The problem of the migration of additives from plastic packaging materials into foods is discussed in Chapter 22. In this section, the major additives that could be encountered in plastic food packaging materials will be briefly discussed, together with the reasons for their inclusion in the packaging materials.

2.3.7.1 Processing Additives

The degradation of polymers frequently involves oxidation reactions by a free radical mechanism, and at high temperatures, interaction of O_2 with C–H bonds leads to the formation of hydroperoxide groups. These decompose into very reactive OH radicals and lead to molecular scissions. Because it is practically impossible to eliminate O_2 from the system, additives are used to inhibit oxidation reactions.

This is accomplished by using primary stabilizers or antioxidants such as hindered phenols or aromatic amines, which interrupt the chain reaction by combining with the free radicals; secondary stabilizers or peroxide decomposers such as organic thioesters, phosphites and metal thiocarbamates, which react with hydroperoxides as they are formed; and chelating agents or metal deactivators such as organic phosphites and hydrazides, which protect the polymer by immobilizing metal ions through coordination reactions.

With PVC, heat stabilizers or acid absorbers that retard the decomposition of PVC into HCl and dark, degraded polymers must also be used, and octyltin mercaptide, calcium-zinc compounds and methyltin have been given FDA clearance.

The tendency for polymers such as PVC and polyolefins to stick to metal parts during processing can be reduced by adding lubricants such as PE waxes, fatty acid esters and amides, metallic stearates such as zinc and calcium stearate, and paraffin.

2.3.7.2 Plasticizers

Brittle polymers such as PVC must be plasticized to obtain flexible films and containers. The plasticizer also gives the material the limp and tacky qualities found in “cling” films. About 80% of all plasticizers are used in PVC. Typically, phthalic esters such as dioctyl phthalate (DOP), also known as di-2-ethylhexylphthalate (DEHP), and dioctyl adipate (DOA), also known as di-2-ethylhexyladipate (DEHA), are used, as well as epoxidized oils and low-MW polyesters. Safety concerns about the use of phthalates in food packaging have been raised and are discussed in Chapter 22. Internal plasticization may be brought about by copolymerization as in the case of PVC, which can be copolymerized with vinyl acetate, ethylene or methylacrylate.

2.3.7.3 Antiaging Additives

Aging is the process of deterioration of materials resulting from the combined effects of atmospheric radiation, temperature, O_2, water, microorganisms and other atmospheric agents (e.g., gases), indicating that a chemical modification in the structure of the material has occurred. Antioxidants have already been mentioned under processing aids, but they are also necessary in polymeric films such as PP, which degrade in the atmosphere. BHT has been cleared by the FDA and acts as a free radical scavenger. Organophosphites act as hydroperoxide decomposers. It is common for different antioxidants to be used together for synergistic effects.

UV stabilizers are used to prevent the deterioration of polymeric films by photooxidation. They act by absorbing high-energy UV radiation and releasing it as lower-energy radiation.

2.3.7.4 Surface Property Modifiers

Static electricity is generated on a polymer surface by friction or by rubbing it against another surface. It can also be generated on fast-moving film during converting operations or on filling lines. Antistatic agents are used to prevent the accumulation of electrical charges in polymeric films, an undesirable effect caused by the fact that polymers are nonconductors of electricity. Electrification of films results from a segregation of charges (electrons and ions), which occurs when two surfaces are parted after close initial contact. The addition of ethoxylated fatty amines, polyhydric alcohols and derivatives, and nonionic and quaternary ammonium compounds overcomes the problem; they migrate to the surface and form a conducting layer through the absorption of atmospheric moisture, which permits the discharge of electrons.

In some food packaging applications, moisture tends to condense as small droplets on the internal surface and prevent a clear view of the package contents. The droplets are formed when the polymer surface tension is lower than the surface tension of water, which prevents the formation of a continuous layer of water. The addition of nonionic ethoxylates or hydrophilic fatty acid esters such as glycerol and sorbitol stearate promotes the deposition of continuous films of moisture by increasing the critical surface tension of the polymer surface. These so-called antifogging agents can be applied on the surface of the material or compounded internally in the packaging material at levels ranging from 0.5% to 4%.

Many packaging films or sheets tend to stick together because they are nonconductors of electricity, a phenomenon known as blocking. Blocking (which may develop under pressure during storage or use) can be reduced by incorporating chemicals such as stearamide, calcium stearate, alkylamines and alkyl quaternary ammonium compounds in the polymer prior to processing. Other materials such as colloidal silica, clays, starches and silicones may be applied to the surface either during or after processing to reduce blocking. Anti-blocking agents are used at levels ranging from 0.1% to 0.5%.

2.3.7.5 Optical Property Modifiers

The optical properties of a material from a technological aspect are normally described in terms of their ability to transmit light, exhibit color and reflect light from the surface (i.e., gloss). The majority of food packaging films are not pigmented, although some are colored by the addition of colorants that can be dyes (which are soluble in the plastic and tend to migrate, thus limiting their use) and pigments (which are insoluble in the plastic matrix). The principal pigments for use as colorants in packaging are carbon black, white titanium dioxide, red iron oxide, yellow cadmium sulfide, molybdate orange (consisting of a solid solution of sulfate, molybdate and chromate compounds of lead), ultramarine blue (consisting primarily of a double silicate of aluminum and sodium with some sulfides or sulfates), blue ferric ammonium ferrocyanide, chrome green (Cr_2O_3) and blue and green copper phthalocyanines (Rosato, 1997). The FDA has questioned the use of some of these colorants in packaging material in contact with food, its concern being with colorants that can migrate from the packaging into the food.

2.3.7.6 Foaming Agents

Foaming or blowing agents are used for the production of cellular products and are normally classified into physical and chemical types, according to whether the generation of gases to produce the cells takes place through a physical transition (i.e., evaporation or sublimation) or by a chemical process (i.e., decomposition reactions that result in evolution of gases). In food packaging applications, physical blowing agents are commonly used. After the Montreal Protocol on Substances That Deplete the Ozone Layer entered into force in 1989, chlorofluorocarbons (CFCs) that had been used as blowing agents were replaced by butane and pentane. These have now been largely replaced by CO_2, which results in improved organoleptic properties that have opened up new applications in food packaging. Today, expanded and extruded PS foams are made using mainly CO_2 or sometimes a light aliphatic hydrocarbon such as pentane or butane as the blowing agent. Expanded PET, PP and PVC foams are produced using chemical blowing agents.

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3 Edible, Biobased and Biodegradable Food Packaging Materials

3.1 INTRODUCTION

With the exception of paper-based products, food packaging materials have traditionally been based on nonrenewable materials. This was not always so, and up until the beginning of the twentieth century, packaging materials, together with other industrial products such as inks, dyes, paints, medicines, chemicals, clothing and plastics, were made from biologically derived resources. During the twentieth century, petrochemical-based chemicals replaced biologically derived resources for most of these industrial products. Now, at the beginning of the twenty-first century, increasing attention is being given to sustainability (discussed further in Chapter 23) and the replacement of nonrenewable resources (particularly those derived from petroleum) with those from renewable sources, essentially plant-derived products and by-products from their fermentation.

Every year, about 170 billion tonnes (1 billion = 10^9) of biomass are produced by nature of which only 3.5% (6 billion tonnes) are utilized by mankind. Most of the 6 billion tonnes are used for food, with a third used for energy, paper, furniture and construction, and only 5% for other nonfood purposes such as chemicals and clothing (Shen et al., 2009).

Biobased packaging materials have been defined (Robertson, 2008) as materials derived from primarily annually renewable sources, thus excluding paper-based materials since trees used for papermaking generally have a renewal time of 25–65 years depending on species and country. However, regenerated cellulose film (referred to as cellophane in many countries) and cellulose acetate, which have been available for over a century, will be discussed in this chapter, even though the cellulose is typically derived from trees. Edible films and coatings are included in this definition and they are discussed later.

While it could be argued that fossil resources are biobased and renewable, it takes more than a million years for biomass to be converted into oil that is used as feedstocks to produce plastics. Since the rate of consumption is much greater than the rate of replenishment, mass imbalance is produced in the carbon cycle. In contrast, biobased polymers made from materials such as corn starch can be produced and then converted back into biomass in similar time frames (Kijchavengkul and Auras, 2008).

In this book, the term “bioplastics” is avoided due to ambiguity: it is sometimes used for plastics that are biobased, and sometimes for plastics that are biodegradable, including those that are made from petrochemical-based rather than renewable resources. Instead, the term “biobased plastics” is used to mean plastics derived from biobased materials.

At present, biobased plastics are made from biopolymers such as starch and cellulose and monomers produced from fermented organic materials. There is a large amount of research underway in both academia and industry to improve the performance of packaging materials made from renewable resources, although commercial use of these materials for the packaging of food is still in its early stages. This situation is likely to change quite quickly over the next decade.

Global biobased plastic packaging consumption in 2010 was about 125,000 tonnes with a market value of $454 million (Pira, 2010). This compares with the global annual production of petrochemical-based plastics that exceeds 250 million tonnes of which approximately 40% or 100 million tonnes is used for packaging. North America produces about 26 million tonnes of plastics for packaging; Europe, about 28 million tonnes; Japan, 7 million tonnes and Asia, (excluding Japan) 34 million tonnes. Even with rapid expansion of manufacturing capacity (and assuming equivalent performance), it will be many years before the packaging industry can switch a significant quantity of its production to biobased materials.

Although biobased packaging materials may be biodegradable, this is not the main driving force behind their development. Rather, it is driven by the ambition to replace nonrenewable with renewable resources, thus leading to a more sustainable packaging industry. However, from the public's point of view, the main drivers for the development of biobased packaging are the solid waste problem (particularly the perception of a lack of landfills), the litter problem (which the public feel would be solved if biodegradable packaging were used), and pollution of the marine environment by nonbiodegradable packaging (Ryan et al., 2009). The petrochemical-based plastics used today may take up to 100 years to degrade if exposed to the atmosphere, and longer if placed in a landfill. Of course, glass and metal packaging never degrade, although metal packaging may oxidize (rust) and lose its mechanical integrity.

3.2 EDIBLE PACKAGING MATERIALS

Edible packaging consists of edible films, sheets, coatings and pouches. Edible films (thickness <254 μm) or sheets (thickness >254 μm) are stand-alone structures that are preformed separately from the food and then placed on or between food components or sealed into edible pouches, whereas edible coatings are thin layers of edible materials formed directly onto the surface of the food (Janjarasskul and Krochta, 2010). The function of edible packaging is to offer a selective barrier to retard the migration of moisture, gas transport, oil and fat migration and solute transport; improve the mechanical handling properties of foods; improve the mechanical integrity or handling characteristics of the food; retain volatile flavor compounds and carry food additives such as antioxidants and antimicrobials (Falguera et al., 2011). Many of these functions are identical to those of synthetic, inedible packaging films. Although the most important functional characteristics for a particular application depend on the food product and its primary mode of deterioration, the resistance of an edible film or coating to the migration of water vapor is often a paramount characteristic. Edible packaging materials are inherently biodegradable, which is considered one of their greatest benefits but is also one of their greatest limitations.

The concept of using an edible film or coating to extend the shelf life of fresh foods and protect them from harmful environmental effects is not a novel one. In fact, the idea derives from the natural protective coating such as the skin of some fruits and vegetables. Covering foods with lipid substances such as waxes and fats to retard desiccation is a very old practice. For example, hot-melt paraffin waxes became commercially available in the 1930s for coating citrus fruits to retard moisture loss, and carnauba wax oil-in-water emulsions were developed in the early 1950s for coating fresh fruits and vegetables. Edible collagen casings for meat products such as sausages and sugar or chocolate coatings for confectionery products are both currently used commercially.

Edible coatings and films are not meant to, nor could they ever, replace nonedible, petrochemical-based packaging materials for prolonged storage of foods. The utility of edible films lies in their capacity to act as an adjunct for improving overall food quality, extending shelf life and improving economic efficiency of packaging materials.

The advantages of edible films over traditional petrochemical-based polymeric packaging materials have been listed as follows (Gennadios, 2002):

1. They can be consumed with the packaged product, leaving no residual packaging to be disposed of.
2. Even if the films are not consumed, they could still contribute to the reduction of environmental pollution since they are likely to degrade more readily than petrochemical-based polymers and are produced exclusively from renewable, edible ingredients.

3. They can enhance the organoleptic properties of packaged foods provided that various components such as flavorings, colorings and sweeteners are incorporated into them.
4. They can supplement the nutritional value of foods (this is particularly true for films made from proteins).
5. They can be used for individual packaging of small portions of food, particularly products that currently are not individually packaged for practical reasons such as peas, beans, nuts and strawberries.
6. They can be applied inside heterogeneous foods at the interfaces between different layers of components and tailored to prevent deteriorative intercomponent moisture and solute migration in foods such as pizzas, pies and candies.
7. They can function as carriers for antimicrobial and antioxidant agents and be used at the surface of foods to control the diffusion rate of preservative substances from the surface to the interior of the food.
8. They can be very conveniently used for microencapsulation of food flavoring and leavening agents to efficiently control their addition and release into the interior of foods.
9. They could be used in multilayer food packaging materials together with inedible films, in which case the edible films would be the inner layer(s) in direct contact with the food.

The majority of edible films and coatings contain at least one component that is a high-MW polymer, particularly if a self-supporting film is desired. Long-chain polymeric structures are required to yield film matrices with appropriate cohesive strength when deposited from a suitable solvent. Increased structural cohesion generally results in reduced film flexibility, porosity and permeability to gases, vapors and solutes. As polymer chain length and polarity increase, cohesion is enhanced. A uniform distribution of polar groups along the polymer chain increases cohesion by increasing the likelihood of interchain hydrogen bonding and ionic interactions.

A variety of polysaccharides, proteins and lipids derived from plants and animals have been utilized, either alone or in mixtures, to produce edible films and coatings and these will be briefly described.

3.2.1 POLYSACCHARIDES

Polysaccharides are complex carbohydrates consisting of monosaccharides joined together by glycosidic bonds; they are the most abundant macromolecules in nature and often have a key role in plant energy storage (e.g., starch) or as one of the main structural elements of plants and animal exoskeletons (e.g., cellulose and chitin).

A variety of polysaccharides and their derivatives have been evaluated for potential use as edible packaging because they are abundant, low cost and easy to handle, as well as possessing good film-forming properties. Polysaccharide films exhibit good mechanical and gas barrier properties and are efficient barriers against oil and lipids but offer little resistance to water migration. In common with other hydrophilic films, their functional properties are greatly affected by humidity.

3.2.1.1 Starch

Starch is the main polysaccharide energy storage material in the plant kingdom. It is a mixture of amylose, a linear polymer composed of α-(1→4)-D-glucopyranosyl monomers, and amylopectin, a highly branched, high-MW molecule that contains the amylose backbone with side units of D-glucopyranosyl linked by α-(1→6) glycosidic bonds. Due to its predominantly linear nature, amylose forms coherent, relatively strong, free-standing films in contrast to amylopectin films that are brittle and noncontinuous.

To enhance water solubility, partial etherification of high-amylose starch with propylene oxide can be performed to yield hydroxypropylated derivatives. Amylose, high-amylose starch and hydroxypropylated high-amylose starch have been used as protective edible coatings on foods and encapsulating agents to provide an O_2 or lipid barrier and to improve appearance, texture and handling. Edible starch films and coatings are commonly used in bakery, confectionary, batters and meat products (Janjarasskul and Krochta, 2010).

Dextrins (a group of low-MW carbohydrates produced by the hydrolysis of starch) are often used to make various types of coatings on confections as well as edible glues and sealants (Kramer, 2009). The traditional method of manufacturing dextrins is in a dry, heated environment where glucose polymers partially depolymerize and then repolymerize; acid may also be employed. These dextrin products can be soluble in cold water and have fair film formation properties and good adhesive properties. When used in confectionery products, an aqueous coating of dextrins is applied to the outside of chocolate prior to coating with a solvent-based coating such as edible shellacs, often referred to as confectioners' glaze. The undercoating here prevents solvent flavors from migrating from the coating into the chocolate, thus spoiling the flavor (Kramer, 2009).

3.2.1.2 Cellulose

Plant materials are primarily made up of three main types of biopolymers: cellulose, lignin and hemicellulose. Cellulose is the most abundant, naturally occurring polymer on earth and is composed of linear chains of β-(1→4)-D-glucopyranosyl monomers; unlike starch, it is a straight chain polymer with no coiling or branching. The numerous hydroxyl functions in cellulose result in strong hydrogen bonds, creating a physical network that makes the material non-fusible; cellulose is insoluble in aqueous solution. To produce plastic materials from cellulose, a chemical modification has to be performed. This modification often involves the substitution of the cellulose hydroxyl functions (etherification) by acetate or methyl functions, the objective being to decrease the intensity of the hydrogen bonds. The degree and type of substitution and polymer chain length affect permeability, mechanical properties and solubility. The most common cellulose ethers are methylcellulose (MC), hydroxypropyl cellulose (HPC), hydroxypropyl methylcellulose (HPMC) and carboxymethylcellulose (CMC) and all have good film-forming properties. MC has excellent film-making properties, as well as high solubility and efficient O_2 and lipid barrier properties. They have been used commercially to form edible films that provide barriers to O_2, oil and moisture, with MC and HPMC finding use as batter ingredients to lessen oil uptake and moisture loss during deep-fat frying. Water-soluble, edible pouches from MC and HPMC are used commercially to deliver pre-weighed dry food ingredients (Janjarasskul and Krochta, 2010).

3.2.1.3 Hemicellulose

Hemicellulose is a polysaccharide that comprises about 20% of the biomass of most plants, the term hemicellulose being used to describe a number of noncrystalline hexose and pentose sugars including glucose, xylose, mannose, galactose, rhamnose and arabinose. Four main groups of hemicelluloses may be defined according to their primary structure: xyloglycans (xylans), mannoglycans (mannans), β-glucans and xyloglucans. Subgroups are further defined within the main groups. There have been a number of studies on hemicellulose for edible food coatings based on β-glucan extracts from hulled barley, hull-less barley and oats, and corn hull or maize bran arabinoxylan. Xylans from birchwood, grass and corncob have been used as additives in wheat gluten to form potentially edible composite films (Hansen and Plackett, 2008).

3.2.1.4 Chitosan

Chitin is, after cellulose, one of the most abundant polysaccharides produced in nature and is particularly abundant in the exoskeleton of arthropods and the cell walls of insect cuticles. It is an acetylated polysaccharide composed of N-acetyl-D-glucosamine groups linked by β-(1→4) linkages and can be described as cellulose with one hydroxyl group on each monomer substituted with an acetyl amine group.

Chitosan is a versatile, nontoxic, nonantigenic hydrophilic polysaccharide derived from chitin by deacetylation with alkalis; typical commercial chitosan is about 85% deacetylated. It is not currently approved for use in the United States as a food additive. Chitosan films can be formed by casting acidic aqueous solutions, the film properties being strongly dependent on the MW and the degree of acetylation. Chitosan has a broad antimicrobial spectrum to which gram-negative and gram-positive bacteria and fungi are highly susceptible. The effectiveness of chitosan varies and is dependent on the species of microorganisms (Goy et al., 2009). The antimicrobial performance of chitosan has been related to the release or positive migration of protonated glucosamine fractions from the biopolymer into the food (Fernandez-Saiz et al., 2009). A recent review (Aider, 2010) summarized the most important information on chitosan from its bioactivity point of view and highlighted various preparative methods used for chitosan-based active biofilms and their potential for applications in food packaging.

Another recent review (Friedman and Juneja, 2010) suggested that low MW chitosans below pH 6 present optimal conditions for achieving desirable antimicrobial and antioxidative–preservative effects in liquid and solid foods. The effects of chitosan coating on the shelf life of fresh-cut products such as strawberries, carrot, mango, cantaloupe, pineapple and mushroom have been reported (Tamer and Çopur, 2010); in all cases, microbial growth was inhibited and shelf life increased.

3.2.1.5 Gums

Alginates are extracted from brown seaweeds of the *Phaeophyceae* family and are the salts of alginic acid, a linear copolymer of D-mannuronic and L-guluronic acid monomers. Films produced by the evaporation of water from a thin layer of alginate solution are impervious to oils and greases, good barriers to O_2 but have high water vapor permeabilities. Calcium ions are used as gelling agents to bridge alginate chains together via ionic interactions. Alginate coatings effectively lessen desiccation in enrobed meats by acting as a sacrificing agent and, because of their good O_2 barrier properties, can protect foods against oxidation.

Carrageenan is a collective term for polysaccharides extracted from certain species of red seaweed of the *Rhodophycae* family, the species known as Irish moss (*Chondrus crispus*) being the most well known. Carrageenan is a complex mixture of at least five distinct polymers based on galactose. Carrageenan has been applied to a variety of foods to carry antimicrobials and to reduce moisture loss, oxidation or disintegration (Nieto, 2009).

Agar is a gum derived from a variety of red seaweeds of the *Rhodophyceae* family and, like carrageenan, is a galactose polymer. It forms strong gels characterized by melting points far above the initial gelation temperature. Agar coatings containing water-soluble antibiotics and the bacteriocin nisin have been used on flesh foods.

Pectins are water-soluble, anionic polymers composed mainly of α-(1→4)-D-galacturonic acid units that can be methylated to varying degrees. The differences in methyl ester content and degree of esterification affect solubility and gelation properties of pectin. Although pectinate coatings are not adequate moisture barriers, they can retard water loss from enrobed food by acting in a sacrificial manner when moisture evaporates from their gel matrix rather than dehydrating the food significantly. Pectin coatings have also been investigated for their ability to retard lipid migration and improve handling and appearance of foods.

3.2.2 LIPIDS

Lipid compounds have been utilized as protective coatings for many years but since they are not polymers, they do not generally form coherent, stand-alone films. However, they can provide gloss and, because of their relatively low polarity, a moisture barrier (Debeaufort and Voilley, 2009). Waxes (esters of a long-chain fatty acid with a long-chain alcohol) including natural waxes such as carnauba wax, candelilla wax, rice bran wax, beeswax and synthetic waxes such as paraffin and petroleum wax, as well as mineral and vegetable oils, have been used commercially since the 1930s as protective coatings for fresh fruits and vegetables. Generally, wax coatings are substantially more resistant to moisture transfer than most other lipid or nonlipid edible coatings. Wax-, fat- and oil-based coatings can be difficult to apply due to their thickness and greasy surface, and may also confer a waxy or rancid taste (Baldwin, 2007).

Mono-, di- and triglycerides are the mono-, di- and triesters of glycerin with fatty acids and have been used as coatings, as have acetylated glycerides. Acetylated glycerol monostearate coatings are slightly more permeable to water vapor than PA and PS films and significantly more permeable than LDPE films; they are less permeable to O_2 than PS films. Certain application and sensory problems have been reported with acetylated monoglyceride edible coatings, including a tendency to crack and flake during refrigerated or frozen storage, to pick up foreign odors and to exhibit an acidic or bitter aftertaste (Bourlieu et al., 2009). Unsaturated glycerides and acetylated glycerides may be susceptible to oxidation. Fatty acids, fatty alcohols and sucrose fatty acid esters can also be used as lipid coatings.

Edible resins such as shellac, terpene resin and wood rosin are used to impart gloss to food commodities. Shellac has been used extensively as an edible coating for confectionary and fresh produce (Baldwin, 2007).

3.2.3 PROTEINS

Films and coatings are made from animal and plant proteins including collagen, gelatin, wheat gluten, corn zein, soy protein, whey protein (WP) and casein. Due to their inherent hydrophilicity and the significant amounts of hydrophilic plasticizers such as glycerin and sorbitol incorporated into protein films to give them flexibility, they have limited resistance to water vapor. Protein-based films generally have good mechanical and optical properties, are good barriers against the transport of O_2, CO_2, aroma and lipids but have high WVP. The barrier and mechanical properties of protein films are compromised by moisture owing to their inherent hydrophilic nature (Janjarasskul and Krochta, 2010). To improve the barrier and mechanical properties of protein films, physical, chemical and enzymic protein cross-linking treatments have been used.

When used as coatings on flesh foods, protein materials are susceptible to proteolytic enzymes present in these foods. Also, given the increasing number of individuals who are allergic to specific protein fractions from milk, egg white, peanuts, wheat, soybeans and so on, the use of protein films and coatings must be clearly identified on the label.

Collagen sausage casings are made from the regenerated corium layer of beef hides; gelatin is derived from partial hydrolysis of collagen. Collagen film overwrap on refrigerated and thawed beef round steak reduces exudation without significantly affecting color or lipid oxidation; collagen-based films have been proposed for processed meats to reduce shrink loss, increase juiciness, allow for easy removal of nets after cooking or smoking and absorb fluid exudates for a variety of cooked meat products. Gelatin coatings can reduce O_2, moisture and oil migration or carry bioactive ingredients. Gelatin is widely used as an encapsulating agent in hard and soft gel capsules for low moisture or oil-based food ingredients and dietary supplements (Baldwin, 2007).

Milk proteins used as edible films and coatings are made from casein as well as WP. WP films and coatings have been used as protective barriers to reduce O_2 uptake and rancidity in roasted peanuts and frozen salmon, as well as disintegration of fragile freeze-dried foods. Incorporating ascorbic acid into WP films confers an O_2-scavenging function and such films reduce the OTR and retard lipid oxidation in coated peanuts, baby formula, peanut butter and mayonnaise (Janjarasskul and Krochta, 2010). WP isolate reduced fat uptake in fried chicken breasts by 30% (Dragich and Krochta, 2010).

Cereal proteins used to form edible films include corn zein (made from the prolamin (alcohol-soluble) fraction of corn proteins) and wheat gluten (a mixture of the prolamin and glutelin fractions of wheat proteins). Zein is insoluble in water except at very low or high pH and is insoluble in anhydrous alcohols. Zein is one of a few proteins used as a commercially successful finishing agent imparting surface gloss and acting as an O_2, lipid and/or moisture barrier for nuts, candies, confectionery products and other foods (Janjarasskul and Krochta, 2010).

Edible films and coatings have also been made from the globulin protein fractions of soybeans and peanuts, fish myofibrillar protein, egg white protein, keratin, peanut protein, rice protein, pea protein and sorghum protein.

3.2.4 COMPOSITE MATERIALS

Multicomponent or edible composite packaging materials have been developed by blending biocomponents for specific applications with the aim of taking advantage of complementary functional properties or to overcome their respective flaws (Janjarasskul and Krochta, 2010). Edible films based on polar biopolymers (polysaccharides and proteins) are generally efficient gas barriers and have moderately good mechanical properties at low RH, but both properties markedly degrade at high RH. In addition, proteins and polysaccharides give water-sensitive films with poor moisture-barrier performance. In contrast, hydrophobic lipids are effective against moisture migration but their mechanical properties are much inferior to those of hydrocolloid films because of their nonpolymeric nature. Most of the composite films studied to date consist of a lipid layer supported by a polysaccharide or protein layer, or lipid material dispersed in a polysaccharide or protein matrix. The lipid components in the formulation reduce water transmission while the other components serve as selective gas barriers and provide strength and structural integrity.

Multicomponent films are formed by two basic techniques. The coating technique involves casting or laminating a lipid onto a dried edible base film to form a bilayer or laminated film. The emulsion technique involves adding a lipid to a film-forming solution prior to film casting and creating an emulsified film (Wu et al., 2002).

Considerable data are available on the water vapor and O_2 permeabilities of edible films (Krochta, 2009; Janjarasskul and Krochta, 2010). However, a comparison of edible film properties must be approached with caution as plasticizer content and test conditions (in particular RH and temperature) have a significant effect on film properties and are not always clearly indicated in the published literature.

Compared to LDPE, polysaccharide and protein films are poor moisture barriers. However, when they are combined with edible waxes or fatty acids, relatively good moisture barrier properties are obtained (in the best cases, approximately twice the WVTR of LDPE). Protein films appear to be better O_2 barriers than polysaccharide or lipid films, with permeabilities approaching that of EVOH at low-to-intermediate RH.

The mechanical and permeability properties of edible films and coatings have recently been reviewed (Lacroix, 2009). Table 3.1 presents data on the permeability of a range of edible films to O_2, CO_2 and water vapor; the significant influence of RH on permeability is clearly evident.

3.2.5 FILM ADDITIVES

A number of materials are incorporated into edible films to enhance structural, mechanical and handling properties or to provide active functions to the films (Janjarasskul and Krochta, 2010).

3.2.5.1 Plasticizers

To improve film flexibility and durability, plasticizers are generally added to edible films. These include mono-, di-, or oligosaccharides such as glucose, fructose–glucose syrups and sucrose; polyols such as glycerol, sorbitol, glyceryl derivatives and polyethylene glycols; lipids and derivatives such as phospholipids, fatty acids and surfactants and, in the case of polysaccharide and protein films, water.

3.2.5.2 Emulsifiers

Emulsifiers are essential to achieve sufficient surface wettability to ensure proper surface coverage and adhesion to the coated surface as well as for the formation and stabilization of well-dispersed lipid

TABLE 3.1
Reported Permeability Coefficients of Edible Films

Film	Temperature (°C)	RH (%)	Permeability (*Barrer*)		
			O_2	CO_2	H_2O
Beeswax	25	0	0.72		
Beeswax	26	100			0.137
Carnauba wax	25	0	0.12		
Carnauba wax	28	100			0.150
Chitosan	25	0	0.0009		
Chitosan	25	93	0.71	23.9	
Corn zein	38	0	0.052	0.64	
Methylcellulose	30	0	0.78	89.3	
Methylcellulose	24	50	0.15		
Pectin	25	96	2.0	63.6	
Sodium caseinate	25	81			57.0
Starch	25	100	1.62		
Wheat gluten	25	0	0.0015	0.021	
Wheat gluten	25	95	1.93	10.97	
Bilayer films					
Methylcellulose/beeswax	25	0–100			0.077
Methylcellulose/carnauba wax	25	0–100			0.045
Methylcellulose/paraffin wax	25	22–84			0.27–0.53
Emulsion-based films					
Gluten + oleic acid	30	0–100			10.5
Gluten + paraffin wax	25	22–84			2.27
Sodium caseinate + beeswax	25	0–100			14.8–56.6
Whey protein + beeswax	25	0–90			31.9–63.7

Source: Adapted from Debeaufort, F. and Voilley, A., Lipid-based edible films and coatings, in: *Edible Films and Coatings for Food Applications*, Embuscado, M.E., Huber, K.C. (Eds), Springer Science + Business Media, New York, pp. 135–168, 2009; Janjarasskul, T. and Krochta, J.M., *Annu. Rev. Food Sci. Technol.* 1, 415, 2010.

particles in composite emulsion films. Common emulsifiers include acetylated monoglyceride, lecithin, glycerol monopalmitate, glycerol monostearate, polysorbate 60, polysorbate 65, polysorbate 80, sodium lauryl sulfate, sorbitan monooleate, and sorbitan monostearate. In addition, many proteins have emulsifying properties owing to their amphiphilic nature (Janjarasskul and Krochta, 2010).

3.2.5.3 Antimicrobials

One of the important emerging functions of edible films and coatings is their use as carriers of antimicrobials and antifungal agents to increase the shelf life of foods; they may also be used as carriers of nutrients to increase nutritional value of processed food products (Quezada-Gallo, 2009). Use of edible films and coatings as active delivery systems in foods is a relatively recent concept, although this function has been widely studied and used for pharmaceuticals. The more commonly used antimicrobials are organic acids, chitosan, nisin, the lactoperoxidase system and some plant extracts and their essential oils and these are discussed further under active packaging in Section 15.3.2.4. In selecting an antimicrobial, its effectiveness against the target microorganism and possible interactions among the antimicrobial, the film-forming biopolymer and other food components present must be considered. These interactions can modify the antimicrobial activity and the characteristics of the film (Campos et al., 2011).

The primary advantage of antimicrobial edible films is that the inhibitory agents in these films can be specifically targeted to post-processing contaminants on the food surface (Zaritzky, 2011). Controlling the antimicrobial release from edible films is very important, and, therefore, measurement of the diffusion coefficients of the antimicrobials in edible films is a necessary prerequisite. While antimicrobial coatings may extend the shelf life of foods, their use is never a substitute for proper handling, storage and good manufacturing practices.

Chitosan naturally has antimicrobial activity and is most effective against yeasts and molds, followed by gram-positive and gram-negative bacteria (Fernandez-Saiz et al., 2010). Chitosan also chelates trace metals, thus preventing microbial growth and toxin production.

3.2.5.4 Antioxidants

Antioxidants are added to edible films to delay the start, or slow the rate, of oxidation reactions. Primary or chain-breaking antioxidants are free radical acceptors that delay the initiation or propagation step of autoxidation, for example, butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate and tertiary butylhydroquinone. Secondary or preventive antioxidants retard oxidation by several different actions including chelating pro-oxidant metals, deactivating singlet O_2, absorbing UV radiation, scavenging O_2 or promoting antioxidant activity of primary antioxidants, for example, citric acid, ascorbic acid, ascorbyl palmitate and tartaric acid. As well, numerous plants have been identified as sources of natural phenolic compounds with antioxidant activity, for example, herb extracts from rosemary, sage and thyme, and tea catechins (Janjarasskul and Krochta, 2010).

In a recent review of the effectiveness and application of antioxidant films and coatings, Bonilla et al. (2012) emphasized that the efficiency of films and coatings is greatly affected by the water availability in the film. Although an increase in film water content reduces the O_2 barrier properties, it can enhance the chemical action of antioxidants. For this reason, the a_w of the food and the RH of the ambient environment should be taken into account in order to develop effective films and coatings with antioxidant activity.

3.2.6 BIONANOCOMPOSITES

Following on from the extraordinary success of the nanocomposite concept in the area of synthetic polymers (see Section 5.6), considerable research on nanocomposites based on edible polymers has been reported. The use of bionanocomposite materials for edible packaging promises to improve barrier and mechanical properties (Rhim and Ng, 2007; Sorrentino et al., 2007; Azeredo et al., 2009; De Moura et al., 2009). The beneficial effects of inorganic nanofillers on edible materials include improved retention of flavor, acids, sugars, texture and color; increased stability during shipping and storage; improved appearance and reduced spoilage. Additionally, nanoparticles can be used as carriers of antimicrobials and additives.

Azeredo et al. (2009) reported that the incorporation of cellulose nanofibers into a mango puree matrix noticeably enhanced the performance of the resulting films with, for example, a 24% reduction in water vapor permeability at 10% concentration; however, no consumer sensory results were reported.

3.2.7 COMMERCIALIZATION

Despite a considerable amount of published research over the past 20 years, the production of edible films remains largely at the laboratory scale for two major reasons: performance and cost compared with synthetic plastic films. Research on cost reduction and production on larger scales are necessary to promote the feasibility of commercialized edible packaging. Additionally, food manufacturers demand a long shelf life for products in interstate or international commerce. Because edible packaging materials are inherently susceptible to biodegradation, their protective functions are stable for shorter durations than conventional packaging. Therefore, the stability and safety of edible packaging under the intended storage/use conditions require investigation (Janjarasskul and Krochta, 2010).

Converting aqueous solutions into edible films is essentially a coating operation and two converting methods are typically used to manufacture edible films: casting on steel belt conveyors and casting on a disposable substrate (e.g., release paper) on a coating line. Melt extrusion using thermoplastic, edible polymers is also possible, but inherent limitations in the materials and in the process render it impractical for most applications (Rossman, 2009).

Both fresh and minimally processed fruits are highly perishable products and new technologies designed to extend their shelf life and ensure their safety are in demand both in the food industry and by consumers. The main problems when applying edible coatings to minimally processed fruits are the low adherence to the highly hydrophilic cut surface of the fruit as it remains wet for a long time and also the possible presence of liquid exudates. As a consequence, the drying process of the coating on the fruit surface slows down (if drying is possible) and a partial loss of coating integrity could occur (Vargas et al., 2008).

Martin-Belloso et al. (2009) reported on the development of vegetable and fruit edible films as alternatives to the seaweed sheets (nori) traditionally used for sushi and other Asian cuisine. These wraps, produced as soft and pliable sheets using infrared drying, can be made from broccoli, tomato, carrot, mango, apple, peach and pear, as well as a variety of other fruit and vegetable products. They can also be used to contain spices, seasonings, colorants, flavors, vitamins and other beneficial plant-derived compounds. These food films are commercially available in the United States for use in a growing number of food applications such as wraps. Other uses might include snack crackers wrapped with fruit and vegetable films, apple wedges wrapped in peach film and tempura strawberry-wrapped bananas.

3.3 BIOBASED AND BIODEGRADABLE PACKAGING MATERIALS

3.3.1 Classification

Biobased packaging materials are by definition made from renewable raw materials and can be classified according to their origin and method of production as illustrated in Figure 3.1. However, not all of these materials are biodegradable (e.g., biopolyethylene made from sugar) and it excludes biodegradable packaging materials produced from petrochemical-based materials (e.g., poly(butylene adipate-*co*-terephthalate) [PBAT]). Biodegradability is not dependent on the origin of the raw materials but only on the chemical composition of the polymers, and, therefore, biodegradable polymers can be made either from renewable or petrochemical-based raw materials. Therefore, for some purposes, it is helpful to classify biodegradable packaging materials according to their origin and method of production as illustrated in Figure 3.2. While some materials from all four categories are already used for food packaging, others have considerable potential as food packaging materials.

Biobased and/or biodegradable packaging materials can be classified into four main categories according to their method of production:

Category 1: Polymers directly extracted from biomass such as starch, cellulose and chitin
Category 2: Polymers produced by classical chemical synthesis from biomass monomers such as polylactic acid (PLA) and biopolyethylene (bioPE)
Category 3: Polymers produced directly by natural or genetically modified organisms such as the polyhydroxyalkanoates (PHA)
Category 4: Polymers whose monomers are obtained from petrochemical-based monomers such as poly(caprolactone) (PCL), poly(butylene succinate-*co*-adipate) (PBSA) and PBAT

The classification is complicated by the fact that some materials can be produced from either petrochemical-based or biobased monomers (e.g., PGA) and the trend is for more to be produced

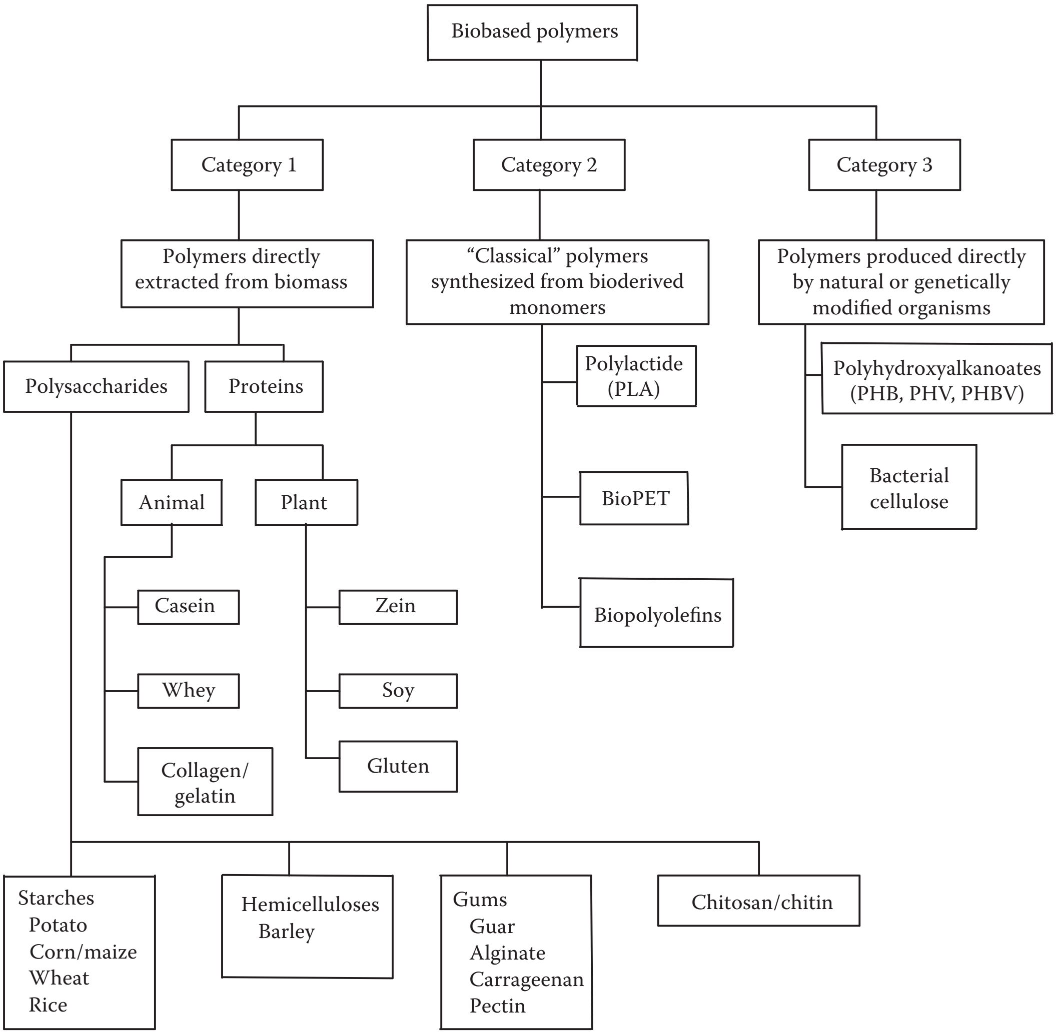

FIGURE 3.1 Classification of biobased packaging materials based on their origin and method of production.

from the latter instead of the former. Vroman and Tighzert (2009) have presented very useful details about many of the biodegradable polymers available commercially.

The major petrochemical-based monomers are butanediol (BDO) and the dicarboxylic acids adipic acid, terephthalic acid and succinic acid. BDO is produced in world-scale plants with different processes and feedstocks including acetylene, butane and butadiene. Compared to BDO, succinic acid is produced on a smaller scale based on maleic acid anhydride (MSA). Adipic acid is based on cyclohexane derived from benzene, and terephthalic acid is based on *p*-xylene (Breulmann et al., 2009).

The production and application of both biobased and/or biodegradable packaging materials is discussed later, but first it is important to clarify exactly what degradability means.

3.3.2 DEGRADABILITY DEFINITIONS

Degradable refers to a material capable of undergoing a significant change in its chemical structure under specific environmental conditions, resulting in a loss of structural integrity and other properties. Degradation is a process that takes place in all materials, the speed depending on the environment. It is important to distinguish between degradability (mechanical disintegration) and biodegradability

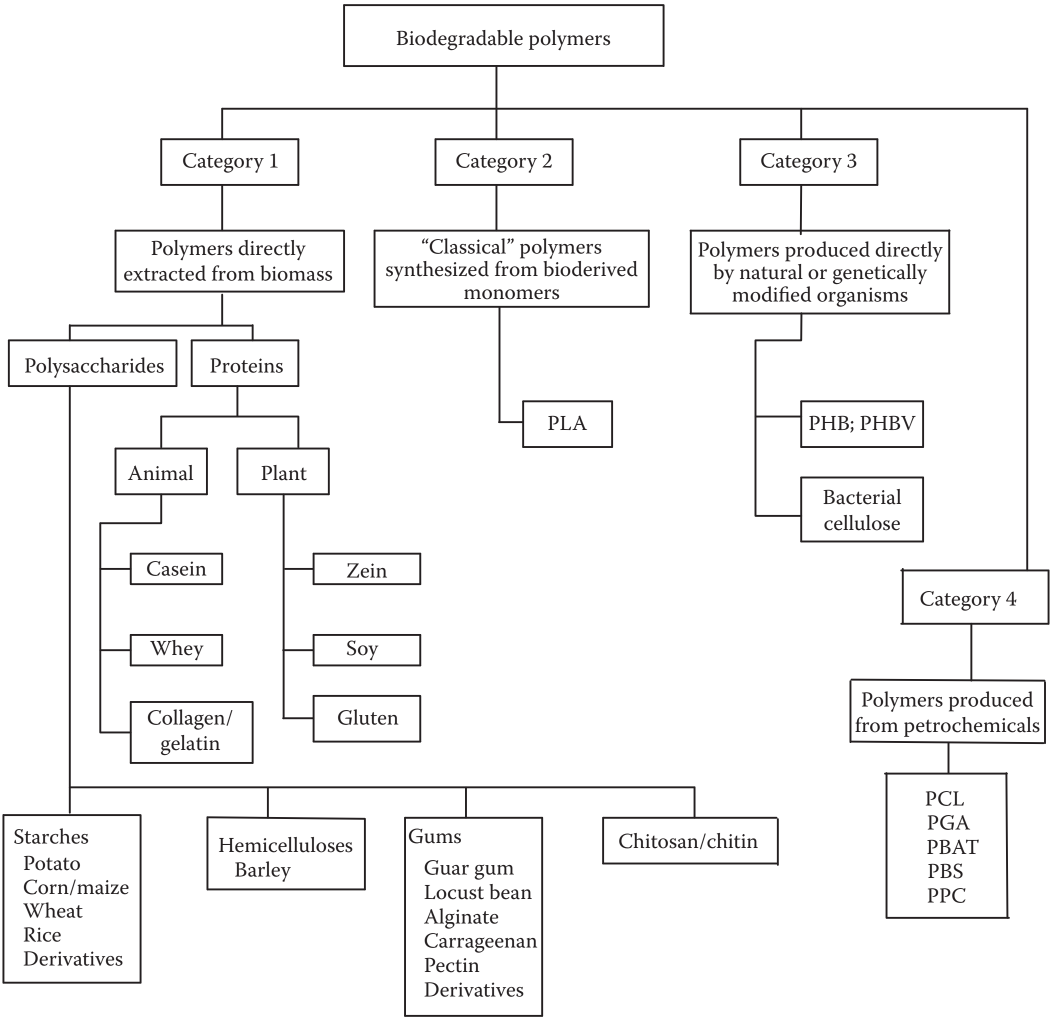

FIGURE 3.2 Classification of biodegradable packaging materials based on their origin and method of production.

(metabolism) because not every polymer that can no longer be seen after a few weeks because it has disintegrated into small pieces has actually been biologically degraded. Two general mechanisms are usually considered for degradable plastics: photodegradation and biodegradation.

Photodegradation is the process by which sunlight (of which UV light is the most significant component), through photooxidation and direct bond cleavage, reduces the MW of polymers so that plastic materials become brittle and disintegrate.

Biodegradation is a process whereby microorganisms such as bacteria, fungi and algae consume a substance as a food source so that its original form disappears and it is completely converted into water, CO_2 and biomass. A standard definition for biodegradable plastics can be found in ISO 472 *Plastics vocabulary and ASTM D883 Standard terms relating to plastics*:

> Biodegradable plastic: a degradable plastic in which the degradation process results in lower MW fragments produced by the action of naturally-occurring micro-organisms such as bacteria, fungi and algae. Under appropriate conditions of moisture, temperature and O_2 availability, biodegradation is a relatively rapid process. In landfills the degradation of even highly biodegradable materials takes place only slowly. Biodegradability has no practical meaning unless the environment, timeframe and context are specified.

Composting is the accelerated degradation of heterogeneous organic matter by a mixed microbial population in a moist, warm, aerobic environment under controlled conditions. Temperatures in a typical compost system are in the range of 40°C–70°C. A compostable plastic is a plastic that undergoes degradation by biological processes during composting to yield CO_2, water, inorganic compounds and biomass at a rate consistent with other known compostable materials and leaves no visually distinguishable or toxic residues (Kale et al., 2007). Therefore, while all compostable plastics are biodegradable, the reverse is not true.

3.3.3 Assessing Biodegradability of Biobased Polymers

Two key steps occur in the biodegradation of polymers. First, a depolymerization or chain cleavage step (hydrolysis and/or oxidation may be responsible) converts the polymer chain into smaller oligomeric fragments. The hydrolytic or oxidative processes may be promoted biotically (in biological pathways) and abiotically (in nonbiological pathways), with oxidation usually a slower process than hydrolysis. The second step (known as mineralization) occurs inside the cell, where oligomeric fragments are converted into biomass, minerals and salts, water and gases such as CO_2 and CH_4.

The biodegradation of plastics depends on both environmental factors (i.e., temperature, moisture, oxygen and pH) and the chemical structure of the polymer or copolymer. Biodegradable polymers usually contain ester, amide or carbonate hydrolyzable bonds in the polymer backbone. The presence of these hydrolyzable functional groups increases their susceptibility to biodegradation. Other factors that affect biodegradability are crystallinity and MW (Tokiwa et al., 2009).

Carbon dioxide that is released as the final mineralization product of biopolymers originates from the renewable carbon source for their biosynthesis. Photosynthetic fixation of the released CO_2 by plants generates renewable carbon sources again. Thus, the carbon flux in the synthesis and degradation of biopolymers is balanced. The main problem arising from incineration is the same as for energy recovery from fuel oil, petrol, gasoline, natural gas and coal: carbon that was fixed over millions of years and that within this time was not part of the natural carbon cycle is converted to CO_2 that eventually accumulates in the atmosphere.

The development of biodegradable polymers has been beset by misinterpretation of the way in which Nature deals with its waste products. In particular, the importance of abiotic (nonbiological) processes has not been given sufficient emphasis in the process of bioassimilation, with the consequence that standards for biodegradable polymers tend to be based on folklore rather than scientific evidence since they ignore completely the environmental role of abiotic chemistry (Scott, 2005).

Complete biodegradation of the product is commonly measured through respirometric tests such as in ASTM D5338, which is equivalent to ISO 14852. In this method, the aerobic biodegradation of polymer materials is determined under controlled composting conditions. This test is more suitable for packaging materials as the inoculum is obtained from composted MSW. Difficulties associated with maintaining the complicated temperature profile of this test have been eliminated in ISO 14855, where a constant temperature of 58°C ± 2°C is specified. This is the most widely used standard test method for the determination of the rate and degree of biodegradation of packaging materials under conditions simulating an intensive aerobic composting process (Jayasekara et al., 2005). The percent biodegradation does not include the carbon converted to cell biomass and not metabolized to CO_2 during the course of the test.

The aforementioned methods all require that the biodegradation of a test material, under aerobic conditions, be determined as the extent of conversion of the carbon substrate to CO_2 as a consequence of microbial attack. The amount of CO_2 evolved is quantitatively compared to the value reached by cellulose, usually taken as a positive control, under the same operating conditions and time. However, it must be recognized that the heterotrophic (organisms that cannot fix carbon and use organic carbon for growth) soil microbial community metabolizes carbon substrates under aerobic conditions both to CO_2 and in the production of new biomass, while some carbon is converted, through chemo-enzymic reactions, to humic substances

(Chiellini et al., 2007). The metabolism of different kinds of carbon substrates, especially in soil, showed that the conversion of highly oxidized materials such as the commonly used reference materials (cellulose or starch) to CO_2 may be significantly overestimated. Therefore, they recommended the use of different reference materials representative of the different classes of carbon substrates in standardized soil biodegradation tests.

The European standard EN13432 *Requirements for packaging recoverable through composting and biodegradation – test scheme and evaluation criteria for final acceptance of packaging* corresponds to D6400. It is worth noting that both the D6400 and EN13432 standards were originally developed for starch-based biopolymers, or hydrobiodegradable polymers, where the mechanism inducing biodegradation is based on a reaction with water. The inherent biodegradation measures the conversion of carbon to CO_2 but there is one significant difference between the two standards: complete biodegradation in the compost as measured by CO_2 evolution in 180 days in D6400 and 90 days in EN13432 (Swift and Baciu, 2006). ISO 17088 *Specifications for compostable plastics* specifies procedures and requirements for the identification and labeling of plastics, and products made from plastics, that are suitable for recovery through aerobic composting. It addresses biodegradation, disintegration during composting, negative effects on the composting process and facility, and negative effects on the quality of the resulting compost, including the presence of high levels of regulated metals and other harmful components. This specification is intended to establish the requirements for the labeling of plastic products and materials, including packaging made from plastics, as “compostable” or “compostable in municipal and industrial composting facilities” or “biodegradable during composting” (for the purposes of this standard, these three expressions are considered to be equivalent).

A major problem with the aforementioned standards is that they evaluate samples of biodegradable materials under laboratory conditions rather than a complete package under real commercial conditions. Kale et al. (2007) determined the degradation process of two PLA packages (a bottle and a delicatessen container) over 30 days under real composting and ambient exposure conditions. Bottles made of 96% L-lactide exhibited less degradation than trays made of 94% L-lactide, mainly due to their highly ordered structure and, therefore, their higher crystallinity.

The procedure to have a package certified as “compostable” is very elaborate (Kale et al., 2007). As well as passing test methods D5338 or ISO 14855, it must meet various other requirements such as the disintegration test, have heavy metals below certain limits and pass the plant growth test for ecotoxicity (based on OECD guideline 208 and included in ISO 13432).

It comes as a surprise to many people to learn that certain natural materials do not meet these standards, for example, a leaf will not naturally biodegrade within the time frame allotted by either D6400 or EN13432.

To identify and quantify the biobased content in a biobased material, the ^{14}C signature is measured. Carbon has three main isotopes: carbon-12 (99%), carbon-13 (1%) and carbon-14 (present at very low concentrations: $^{14}C/^{12}C = 1 \times 10^{-12}$). The CO_2 in the atmosphere is in equilibrium with radioactive $^{14}CO_2$ that is formed in the upper atmosphere through the effect of cosmic ray neutrons on ^{14}N. It is rapidly oxidized to radioactive $^{14}CO_2$, and enters plants and animals on Earth through photosynthesis and the food chain. Plants and animals that utilize carbon in biological food chains take up ^{14}C during their lifetimes and the number of C-14 atoms and nonradioactive carbon atoms stays approximately the same over time. As soon as a plant or animal dies, carbon uptake ceases and there is no replenishment of radioactive carbon, only decay. Since the half-life of carbon is around 5730 years, petrochemical-based feedstocks formed over millions of years will have no ^{14}C signature, the ^{14}C changing to ^{14}N by radio decay. Test method D6866 entitled “Standard test methods for determining the biobased content of solid, liquid, and gaseous samples using radiocarbon analysis” involves combusting the test material in the presence of O_2 to produce CO_2 gas; the $^{14}C/^{12}C$ ratio is compared directly using accelerator mass spectrometry (AMS) with an oxalic acid radiocarbon standard reference material (SRM 4990c) that is 100% new (bio) carbon—actually 0.93 of the reference material to correct for the post-1950 ^{14}C injection into the atmosphere from nuclear testing (Song et al., 2009). The biobased or renewable content of a product is the amount of biobased carbon in the product as a fraction weight (mass) or percent weight (mass) of the total carbon in the product.

3.3.4 OXO-BIODEGRADABLE (OBD) POLYMERS

OBD plastic is typically polyolefin plastic to which has been added a prodegradant (very small [catalytic] amounts of metal salts) to accelerate the reaction of the plastic with atmospheric O_2. Transition metal ions such as iron, cobalt and manganese are the most widely reported prodegradant additives currently in use. OBD plastics are designed to address the problem caused by plastic waste that gets, deliberately or accidentally, into the open environment where it could lie or float around for decades. If collected during its useful life it can be reused and recycled but if not collected, it self-destructs without human intervention, leaving no harmful residues.

As long as the plastic has access to O_2 (as it does in a littered state), these additives catalyze the natural degradation process to speed it up so that the OBD plastic will degrade. Once degraded to small enough particles, they can interact with biological processes to produce water, CO_2 and biomass. The process is shortened from hundreds of years to months for degradation and, thereafter, biodegradation depends on the microorganisms in the environment. However, this process is not fast enough to meet the D6400 standard for definition as compostable plastics.

Oxo-biodegradation is defined as "degradation identified as resulting from oxidative and cell-mediated phenomena, either simultaneously or successively." The first stage is an abiotic process and involves the reaction of O_2 in the air with the polymer resulting in hydroxyl (OH), carbonyl (C=O) and carboxyl (COOH) groups being introduced into the polymer chain; this leads to further oxidation resulting in the formation of smaller molecular fragments. The main factors that influence abiotic oxidation are heat and sunlight. The hydrocarbon polymers change their behavior from hydrophobic to hydrophilic, thereby allowing the fragmented polymer to absorb water. The second stage is the biodegradation of the oxidation products by microorganisms that consume the oxidized carbon backbone fragments to form CO_2, H_2O and biomass (Ammala et al., 2011). Recently, Roy et al. (2011) reviewed the state of the art on the degradability of polyethylene containing pro-oxidants, and the effect these polymers could have on the environment in the long run. They raised questions, particularly in terms of the timescale of complete degradation, environmental fate of the polymer residues, and possible accumulation of toxins. In their view, the answers need to be established prior to accepting these polymers as environmentally benign alternatives to their non-degradable equivalents.

There is a single ASTM standard test method for OBD plastics, namely, D6954 *Standard guide for exposing and testing plastics that degrade in the environment by a combination of oxidation and biodegradation*. The standard compares and ranks controlled laboratory rates of degradation and degree of physical property losses of polymers by thermal and photooxidation processes, as well as the biodegradation and ecological impacts in defined applications and the disposal environments after degradation. The conditions selected for oxidation (UV or thermal at 20°C–70°C) accelerate the degradation likely to occur in a chosen application and disposal environment. The residues resulting from abiotic oxidation are then exposed to appropriate disposal or use environments in standard biometric test methods to measure the rate and degree of biodegradation. Finally, the end-residues must be submitted to aquatic and terrestrial toxicity tests (OCED guidelines 207 and 208) to ensure that they are environmentally benign and not persistent. There is as yet no ISO standard that is the equivalent of this standard, but in 2010, the British Standard BS8472 *Method for the determination of compostability (including biodegradability and eco-toxicity) of packaging materials based on oxo-biodegradable plastics* was released.

Since 2009, PET bottles containing Reverte™ additive have been marketed; it is claimed that they will oxo-biodegrade in a 10–20 year time frame (www.theplanetbottle.net). However, to date, no peer-reviewed studies have confirmed these claims.

It has been reported that montmorillonite (MMT) clay in OBD polyethylene nanocomposites promoted the growth of microbes by keeping the pH of the environment at levels conducive to growth. Reddy et al. (2009) showed that nanoclay, by providing a favorable environment, helped in the growth of microorganisms and their utilization of the polymer surface and the bulk of the polymer volume.

3.3.5 CATEGORY 1

Most of the commonly available Category 1 polymers are extracted from marine and agricultural products; examples include polysaccharides such as cellulose, starch and chitin and proteins such as collagen and soy. They can be used alone or in a mixture with a synthetic biodegradable polymer such as PCL or a biobased, biodegradable polyester such as PLA. In contrast to thermoplastic petrochemical-based polymers that can be melt processed by simply applying heat and shear, the high crystallinity and strong intermolecular interactions present in proteins and polysaccharides lead to their thermal degradation before achieving melt flow (Mensitieri et al., 2011). Therefore, a thermoplasticization process based on a combination of heat, mechanical shear and suitable plasticizers is necessary. The use of plasticizers such as water, glycerol or lactic acid is required to act as internal lubricants, leading to an increase of molecular mobility that promotes melt flow before the occurrence of degradation phenomena. However, using water-soluble plasticizers can result in migration toward and contact with the product (food), leading to either a loss of material properties or pollution of the product (Guilbert et al., 2010).

3.3.5.1 Starch

Of the annually renewable raw materials, those based on starch are the most common. Starch is mainly extracted from cereals (wheat, corn, rice and so on) and tubers (potatoes, manioc and so on). Depending on the botanical origin of the plant, starch granules can have very different shapes (sphere, platelet, polygon and so on) and size (from 0.5 to 175 μm). These granules are composed of amylose, a linear polymer composed of α-(1→4)-D-glucopyranosyl monomers, and amylopectin, a highly branched, high MW molecule that contains the amylose backbone with side units of D-glucopyranosyl linked by α-(1→6) glycosidic bonds. Their proportions in the granules depend directly on the botanical source. Native starch is not a true thermoplastic but can be converted into a plastic-like material called "thermoplastic starch" (TPS). In the presence of plasticizers at high temperature (90°C–180°C) and under shear, starch readily melts and flows, allowing for its use as an extrusion, injection molding or blow molding material, similar to most conventional petroleum-based thermoplastic polymers. Although TPS can be processed in the same way as traditional plastics, its sensitivity to water vapor and poor mechanical properties make it unsuitable for many applications. TPS properties reach equilibrium only after several weeks.

Blending of starch with aliphatic polyesters improves their processability and biodegradability, with PCL and its copolymers being particularly suitable. The combination of starch with a water-soluble polymer such as PVOH has been widely studied since 1970 and is currently used to produce starch-based loose fillers as a substitute for expanded PS, as well as sheet extrusion and thermoforming. To decrease the water sensitivity of starch-based materials, another approach is the chemical modification of the starch chains. The objective of this chemical modification is the substitution of hydroxyl groups by less hydrophilic functions such as acetate groups.

Commercial water-resistant, starch-based bioplastics are produced by using blends of biodegradable petroleum-based polymers and starch. These materials are made with gelatinized starch (60–85%) and hydrophilic (e.g., EVOH) or hydrophobic petroleum-based biodegradable polymers (e.g., PCL or PBAT known as Ecoflex®) and compatibility agents. The polyesters form the continuous phase leading to materials having relative water resistance and acceptable barrier and mechanical properties. The most important starch/polyester-based materials on the market are those produced by Novamont as Mater-Bi® (starch/PCL), Sphere as Bioplast® (starch/PCL), Showa Highpolymer as Bionolle™-Starch (starch/PBSA) and Plantic® (starch/PVOH).

3.3.5.2 Cellulose

Numerous cellulose derivatives can be produced by the dissolution of normally insoluble cellulose, replacement of the hydroxyl groups with different radicals and reclamation from solution to produce films for packaging. Although the cellulose is usually derived from trees and, therefore, does not meet the definition of an annually renewable biobased material, it is biodegradable and, therefore, will be discussed in this chapter.

3.3.5.2.1 Regenerated Cellulose Film

In 1908, the Swiss chemist Jacques E. Brandenburger tried spraying a tablecloth with a viscose solution so that it would repel liquids such as wine rather than absorb them. Although the coated tablecloth was far too stiff, he found that the coating could be peeled off like skin. Three years later, he designed a machine to produce a material he called “cellophane” from the first syllable of “cellulose” and the last syllable of the French word “diaphane” meaning transparent. Although the word cellophane has become a generic term for regenerated cellulose film (RCF), it is a registered trademark of Innovia Films Ltd, United Kingdom. It is important to note that RCF is not a plastic as it will not melt and cannot be formed by pressure and heat.

3.3.5.2.1.1 Manufacturing Process Regenerated cellulose is manufactured from highly purified cellulose usually derived from bleached sulfite wood pulp or, to a limited extent, cotton linters. The pulp, in sheet or roll form, is steeped in sodium hydroxide to form soda cellulose and then shredded. The alkali cellulose is then aged to begin the molecular depolymerization process, after which carbon disulfide is added to form sodium cellulose xanthate.

Viscose is formed by adding dilute sodium hydroxide to the xanthate, causing the cellulose to dissolve into solution. The viscose is then allowed to age or ripen, after which it is extruded through a slot die into acid-salt coagulating and regenerating tanks to give an RCF. Subsequent tanks contain various solutions designed to complete the regeneration, wash out acid carried over from the coagulating bath, remove any elemental sulfur, carbon disulfide or hydrogen sulfide, and bleach the now transparent but still slightly colored film. The film is then run through a bath containing glycerol or ethylene glycol (EG), which act as plasticizers and confer flexibility on the film. Finally, it is passed through a drying oven and wound up as plain, non-moisture-proof film.

RCF can be regarded as transparent paper. If uncoated, it is highly permeable to steam, and when immersed in water, can absorb its own weight of water. Although impervious to gases when dry, in a wet state it is pervious to varying degrees. It is impervious to fats and oils and insoluble in organic solvents. It does not have the same tensile strength as plastic films, and is nonresistant to strong acids and alkalis. As it is flammable, it cannot be heat sealed. Therefore, it is not surprising that it has very few uses in its plain uncoated form.

For food packaging applications, it is always used after various coatings have been applied to one or both sides. The type of coating largely determines the protective properties of the film. Where alternative thicknesses of the film are available, it is the thickness of the cellulose portion that is altered and only minor changes are made to the coating thickness.

3.3.5.2.1.2 RCF Film Coatings There are four types of coatings that can be applied to RCF to confer on it properties that make it a desirable film for food packaging applications:

1. Nitrocellulose—these lacquers contain nitrocellulose, resins, plasticizers, waxes and agents to prevent surface blocking. This is the commonest type of coating and provides a moisture barrier.
2. Poly(vinyl chloride-*co*-vinyl acetate) copolymer coating provides a heat sealable film with an intermediate barrier to water vapor, gases and aromas. It is commonly referred to as copolymer-coated cellophane and certain grades have been approved for use in ovens and microwaves up to 200°C.

3. PVdC copolymer coating is used where protection from moisture ingress is crucial. To increase the moisture barrier further, the film can be metallized.
4. LDPE—this coating is used for premium packaging such as fresh meats where no moisture loss but high O_2 permeability and heat sealability is required.

It should be noted that creasing of moisture-proof cellulose film can adversely affect its water vapor permeability because of damage to the coating. Uncoated RCF is used for twist wrap and lamination applications for products where protection from moisture is not required. In recent years, RCF has been replaced in many food packaging applications by plastic films (especially BOPP), but the recent interest in sustainability has seen a revival in demand.

3.3.5.2.2 Cellulose Acetate

When cellulose is acetylated, all three hydroxyl groups are replaced by acetate ones, that is, cellulose triacetate is formed. This is soluble only in expensive solvents. However, the American chemist Miles found in 1903 that if cellulose acetate is subjected to mild acid hydrolysis such that one of the three acetyl groups is hydrolyzed back to hydroxyl, a cellulose acetate that is soluble in acetone is formed. The product is known as secondary cellulose acetate and will be abbreviated as CA in this book. It appears that it is a sesteracetate (2.5 acetate groups per monomer unit) or, in reality, a primitive form of copolymer, since equal numbers of triacetate and diacetate monomer units must be present.

CA is made in a two-stage process. First, the cellulose is activated by swelling it in a mixture of sulfuric and acetic acids. Second, some acetic acid is removed, and acetic anhydride is added to begin the reaction. When the reaction has proceeded to completion, water is added and hydrolysis occurs until at equilibrium the CA remaining in solution has a DS of approximately 2.5. If the DS falls below 1.88, CA loses its solubility, even in acetone. In the range of DS between 0.85 and 1.35 it becomes water soluble, presumably because the bulky ester groups break up the ordered structure and create greater accessibility.

Although the properties of CA vary with the degree of acetylation and the type of plasticizers used, it is generally a hard, tough material and possesses a sparkling clarity, good gloss and has a high tensile strength when dry. As it has a very faint brown cast, it is common to add a trace of blue dye to counteract this. CA is sensitive to moisture absorption and so is not dimensionally stable when RH changes. Not surprisingly, it has a high rate of water vapor and gas transmission. This property was used to advantage in the packaging of fresh fruits and vegetables. Because it has a low static attraction for dusts, it was also used as a window in products that dust off such as pastas. Although CA is softened by heat, it is not readily heat sealable. Commercially, it is sealed with solvent adhesives such as cellulose acetate dissolved in acetone, or by the use of thermal impulse methods. As well as film form, it can be used as a semirigid container or as a thermoformed blister package. It finds very limited use in food packaging.

Cellulose acetate propionate and cellulose acetate butyrate can be manufactured but their use in food packaging is minimal.

3.3.5.2.3 Microfibrillated Cellulose

Microfibrillated celluloses (MFCs) were first produced in 1983 using wood pulp and a high-pressure homogenizer that promoted the disintegration of cellulosic fibers into substructural fibrils and microfibrils having lengths in the micron scale and widths ranging from 10 nm to a few hundred nanometers. Today, MFCs with diameters in the 10–100 nm range can be produced from various sources such as wood and non-wood fibers, bacterial and animal-derived cellulose. They have generated considerable interest for use in composites, coatings and films due to large specific surface areas, renewability and unique mechanical properties (Spence et al., 2011). They appear to have potential in packaging applications, for example, in transparent films or coatings and as reinforcement in foams and composites. Profitable production of MFC has been restricted by high energy consumption, high cost (due mainly to the difficulties in the extraction of microfibrils without chain cleavage during enzymic or chemical treatment), difficulties with scale-up and runnability problems. However, a plant to produce MFC, which is then used to coat liquid paperboard, commenced production in Finland in 2012.

Cellulose fibrils naturally possess a high surface polarity that prevents them binding well to the hydrophobic surface of the most commonly used petrochemical-based polymers. There are different methods to achieve better adhesion between the two phases and to improve the barrier properties of cellulose materials, for example, chemical modification with acetic anhydride that reacts with the OH groups on the cellulose molecules, thereby making the hydrophilic surface more hydrophobic.

Spence et al. (2011) showed that compared to homogenization, microfluidization with a refining pretreatment and the microgrinding of wood fibers required less energy and produced MFC films with superior physical, optical and water interaction properties than homogenization. They suggested that these materials could be produced in a more economically feasible way for potential packaging applications. To give one example, a more than 700-fold decrease in O_2 permeability of a PLA film when a nanocellulose layer was added to the PLA surface has been reported. The properties of the MFCs also make them interesting materials for reinforcing plastics. Another potential application is the use of MFCs as a surface layer (up to 8% of total basis weight) on base paper to increase the strength of the paper sheets significantly and reduce their gas permeability dramatically. A recent review (Siró and Plackett, 2010) summarized progress in nanocellulose preparation with a particular focus on MFCs; it also discussed recent developments in bionanocomposite fabrication based on nanocellulose.

3.3.5.3 Hemicellulose

There is ongoing research into the use of hemicelluloses for biobased food packaging materials using glucuronoxylan (the primary hemicellulose in hardwood) and arabinoxylan (the primary hemicellulose in annuals such as barley). Surface fluorination of arabinoxylan films has been proposed as a method to produce hydrophobic films with a potential in food packaging. However, no such films have yet been commercialized (Hansen and Plackett, 2008).

3.3.5.4 Chitosan

Although both chitin and chitosan can be extruded to make films for food packaging applications, their main use is as an edible coating to extend the shelf life of fresh fruits and vegetables (see Section 3.2.1.4). Films made only from chitosan lack water resistance and have poor mechanical properties. Both chitin and chitosan have antimicrobial activity, which can be a useful attribute in many food packaging applications to improve quality and extend shelf life.

3.3.5.5 Others

Two of the more common plant proteins used to produce biodegradable plastic films are chickpea and soy protein isolates; other proteins used include those extracted from wheat, pistachio, sunflower and peas. Many other protein-based polymers such as casein, albumin, fibrinogen, silks and elastins have been considered because of their inherent biodegradability but they have not yet found widespread use as food packaging materials since they are difficult to process, do not melt without decomposition, are difficult to blend with most polymers because of their incompatibility and are more expensive than most polysaccharides.

Soy protein isolate films suffer from high moisture sensitivity and low strength. The addition of up to 25% stearic acid results in films with improved tensile and thermal properties as well as reduced moisture sensitivity. Soy protein isolate, glycerol and gellan gum or κ-carrageenan were reported to be suitable to manufacture biodegradable/edible soy-based packaging trays but a moisture barrier must be applied to the trays as they are hydrophilic in nature. Although protein materials have been studied extensively as food packaging materials with recent improvements in properties, a breakthrough leading to commercialization has not yet eventuated. Collagen sausage casings remain the major commercial protein-packaging material. Future packaging applications of proteins are likely to be as edible films.

Recently, biodegradable thermoplastics were developed through graft polymerization of native chicken feather with methyl acrylate. Although poultry feathers are available in large quantities at a low price, natural chicken feathers have poor thermoplasticity, cannot be used to develop thermoplastic products, have very limited industrial applications and are often considered as solid wastes despite being high in β-keratins, a family of fibrous structural proteins. Methyl acrylate was successfully grafted onto functional groups on the surfaces of the chicken feathers, and showed good thermoplasticity; feather films had substantially higher tensile properties than soy protein isolate and starch acetate films (Jin et al., 2011).

3.3.6 CATEGORY 2

3.3.6.1 Poly(lactic acid)

Of all the possible biopolyesters that have been produced from biobased materials, PLA has shown the highest commercial potential and is now produced on a comparatively large scale. Concomitant with commercialization has been a large number of papers published in the scientific literature including a number of reviews (e.g., Avérous, 2008; Jamshidian et al., 2010). There is also a recent book devoted to PLA (Auras et al., 2010) to which the reader is referred for further details.

PLA is a linear, aliphatic polyester synthesized from lactic acid monomers. The ester linkages in the polymer are sensitive to both enzymic and chemical hydrolysis. Lactic acid can be produced cheaply by the fermentation of glucose obtained from the starch in biomass such as corn or wheat, or from lactose in whey or sucrose in molasses.

The dimerization of polycondensed lactic acid into lactide (dilactone of lactic acid) and the ring-opening polymerization (ROP) thereof was reported by the American chemist Wallace Carothers and others from DuPont in 1932. However, because the polymer based on lactyl units was unstable at high humidities, it was not considered to have commercial potential until the 1960s when its advantages in medical applications became apparent.

Lactic acid (2-hydroxypropanoic acid) is one of the smallest optically active molecules; it can be either an L(+) or a D(−) stereoisomer. Lactic acid produced by petrochemical routes is an optically inactive 50:50 mixture of the D and L forms, whereas fermentation-derived lactic acid exists almost exclusively (99.5%) as the L-isomer. Lactide is a six-membered cyclic diester produced from the dehydration of lactic acid and is formed by the condensation of two lactic acid molecules. Because of the chirality of the lactyl unit, lactide exists in three diasteroisomeric forms: L-lactide, D-lactide and *meso*-lactide (Ahmed and Varshney, 2011). These can be in the form of L-lactide (two L-lactic acid molecules), D-lactide (two D-lactic acid molecules) and *meso*-lactide (an L-lactic acid and D-lactic acid molecule).

PLA can be prepared by both direct condensation of lactic acid and by ROP of the cyclic lactide dimer. Because the direct condensation route is an equilibrium reaction, difficulties in removing trace amounts of water during the late stages of polymerization generally limit the ultimate MW achievable by this approach and the focus has been on ROP. In a solvent-free process, a cyclic dimer intermediate called lactide is formed followed by catalytic ROP of the cyclic lactide as shown in Figure 3.3. The ROP requires the use of metal-based catalysts such as oxides or chlorides of zinc and tin or stannous-2-ethylhexanoate, which is the most common. Recently, a one-step production

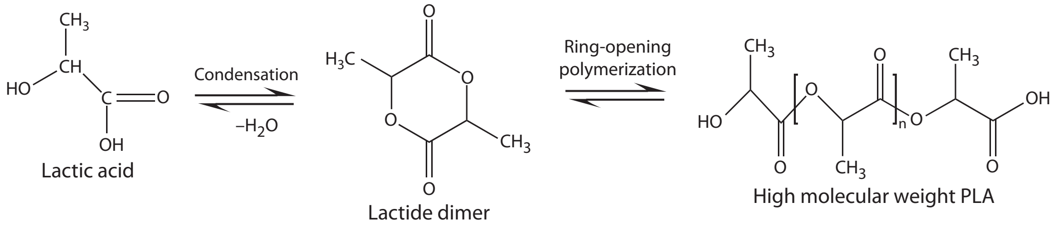

FIGURE 3.3 Reaction scheme to convert lactic acid to PLA.

of PLA homopolymer by direct fermentation of metabolically engineered *Escherichia coli* with a yield of up to 11 wt% PLA from glucose was reported (Jung et al., 2010).

The most common commercial polymers of PLA are optical copolymers of predominantly L-lactide, with small amounts of D- and *meso*-lactides. The properties of polylactides vary to a large extent depending on the ratio and distribution of the two isomers and MW of the polymer.

PLA can be either amorphous or semicrystalline, depending on the stereochemistry and thermal history. Poly(L-lactide) (PLLA) and poly(D-lactide) (PDLA) are semicrystalline polymers, while the atactic polymer, poly(D,L-lactide) (PDLLA) is amorphous. For amorphous PLAs, the T_g determines the upper use temperature for most commercial applications. For semicrystalline PLAs, both the T_g (~58°C) and T_m (130° to 180°C depending on structure) are important for determining the use temperatures across various applications.

The bulk properties of PLA are greatly affected by the MW of the polymer, the chain architecture (branched vs. linear) and the degree of crystallinity, which is determined by the relative proportions of L- and D-lactide in the polymer backbone. The appearance of PLA is also affected by the crystalline content. Amorphous PLA and low crystalline PLA are clear materials with high gloss, while highly crystalline PLA is an opaque white material.

The properties of PLA are similar to LDPE but its rigidity is much higher due to a higher T_g (58°C compared to −25°C for LDPE). PLA biodegrades at temperatures above the T_g; standard PLA is not considered biodegradable according to the ASTM standards but is compostable in industrial composters.

Degradation of PLA is primarily due to hydrolysis of the ester linkages, which occurs more or less randomly along the backbone of the polymer. Two major challenges to the stabilization of PLA with regard to hydrolysis are that it is quite permeable to water and the hydrolysis reaction is autocatalytic. PET is also a polyester that hydrolyzes, but the inherent rate of hydrolysis is slower than PLA and it is not autocatalytic (Henton et al., 2005).

Plasticizers can be added to PLA to decrease its T_g, which results in a lower stress at yield and a higher elongation at break at room temperature, that is, improved flexibility of films and sheets. Citrate derivatives such as tributyl citrate, acetyl triethyl citrate and acetyl tributyl citrate (ATBC) have been added to PLA as well as glyceryl triacetate and acetyl glycerol monolaurate; increases in the elongation at break of 60–100 times have been obtained.

3.3.6.2 Biopolyethylene

Bioethylene is produced by the catalytic dehydration of bioethanol, which can be made by the fermentation of various feedstocks including sugarcane, sugar beet and wheat grain (Morschbacker, 2009). The amount of ethanol needed to make 1 tonne of polyethylene is roughly 2 tonnes since dehydration of the sugarcane-derived ethanol removes half of its weight in water while converting it into ethylene. BioPE has characteristics equivalent to those of conventional polyethylene and can be used in identical applications. From bioethylene it is possible to produce all the polyethylene types: HDPE, LDPE and LLDPE.

The two largest bioethanol from sugarcane producers in the world are based in Brazil and they have formed joint ventures to produce bioPE: Braskem with Toyota Tsusho Corporation and Dow Chemical Company with Crystalsev. Given that polyethylene is the most common polymer used for food packaging, it is expected that many companies will switch to bioPE to lower their carbon footprints and be seen as more sustainable.

Biopropylene (BPP) has been produced via a metathesis (transalkylidenation) reaction of bioethylene with its butane biodimer, a reaction that is presently adopted in countries with a great abundance of natural gas and a shortage of propylene.

3.3.6.3 Biopoly(ethylene terephthalate)

In 2009, The Coca-Cola Company launched PlantBottle™, a PET bottle where the EG is derived from sugarcane rather than from petroleum. EG represents 30% of the total composition of PET plastic by weight.

The remaining 70% is terephthalic acid (TA) derived from petroleum, and research is underway to manufacture biobased TA to make the PlantBottle™ 100% biobased. Research is also underway to extract sugar from plant-based wastes like stems, fruit peels and bark to manufacture EG. The bioPET has identical properties to petrochemical-based PET, that is, it can be recycled but is not biodegradable. The Coca-Cola Company and H.J. Heinz Company have formed a strategic partnership that enables Heinz to produce its ketchup bottles using Coca-Cola's PlantBottle™ packaging technology.

In 2011, PepsiCo announced it had developed the world's first PET plastic bottle made entirely from plant-based, fully renewable resources. The bottle is made from nonfood biomass such as switch grass, pine bark, corn husks and other materials. Ultimately, Pepsi plans to also use orange peels, oat hulls, potato scraps and other leftovers from its food business. In other words, any carbohydrate biomass can serve as the starting material. PepsiCo was to pilot the production of the new bottle in 2012 and move directly to full-scale commercialization on successful completion of the pilot. PepsiCo has found a source of biobased TA, although it have not released details. However, the production of a range of hydrocarbons (including TA) from any carbohydrate source via isobutanol fermentation is being commercialized by several companies and PepsiCo has presumably got access to this technology.

The decision by the two largest users of PET bottles in the world to move toward bioPET is highly significant and effectively signals the demise of rigid, biodegradable, biobased beverage bottles made from PLA. In its 2009/2010 Sustainability Review, Coca-Cola stated that, "A one-use bottle is simply not a viable option for our business. While biodegradable packaging can be a sound choice for products that are not commercially recyclable, the process of capturing the embodied energy and raw materials in beverage bottles for reuse through recycling is, in our view, a much better option." Since recycling streams for PET already exist and are expanding, then by opting for a bioPET bottle, the potential for PLA bottles to contaminate the recycled PET stream is avoided.

In the Netherlands, Avantium is developing a 100% renewable-based polyester like PET by using biobased EG and replacing TA with their platform chemical 2,5-furandicarboxylic acid (FDCA). Dehydration of carbohydrates produces a stable ether derivative of 5-hydroxymethylfurfural (HMF) referred to as RMF. Catalytic oxidation of RMF produces FDCA that can subsequently be polymerized into polyesters by (trans)esterification and polycondensation with a variety of diols.

3.3.7 Category 3

3.3.7.1 Poly(hydroxyalkanoates)

Category 3 polymers consist mainly of the microbial polyesters known generally as PHAs, a family consisting of renewable, biodegradable, biocompatible, optically active polyesters that were first identified in 1925 by the French microbiologist Maurice Lemoigne. They are produced in the form of intracellular particles by many commonly found microorganisms that accumulate PHAs as a carbon and energy sink when grown under nutrient stress in the presence of excess carbon. Under controlled fermentation conditions, some species can accumulate up to 90% of their dry mass as polymer.

PHAs are linear aliphatic polyesters consisting of homo- or copolymers of β-hydroxyalkanoic acids that can be produced from the fermentation of sugars by, for example, *Cupriavidus necator* (originally known as *Alcaligenes eutrophus* and, subsequently, renamed *Ralstonia eutropha* and then *Wautersia eutropha*), the sugar to polymer conversion yield being about 33%. The polymers produced are biodegradable and, due to their characteristics, are suitable for the production of packaging materials. Poly(hydroxybutyrate) (PHB) is the most common and is classed as a short-chain-length PHA (scl PHA) with its monomers containing four to five carbon atoms. By manipulating the growth medium, a random copolymer containing both 3-hydroxybutyrate (HB) and 3-hydroxyvalerate (HV) is obtained: poly(hydroxybutyrate-*co*-hydroxyvalerate) or PHBV (Lu et al., 2009).

PHAs can be decomposed by a PHA-depolymerase detected in several bacteria and fungi in soil, compost or marine sediment. In aerobic environments, the degradation products are CO_2 and CH_4.

In composting trials, up to 85% of the PHA samples degraded within 7 weeks, and PHA-coated paper was rapidly degraded and incorporated into the compost.

PHAs were first developed industrially in the 1960s and commercialized by ICI in the late 1980s under the trade name Biopol®, the first commercial product being a biodegradable, injection blow-molded bottle. Biomer in Munich has produced PHB since 1994 using proprietary bacteria.

Ningbo Tianan Biologic Material Co. Ltd was established in 2000 near Shanghai and is the world's leading producer of PHBV. Other PHA producers include Greenbio in Tianjin, China, and Biocycle in Brazil. Since 2010, Telles, a joint venture between Metabolix and Archer Daniels Midland Company (ADM), has used proprietary technology for large-scale microbial fermentation to produce PHAs under the trade name Mirel® at a commercial-scale plant in Clinton, Iowa.

By changing the ratio of HV to HB, the resulting copolymer can be made to resemble either PP (low HV) or LDPE (high HV) with regard to flexibility, tensile strength and melting point. PHBV has good chemical and moisture resistance as well as good O_2 and aroma barrier properties. The mechanical properties and biocompatibility of PHAs can be further improved by blending with other polymers, modifying the surface or combining PHA with other inorganic materials, thus making them useful for a wider range of applications.

Although the cost of production of PHAs is still quite high, current advances in fermentation, extraction and purification technology, as well as the development of superior bacterial strains, are likely to lower the price of PHAs closer to that of other biodegradable polymers such as PLA and aliphatic polyesters. A combination of more efficient metabolically engineered strains capable of utilizing cheap carbon sources and efficient fermentation strategies will certainly lead to increased efficiency of PHA production (Akaraoyne et al., 2010).

There has been considerable interest in the use of cheap carbon substrates for PHA production since the cost of the carbon source accounts for about 50% of the production costs. Potential substrates include whey, wastewater from olive mills, molasses, corn steep liquor, starchy wastewater and palm oil mill effluent (Koller et al., 2010). Extensive research has begun on the use of CO_2 as the ultimate feedstock for PHA production; *C. necator* has the ability to accumulate a high amount of P(3HB) when CO_2 is employed as a carbon source for PHA production (Akaraoyne et al., 2010).

Because bacterial synthesis is costly, the focus now is on producing PHA plastics and derived chemicals directly in genetically modified crops such as switchgrass (*Panicum virgatum* L.), while concurrently providing biomass for alternative energy generation. Switchgrass grows in high yield on land in the United States, which is of marginal use for other crops. It fixes 2 kg CO_2 in its root system kg^{-1} of biomass aboveground. Sugarcane and soybean are also attractive crops for PHA production. A commercially relevant yield of 7–14% dry weight has been achieved with transgenic sugarcane and switch grass (Guilbert et al., 2010).

Coproduction of energy and PHAs using biomass is seen as the most sustainable approach to biobased material production. It is hoped that direct production of PHAs in plants will achieve economics competitive with those of existing large-volume petrochemical-based polymers. However, the extraction of PHA accumulated in plant materials will not be as easy as extracting PHA from microorganisms. The numerous challenges, both technical and nontechnical, associated with commercializing this technology include achieving a high level of polymer production in the plant without a decrease in crop yield, and economically recovering the polymer from the plant biomass.

3.3.7.2 Bacterial Cellulose

Another Category 3 polymer is bacterial cellulose (BC), an extracellular polysaccharide produced in a highly pure form by several bacteria belonging to the genera *Acetobacter*, *Agrobacterium*, *Alcaligenes*, *Gluconacetobacter*, *Rhizobium* or *Sarcina*. It is considered to have enormous potential within the food packaging industry but so far is unexploited. The cellulose is identical in chemical and physical structure to the cellulose formed in plants but has the advantage that it is not combined with lignin, hemicelluloses and pectin and so can be extracted without the need for harsh chemical treatment. BC is generated as a three-dimensional network of nano- and microfibrils of cellulose with 10–100 nm diameter and possesses unique physical and mechanical properties. In comparison with cellulose from plants, BC has a higher water-holding capacity, crystallinity, tensile strength and Young's modulus. Hydrophilic polymers such as BC normally have very low permeability to gases in the dry state but permeability changes substantially when they are swollen by water. Chemical modification of BC is essentially limited to acetylation, nitration, amination, phosphorylation and hexanoylation, the latter process resulting in a decrease of roughly 50% in both water and gas permeability. No BC films have yet been commercialized for food packaging but this could happen over the next decade. Recent studies have highlighted the potential of BC as a reinforcement in nanocomposites.

3.3.8 CATEGORY 4

The major petrochemical-based monomers are butanediol (BDO) and the dicarboxylic acids TA, adipic acid and succinic acid. BDO is produced from different feedstocks including acetylene, butane and butadiene. Adipic acid is based on cyclohexane derived from benzene, TA is based on *p*-xylene, and succinic acid is produced from maleic acid anhydride. The best known petrochemical-based biodegradable polymers are aliphatic polyesters or aliphatic-aromatic copolyesters.

3.3.8.1 Poly(caprolactone)

PCL (Figure 3.4) is generally prepared from the ROP of ε-caprolactone, which is produced by the oxidation of cyclohexanone produced by the catalytic oxidation of cyclohexane that results from the catalytic reduction of benzene. It is a flexible, aliphatic, semicrystalline polyester that is miscible with many other polymers. PCL has a T_m of 59 to 64°C and a T_g of −60°C. It can be biodegraded aerobically by a large number of microorganisms in various environments. However, the high cost

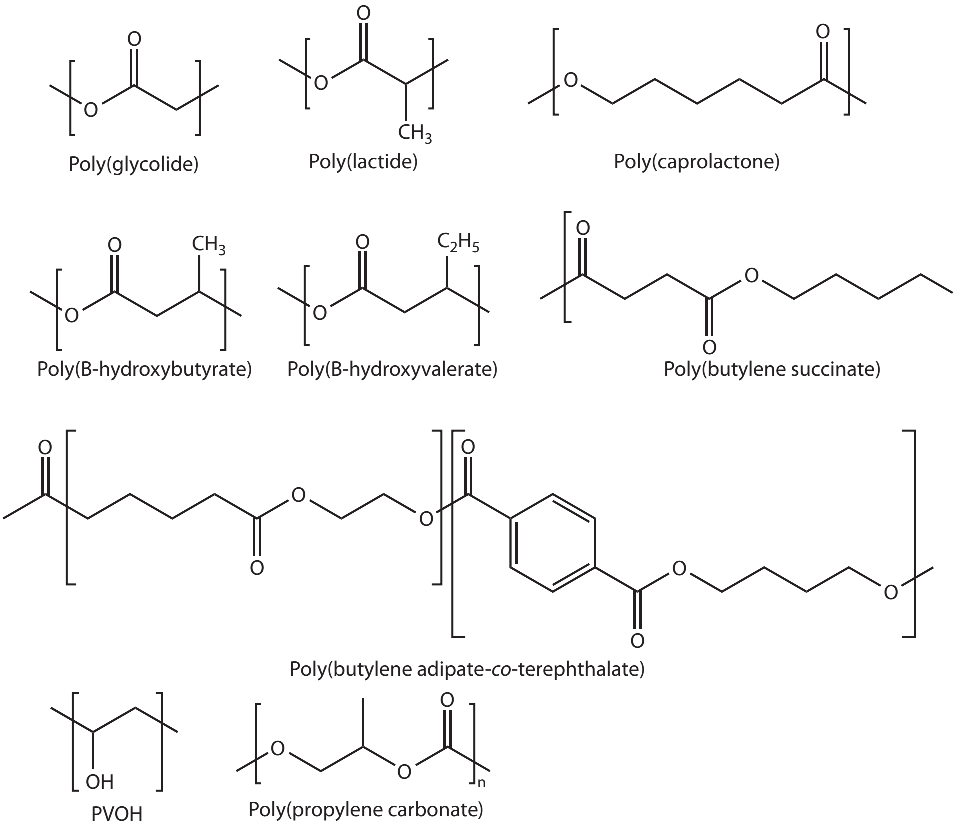

FIGURE 3.4 Structures of some commercially available biodegradable polymers.

and low performance of PCL has prevented its widespread industrial use in food packaging. PCL can be mixed with starch to lower its cost and increase its biodegradability, for example, Mater-Bi produced by Novamont. The PCL limits moisture sensitivity, boosts melt strength and helps plasticize the starch. With PCL contents of up to 20%, starch–PCL films have proved to be excellent O_2 barriers. However, increasing the PCL content beyond this level impaired the O_2 barrier properties while improving the water barrier properties. PCL also finds use as a plasticizer in PVC.

3.3.8.2 Poly(glycolic acid)

Poly(glycolic acid) (PGA) (Figure 3.4) is a biodegradable, thermoplastic polymer and the simplest linear, aliphatic polyester. PGA is highly crystalline (45%–55%), with a high T_m (220°C–225°C) and a T_g of 35°C–40°C. It can be prepared starting from glycolic acid (hydroxyacetic acid) by means of polycondensation or ROP. The reaction also results in the generation of an unwanted by-product (water) that tends to hydrolyze the ester bonds. The Kureha process technology involves creating glycolide rings followed by ROP; this is achieved by maintaining the right solvent at the right concentration. The hydrolysis reaction is also avoided by incorporating proprietary additives and comonomers.

PGA is a polyester resin that offers high gas barrier to both CO_2 and O_2, controllable hydrolysis and excellent mechanical strength, making PGA ideally suited for high performance packaging and industrial applications. The targeted application for PGA is multilayer PET bottles for carbonated soft drinks and beer. Since PGA offers a gas barrier 100 times higher than that of PET, it is possible to reduce the amount of PET used in these bottles by more than 20%, while maintaining the equivalent barrier against CO_2 loss. The multilayer container has sufficient heat resistance to withstand hot filling at 93°C for 20 s.

PGA's unique hydrolytic properties make it highly compatible with widely practiced industrial PET recycling processes, ensuring that the material does not interfere with the purity and quality of recycled PET. In another packaging application, PGA multilayer designs have been shown to enhance the gas and moisture barrier of biobased polymers such as PLA.

Until recently, PGA and its copolymers (poly(lactic-*co*-glycolic acid), poly(glycolide-*co*-caprolactone) and poly(glycolide-*co*-trimethylene carbonate) were widely used only for the synthesis of absorbable sutures. Production of PGA for packaging applications (marketed under the trade name Kuredux®) commenced in the United States in 2011. Kuredux has been certified as a biodegradable plastic in the United States, Europe and Japan and biodegrades into CO_2 and water in compost within 1 month at a similar rate to cellulose.

3.3.8.3 Poly(butylene adipate-*co*-terephthalate)

PBAT (Figure 3.4) is an aliphatic–aromatic copolyester, synthesized from 1,4-BDO, adipic acid and TA. The polymer was developed by BASF especially for applications using compost as the disposal route and was designed to be a strong and flexible material with mechanical properties similar to polyethylene; it is sold under the name Ecoflex. As a consequence, it can be melt-processed on standard polyolefin equipment. Today, these types of polymers offer very good combinations of biodegradation and material properties and can be used for many applications (Eubeler et al., 2010). By adding special additives and optimizing the processing conditions, transparent cling films can be obtained using a blown film process. These films can be used for the packaging of foods, including fresh meats, vegetables and fruits sold in supermarkets. Ecoflex can be blended with starch as well as PLA (e.g., Ecovio® by BASF) to widen its properties while still retaining its biodegradability.

3.3.8.4 Poly(butylene succinate) and Copolymers

PBS (Figure 3.4) and its copolymers are a family of biodegradable polymers with excellent biodegradability, thermoplastic processability and balanced mechanical properties. PBS is usually synthesized via polycondensation of succinic acid (or dimethyl succinate) and BDO. The monomers can be obtained from petrochemical-based or renewable resources. At present, succinic acid is commercially manufactured via hydrogenization of maleic anhydride (which is derived from oxidation of butane or benzene) to succinic anhydride, followed by hydration to succinic acid. Succinic acid can also be obtained from fermentation of microorganisms on renewable feedstocks such as glucose, starch, xylose and so on (Xu and Guo, 2010). While conventional commercial processes for BDO synthesis use petrochemical-based feedstocks, various industrial processes based on renewable feedstocks have been developed and are being commercialized.

Biodegradable aliphatic polyesters, trademarked Bionolle™ and manufactured by Showa Highpolymer, include PBS and PBSA; they are produced through polycondensation reactions of glycols such as EG and 1,4-BDO, and aliphatic dicarboxylic acids such as succinic acid and adipic acid. Bionolle™ polymers are white, crystalline thermoplastics with melting points ranging from 90°C–120°C, T_g's ranging from −45°C to −10°C and density about 1250 kg m^{-3}. They have excellent processability, so they can be processed on conventional equipment commonly used in processing polyolefins at temperatures of 160°C–200°C into various molded products such as injected, extruded and blown ones. A new grade of Bionolle™, which has long chain branches, high melt tension and high recrystallization rate, has been developed to enable stretched blown bottles and highly expanded foams to be made easily.

Terephthalic acid can be copolymerized with succinic acid and BDO to produce the aliphatic–aromatic polyester poly(butylene succinate-*co*-terephthalate) (PBST). 1,3-Propanediol (PDO) can be prepared from four feedstocks: glycerol, ethylene oxide, acrolein and glucose (Kraus, 2008). Polymers based on PDO and TA exhibit a number of advantages over polyesters based on EG or 1,4-BDO and TA. The advantage stems in part from the difference in molecular structure, with the polymer derived from PDO and TA having a zigzag or coil-like shape that translates into a polymer having superior stretching and stretch-recovery characteristics. Recently, bioPDO has been produced commercially from the aerobic fermentation of corn glucose using genetically engineered *E. coli;* it can be copolymerized with succinic acid and BDO to form poly(butylene succinate-*co*-propylene succinate) (PBSPS) copolyester (Liu et al., 2010).

3.3.8.5 Poly(propylene carbonate)

The catalytic coupling of CO_2 with heterocyclic compounds has received considerable attention over the past 40 years, especially the copolymerization of CO_2 and epoxides such as propylene oxide (PO) to form biodegradable polymers. Industrial production of PO starts from propylene and two general approaches are employed: one involving hydrochlorination and the other involving oxidation. PO is produced on a large scale industrially, its major application being the production of polyether polyols for use in making polyurethane plastics.

Poly(propylene carbonate) (PPC) (Figure 3.4) is a form of aliphatic polycarbonate with a backbone consisting of flexible ether linkages (C–O–C) and weak polar carbonate groups; it is hydrophobic. Since PPC is an amorphous polymer with a low T_g, it is common to make polyblends with crystalline biodegradable polymers that can act as physical cross-linking zones to improve the mechanical properties of PPC at elevated temperatures. Many biodegradable crystalline polymers such as PLA, PBS and Ecoflex have been used for such purposes (Qin and Wang, 2010). However, the poor thermal stability and low T_g have limited its applications. To improve the thermal properties of PPC, organophilic montmorillonite (OMMT) has been mixed with PPC by a solution intercalation method to produce nanocomposites (Shi and Gan, 2007). Recently, PPC has been blended with glycerol-plasticized thermoplastic dried starch in a screw extruder to make biodegradable carrier bags.

3.3.9 PROPERTIES OF BIOBASED PACKAGING MATERIALS

3.3.9.1 Barrier Properties

The poor barrier properties (especially under conditions of high humidity) of the traditional and most widely used biobased materials (paper and RCF or cellophane) are well known and it is necessary for them to be coated with synthetic polymers in order to achieve the desired barrier properties necessary for the packaging of many foods. A similar shortcoming limits the use of many of the biobased packaging materials discussed earlier.

Polysaccharide-based films are poor barriers against water vapor and other polar substances at high RH, but at low to intermediate RH, they are good barriers against O_2 and other nonpolar substances such as aromas and oils. WVTRs of starch-based films are four to six times greater than those of conventional films made from petroleum-based polymers. Films based on arabinoxylan from annuals such as barley have low O_2 and CO_2 permeabilities but high water vapor permeabilities; surface fluorination makes them less hydrophilic but such films are not yet commercially available.

PLA has WVTRs four times higher than conventional films; PHAs have WVTRs similar to those of LDPE. The gas barrier properties of many biobased materials depend on the ambient humidity, the two notable exceptions being PLA and PHA. PHB has better O_2 barrier properties than PET and PP, and adequate fat and odor barrier properties for applications with short shelf life products.

The permselectivity β (the ratio of CO_2:O_2 permeability coefficients) of petroleum-based polymers is typically in the range of 4:1–6:1 depending on the nature of the polymer. For PLA, β has been reported as high as 10:1; for starch–PCL as ranging from 4:1 to 14:1 and for wheat gluten 15:1, the latter film being successfully used in laboratory trials for the MAP of mushrooms.

Unfortunately, PLA is a relatively poor barrier to water vapor with a WVTR significantly higher than those of PET, PP or PVC. Biaxially oriented PLA (BOPLA) films have been developed to improve barrier properties. Recently, permeation, sorption and diffusion in PLA were reviewed (Almenar and Auras, 2010). The ratio of L-enantiomers to D-enantiomers (L/D ratio or L:D) has a large effect on barrier properties of PLA. Auras et al. (2004) studied the effect of temperature on the O_2 permeability coefficient P in PLA films containing different L-lactide content (94% and 98%) and exposed to 5, 23, and 40°C; PET films were used as a comparison. A significant increase in P with increasing temperature was observed for both types of PLA, the P values increasing by approximately 10% with each temperature step; PET films showed a similar behavior. The addition of regrind material has been reported to have an effect on the O_2 permeability of OPLA sheets, with a higher value of P for OPLA with 40% regrind content compared to OPLA without regrind. The values of P for CO_2 in PLA films at 0% RH were 1 order of magnitude higher than those of PET and 1 order of magnitude lower than those of amorphous PS.

Bao et al. (2006) used a time-lag method for the determination of gas permeation in amorphous PLA; they found that annealing the PLA film was necessary for reproducible results. Their permeability values were lower than those previously reported by about 1 order of magnitude. For example, at 30°C, O_2 and CO_2 permeabilities in PLA (98.7% L; 1.3% D) were 2.6 and 11.0 *barrer*, respectively, giving a β value of 4.2:1. The differences may be explained by differences in the crystallinity and processing conditions used to produce the films.

The OTR and WVTR of single-screw extruded PHB and PHBV films showed that the PHBV film samples had a higher barrier to O_2 and water vapor than the three PHB copolymer film samples. These results could be attributed to the crystallinity and amount of amorphous content in the samples (Thellen et al., 2008).

The barrier properties of some biobased and petrochemical-based polymers are shown in Tables 3.2 and 3.3. The wide variation in the values reported are due in large part to the physical nature of the films (e.g., some are handmade; others extruded commercially) and variations in test methodology, rather than their inherent barrier properties. Many values reported in the literature are incomplete, with missing data on sample thickness and the temperature and humidity at which measurements were made. Therefore, all the values in these tables should be used with caution. PLA has WVTRs three to five times higher than PET, LDPE, HDPE and OPS; PHAs have WVTRs similar to those of petrochemical-based polymers. PLA has better O_2 barrier properties than PS but not as good as PET; PHB has better O_2 barrier properties than PET and PP and adequate fat and odor barrier properties for applications with short-shelf-life products. Although the gas barrier

TABLE 3.2
WVTR of Some Biodegradable and Nonbiodegradable Polymers

	WVTR (g m^{-2} day^{-1}) at 100% RH			Crystallinity (%)
Polymer (Normalized to 25 μm Thickness)	**6°C**	**25°C**	**49°C**	
Poly(L-lactic acid) (PLA) (crystal)	27	82	333	66
Poly(L-lactic acid) (PLA) (amorphous)	54	172	1100	0
Poly(ε-caprolactone) (PCL)	41	177	1170	67
Poly(butylene-succinate) (PBS) Bionolle™	59	330	2420	41
Poly(butylene adipate-*co*-polycaprolactam)	134	680	3070	
Poly(butylene adipate-*co*-terephthalate) (PBAT) Ecoflex®		272[b]		
Poly(propylene carbonate) (PPC)		64–96[b]		
Poly(glycolic acid) (PGA)			11[d]	
Poly(3-hydroxybutyrate) (PHB)			158–217[e]	
Poly(3-hydroxybutyrate-*co*-3-valerate) (PHBV)-6[a]	1.8	13	124	74
Poly(3-hydroxybutyrate-*co*-3-valerate) (PHBV)-12[a]	3.1	21	204	69
Poly(3-hydroxybutyrate-*co*-3-valerate) (PHBV)-18[a]	3.5	26	245	62
Cellulose acetate (CA)	1020	2920	7900	
Cellulose acetate propionate (CAP)	590	1700	5200	
Ecoflex/PPC/PBS three-layered film		83[b]		
LDPE		4[c]		
Poly(ethylene terephthalate) (PET)		7[c]		
LDPE/PPC/LDPE three-layered film		8.5[b]		

Source: Adapted mainly from Qin, Y. and Wang, X., *Biotechnol. J.*, 5, 1164, 2010; Shogren, R., *J. Environ. Polym. Degrad*., 5, 91, 1997; Thellen, C. et al., *J. Polym. Environ*., 16, 1, 2008.

[a] mol percentage valerate.

[b] 20°C.

[c] 75% RH.

[d] 40°C/90% RH.

[e] 37.8°C/90% RH.

properties of most biobased materials depend on the ambient humidity, PLA and PHA are two notable exceptions. PHBV has good chemical and moisture resistance as well as good O_2 and aroma barrier properties.

The sorption of ethyl acetate and D-limonene in PLA polymers has been determined (Auras et al., 2006). Ethyl acetate permeability coefficients in PLA are lower than those for PP and LDPE and slightly higher than PET. The permeability coefficient for D-limonene in PLA is much lower than for PET, PP and LDPE, thus confirming that PLA is a good aroma barrier when used in food packaging; there is also minimal scalping.

3.3.9.2 Mechanical Properties

The mechanical properties of PLA are determined by the MW of the polymer, chain architecture (linear vs. branched) and degree of crystallinity, with the achievable crystallinity being determined by the relative proportions of L-, D- and *meso*-lactide in the polymer backbone. PLA is a brittle material (tensile strength 40–63 MPa) with a high Young's modulus (2050 MPa) and low elongation at break (EB) (9%) (Table 3.4). Orientation of PLA improves mechanical strength and heat stability, and varying crystallinity and MW results in films ranging from soft and elastic to stiff and high strength. Some limitations do still exist, including the low melt strength (extensibility without breaking of the molten state) and the relatively low temperature at which heat distortion begins to occur. Since PLA is rigid and brittle with a low ability to plastic deformation below its

TABLE 3.3
Oxygen Transmission Rate (OTR) of Biobased and Petrochemical-Based Polymers

Polymer (Normalized to 25 μm Thickness)	OTR (mL m^{-2} day^{-1}) at 0% RH	Temperature (°C)
OPLA	1036	22
PLA	800	23
PLA/NC[a]	336–400	23
PLA-PCL[b]	420	23
PLA (IM)[c]	930	23
PLA-PCL/NC[a]	730	23
PGA	0.9	20
PGA	1.1[d]	20
PHB	269–410	23
PHBV (5%)	193	23
PHBV (8%)	246	23
PHBV (12%)	156	23
PPC	3.4–6.7	20
PBS	403	20
PBAT	470	20
BOPET	20–33	20
BOPP	672	20
PET	174	22
LDPE	7400	23
OPS	9800	22

[a] 5% nanoclay.
[b] 3%–4% caprolactone.
[c] Impact modified.
[d] 90% RH.

T_g (58°C), it is necessary to plasticize PLA in order to produce flexible films. Plasticizers such as water, poly(ethylene glycol) (PEG), lactide, lactic acid, nontoxic citrates, glycerol and sorbitol have been tested and reported as effective for PLA (Almenar and Auras, 2010). The advantage of PEG is that it does not crystallize, has low T_g, and is easily miscible with PLA. The transition from brittle to ductile behavior in plasticized PLA occurs when the T_g is lowered to 35°C.

Amorphous and low-crystalline PLA are clear with a high gloss, while highly crystalline PLA is an opaque white material. PLA has a heat seal initiation temperature of 80°C, and mechanical properties similar to those of PET. It has been shown that hydrolysis of PLA ester linkages results in a 75% decrease in MW and a 35% loss of tensile strength over 130 days at 25°C and 98% RH; no decrease was observed at 5°C (Holm et al., 2006). Despite the well-known hydrolytic effect of water on PLA (Cairncross et al., 2005), it is used commercially on a limited scale for packaging water, the end of shelf life (typically 3–6 months) being when the sidewalls panel and/or the amount of water remaining in the bottle is less than the quantity declared on the label.

The effect of moisture sorption on the stability of PLA films at 11%–98% RH and 5°C and 25°C was investigated by the decrease in number average MW and the loss of tensile strength (Holm et al., 2006). Hydrolysis of the PLA ester linkages resulted in a 75% decrease over 130 days at 25°C and 98% RH. At lower temperatures, the decrease amounted to 35%. An equilibrium moisture sorption isotherm could not be achieved as the irreversible hydrolysis of PLA induced

TABLE 3.4
Mechanical Properties of BioBased and Petrochemical-Based Polymers

Polymer	Melting Temperature T_m (°C)	Glass Transition Temperature T_g (°C)	Young's Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)
Starch[a]		8	100–400	24–30	200–1000
Starch[b]		−20	200–2000	20–30	20–500
Starch	110–115		600–850	35–80	580–820
PBAT	115–120	−30	80	17–23	470–700
PBS	115	−32	645	35	170–560
PBT	221	20–40			24–29
PCL	65	−61	190	14	500
PGA	225	35	7000		600
PHA	70–170	−30–10	0.7–1.8	18–24	3–25
PHB	178	4	1000–2000	25–40	5–8
PHBV[c]	153	5	900		15
PHBV[d]	145	−1	800	20	50
PLA	152	58	2050	40–63	9
PPC		30–41	990–1250	33	640
PTT	228	45–55	1830	180	28–33
PET	267	69	2800–4100	48–72	30–300
PS	240	100	3000–3500	34–50	3–5
LDPE	105–115	−25	300–500	8–20	500–1000
PP	176	−18	1000–2000	30–40	400–900

[a] Film grade.

[b] Injection molding grade.

[c] 7 mol% HV.

[d] 20 mol% HV.

an ongoing moisture uptake. Up to 12 times more water was absorbed at 25°C than at 5°C when PLA was exposed to low and high temperatures at equal RH and for equal amounts of time. After 189 days at 98% RH, moisture sorption was found to be 7 g per 100 g at 5°C and 86 g at 25°C. The amount of water available (the water concentration) differs substantially at different temperatures at the same RH; for example, air at 100% RH has 6.8 g water m^{-3} at 5°C and 23.0 g water m^{-3} at 25°C. A minimum loss of tensile strength was explained by reversible plasticization by moisture. Only at 98% RH and 25°C did loss of tensile strength become distinct (45%). Consequently, PLA material is, in general, expected to be mechanically stable when packaging foods, covering the region from dry to moist food and storage conditions from chill to ambient temperatures.

Patented technology developed for melt blending PLA with 20% of any of several biodegradable aliphatic copolyesters (McCarthy et al., 1999) is said to achieve dramatic improvements in mechanical properties over PLA alone. Elongation can be 200% versus about 7% for plain PLA. The blends reportedly retained their properties after aging, while PLA alone rapidly became brittle. Such results were obtained with blends of PLA plus PCL, Ecoflex, Bionolle™ or PHA. When amorphous PLA was blended with PCL, it resulted in improved mechanical properties and thermal stability without a significant decrease in barrier properties. The toughness of PLA was substantially increased without a reduction in optical clarity by blending a small amount of ductile PHA with PLA.

The physical properties of PHA copolymers can be regulated by varying their molecular structures and copolymer compositions. In general, PHB is a hard, highly crystalline thermoplastic polymer that most closely resembles isotactic PP with respect to mechanical behavior. Although PHB homopolymer is relatively stiff and brittle, the introduction of HV comonomers greatly improves its mechanical properties by reducing the level of crystallinity and melting point, resulting in a decrease in stiffness but an increase in toughness or impact resistance. As a consequence, the PHA family of polyesters displays a wide variety of properties, from hard crystalline plastics to elastic rubbers with melting temperatures of 50°C–180°C.

A random copolymer containing both 3-hydroxybutyrate (HB) and 3-hydroxyvalerate (HV) is thermoplastic, being able to be formed by the same techniques as those used for petroleum-based polymers. By changing the ratio of HV to HB, the resulting copolymer can be made to resemble either PP (low HV) or LDPE (high HV) with regard to flexibility, tensile strength and melting point. For example, the melting temperature decreases from 179°C for PHB with no HV to 137°C with 25% HV.

Overcoming the brittleness of starch while achieving full biodegradability in blends can be accomplished with the addition of biodegradable plasticizers (Viera et al., 2011). Hydrophilic compounds such as polyols (e.g., glycerol and sorbitol) are commonly used in starch films and the effect of type and concentration has been extensively investigated.

3.3.10 Current Limitations

The major limitations of most biobased packaging materials for food applications are their performance, processing and cost (Sorrentino et al., 2007). In particular, brittleness, low heat distortion temperature, poor resistance to protracted processing operations and (with the exception of PHAs) their barrier properties, in particular, their barrier to water vapor, have limited their applications. Cost has declined in recent years and will decline further as production volume is increased and process optimization and in-plant efficiencies achieved. Limited availability is another issue, although construction of additional production capacity will address this.

3.3.11 Methods to Improve Functionality

It is possible to improve the barrier properties of biobased materials (as well as petrochemical-based polymers) using various techniques including metallization with aluminum, coating with thin organic or inorganic layers such as silicon oxide (SiO_x), aluminum oxide (Al_2O_3) and diamond-like carbon (DLC), and the addition of nanoclays (see Section 3.3.12). Coating with SiO_x is the most common commercial technology to increase barrier properties of polymers and PLA bottles have been shown to be compatible with coating processes. For example, a SiO_x coating on PLA reduces the WVTR by 60%.

Since PPC is an amorphous polymer with a low T_g, it is common to make polyblends with crystalline biodegradable polymers that can act as physical cross-linking zones to improve the mechanical property of PPC at elevated temperatures. Many biodegradable crystalline polymers such as PLA, PBS and Ecoflex have been used for such purposes. A PBS and PPC polyblend is regarded as an effective way of improving the dimensional stability of PPC at high temperatures, since PBS has a T_d above 100°C (Qin and Wang, 2010).

3.3.12 Bionanocomposites

The commercial use of films based on biopolymers has been limited because of their generally poor mechanical and barrier properties when compared to petrochemical-based polymers. The use of nanocomposites promises to expand the use of biobased packaging. Bionanocomposites are mixture of biopolymers with nanosized inorganic or organic fillers with particular size, geometry and surface chemistry properties (Chivrac et al., 2009). Several bionanocomposites have been developed by adding reinforcing compounds (nanofillers) to biopolymers, improving their properties and enhancing their cost-price efficiency (Sorrentino et al., 2007). A uniform dispersion of nanofillers leads to a very large matrix/filler interfacial area, which changes the molecular mobility and the consequent thermal and mechanical properties of the material. High aspect ratio fillers such as nanofibers are particularly interesting because of their high specific surface area, providing better reinforcing effects. Bionanocomposites exhibit dramatic enhancements of various material properties including mechanical and flexural properties, heat distortion temperature and O_2 permeability. However, the magnitude of the enhancements strongly depends on the structure of the nanocomposites (Bordes et al., 2009). Ray and Bousmina (2005) have reviewed the use of biodegradable polymers in polymer-clay nanocomposites (PCNs). A more detailed discussion of nanocomposites in given in Section 5.5.

The most studied bionanocomposites are based on nanoclay and polysaccharides, namely, starch and its derivatives, cellulose, chitosan and pectin; these nanocomposite films show improved mechanical properties. Starch has been the most studied polysaccharide in bionanocomposite systems, mainly into its plasticized state but also as blends with PLA, PCL, PBS, PHBV and PVOH or with chemically modified (e.g., acetylated) starch matrices (Tang et al., 2008).

When 4% kaolinite nanofillers were blended with amorphous PLA, it resulted in an increase in O_2 barrier of 43%. The O_2 permeability values were less than half when three types of nanoclays were incorporated into PLA. Rhim et al. (2009) reported that the tensile strength and elongation at break of nanocomposite films prepared with 5 wt% clay in PLA decreased 10%–20% and 11%–17%, respectively, depending on the clays used; the WVTR of the nanocomposite films decreased 6%–33% through nanoclay compounding. A study by Ahmed et al. (2010) indicated that a PLA/MMT blend could serve as an effective nanocomposite for packaging applications; T_g remained unaffected, irrespective of clay concentration, due to the immobilization of the polymer chain in the clay nanocomposite. PLA nanocomposites based on organically modified MMT at 5 wt% loading were prepared by melt blending and then degraded in a commercial compost; the addition of nanoclays was found to increase the PLA degradation rate (Fukushima et al., 2009). Nanobiocomposites of PLA plasticized by polyadipates (15 wt%) with 2.1 wt% of an organo-modified MMT showed enhanced ductility and barrier properties with the OTR being reduced by 25% (Martino et al., 2011).

PHB is generally considered to be a very difficult biopolymer to handle because of significant instability during melt processing and excessive brittleness. Sanchez-Garcia et al. (2010) studied the morphological, thermal and barrier properties of nanobiocomposites of PHB, PCL and commercial organo-modified kaolinite and MMT clay additives. The addition of PCL to the blend lead to a reduction in O_2 permeability and a finer dispersion of the clay. PHB/layered silicate nanocomposites showed improved thermal and mechanical properties and the rate of biodegradation of PHB was enhanced dramatically in the nanohybrids (Maiti et al., 2007).

A PCL-based nanocomposite was the first nanobiocomposite studied in the early 1990s; thermal stability increased and water permeability decreased.

PBS presents many interesting properties, including biodegradability, melt processability, and thermal and chemical resistance, but poor gas barrier properties and softness still limit its use. Therefore, particular attention has been paid to the manufacture of PBS-based bionanocomposites to overcome these issues and to improve the material properties.

PBAT is flexible and has a higher elongation at break than most biodegradable polyesters such as PLA and PBS, and, therefore, is more suitable for food packaging films. However, only a few articles report studies of PBAT/clay bionanocomposites.

The thermal stability, T_g and mechanical properties of PPC were improved by adding OMMT. PPC-OMMT nanocomposite with 4 wt% OMMT showed the best thermal and mechanical properties: tensile strength was three times higher and the T_g 13°C higher than that of pure PPC (Shi and Gan, 2007).

Different parameters such as elaboration route, polymer/clay affinity and clay content can affect the structure and properties of bionanocomposites that can, consequently, be fine-tuned as desired by controlling the parameters previously mentioned (Bordes et al., 2009). A recent article described the mathematical modeling of mechanical and barrier properties of bionanocomposites using analytical micromechanics (Kumar et al., 2011).

Recently, Johansson (2011) reviewed applications of bionanocomposites in food packaging. In addition to those mentioned, other types of bionanocomposites with the potential for use in food-packaging applications have been reported recently. These include clay–cellulose acetate nanocomposites by injection molding; organoclay-WP isolate composites and nanocomposites from biobased furfuryl alcohol formed from furfural (an agricultural residue), in combination with cellulose whiskers or MMT.

A recent review of the opportunities, challenges and strategies for nanotechnology in bioplastics (Lagaron and Lopez-Rubio, 2011) revealed that most applications for packaging have made use of laminar clays and, to a limited extent, carbon nanotubes. Other types of reinforcing elements such as biodegradable cellulose nanowhiskers (CNW) and nanostructures obtained by electrospinning are very promising. These nanobiofillers have a very large surface to mass ratios (up to 103 times higher than a microfiber), excellent mechanical strength (this is true for CNW and some reinforced electrospun fibers), flexibility, lightness and, in some cases, edibility since they can be made from food hydrocolloids.

3.3.13 FOOD PACKAGING APPLICATIONS

Despite considerable research and development, the use of biobased packaging materials for the packaging of food remains limited. The major scientific studies on the packaging of foods in biobased materials have been reviewed (Holm, 2010; Gontard et al., 2011). Although the number of published papers is few, they show that there are many potential applications. At the present time, biobased materials are being used for short shelf life foods stored at chill temperatures, due to the fact that the materials are biodegradable. Potential applications include fast food packaging of salads, egg cartons, fresh or minimally processed fruits and vegetables, dairy products such as yoghurt and organically grown foods. The high CO_2:O_2 permeability ratio of certain biobased packaging materials suggests that they could find application in the packaging of respiring foods such as fruits and vegetables, although conflicting permselectivity ratios have been reported.

The relatively poor water vapor barrier of PLA has been shown to be a factor limiting the shelf life of moist foods. For example, semi-hard cheese packaged in PLA lost moisture, and surface drying was observed after 56 days due to the high WVTR of the PLA; cheese packaged in conventional materials had a shelf life of 84 days (Holm, 2010).

Pettersen et al. (2011) compared PLA- and starch-based packaging materials with APET/LDPE and HDPE packages for fresh salmon fillets stored at 4°C in a modified atmosphere (60% CO_2: 40% N_2) for 5, 7, 9 and 14 days. A relatively high level (log 6 cfu g^{-1}) of total viable counts was detected after 9 and 14 days for fillets stored in biobased and petrochemical-based materials, respectively. After 14 days, the salmon stored in starch-based pouches was regarded as having a lower intensity of freshness compared with APET-LDPE trays and PLA-based pouches. The opposite result was obtained regarding the color of the salmon, where the biomaterials resulted in a higher intensity of fresh color compared with the traditional materials, although the surface of the salmon at the end of the experiment was dry and unpleasant.

Joo et al. (2011) compared the retail shelf life of blackberries packaged in OPLA and OPS containers stored at 3°C and 85% RH for 3 weeks. Although the blackberries demonstrated better quality in the OPS container with less weight loss, blackberries in both OPS and OPLA containers met the "U.S. standard No 1" grade for commercialization for more than 12 days at 3°C.

PLA resins can be tailor-made for different fabrication processes and made into films, coextruded into laminates, thermoformed and injection stretch blow molded into bottles. PLA films can be prepared by the blown double-bubble technology or, preferably, cast tentering, the latter having very low haze, excellent gloss and gas transmission rates desirable for consumer food packaging. PLA films also have superior dead fold or twist retention properties, making them suitable for twist wrap packaging. The major application to date has been as food service containers. Other current uses include thermoformed packaging for bakery products and bags for bread, fresh pasta and salads. Now that production costs are being reduced, PLA is expected to find packaging applications in areas such as coatings for paperboard beverage cartons, plastic film wraps for foods, blister packs and plastic windows in cartons.

On Earth Day in April 2010, FritoLay launched its SunChips® in a 100% compostable, BOPLA bag consisting of a six-layer, 20 μm thick film (PLA-print-adhesive-metallized PLA–PLA sealant) that was 90% by weight PLA. The PLA bags made more noise than the BOPP bags they replaced, and after more than 40,000 consumer complaints that the bags were too loud, they were withdrawn (except for one variety) in October 2010. The bags were relaunched in February 2011 after a different adhesive was employed that absorbed some of the noise.

Because the WVTR is significantly higher for PLA compared to PET (at least 10 times), it is recommended by the resin suppliers that PLA bottles for water have reinforcing features such as ribs to help alleviate paneling of the sidewalls due to water loss. Light weighting the bottle is not recommended; a typical weight for a 500 mL PLA bottle should be 22–24 g. Dosing with N_2 is also recommended to help minimize the impact of altitude change and internal pressure loss in the bottle, which can result in paneling. These same issues need to be addressed with products containing high water content such as juices.

In 2010, Telles launched Mirel F3002 for thermoformed nonalcoholic food contact packaging applications, including cold and hot cups, cup lids, yogurt containers, tubs and trays for meats and vegetables, condiment cups and other single-serve and disposable food packaging. The conditions of use range from frozen food storage to boiling water and include microwave reheating. The material is suitable for storage as well as food service. In addition, the injection molded grade is suitable for caps and living hinge closures, and disposable cutlery. To date, no peer-reviewed publications on the packaging of food with Mirel have appeared.

3.4 ENVIRONMENTAL ASPECTS

Development of biobased packaging materials is predicated on a widely held belief that such materials will have lower environmental impacts than existing petrochemical-based materials. Without this advantage, there is less incentive for industry to adopt biobased packaging materials apart from the obvious advantage of replacing nonrenewable with renewable raw materials, thus leading to a more sustainable packaging industry.

To evaluate the environmental performance of biobased products, a standard practice has been developed and presented in D7075 "Standard practice for evaluating and reporting environmental performance of biobased products." ISO 14040 and 14044 detail the use of life cycle assessment (LCA), a cradle-to-grave analysis tool developed to assess the total environmental impacts of a product (or process) and the system used for manufacturing, use and disposal (or recovery) of that product. It is described further in Section 23.3 of Chapter 23.

LCA studies of biobased polymers generally show reduced environmental impacts and energy use when compared to petrochemical-based polymers. For example, in a cradle-to-grave LCA (Vidal et al., 2007), the production of multilayer film from petrochemical-based polymers (PP–PA6–PP) exhibited 90% higher environmental impacts than the production of biodegradable multilayer film (PLA-starch with PCL-PLA); the films were used to package fresh pasta. However, all LCA studies need to be read closely to ascertain exactly where the specific system boundaries were set and what assumptions were made.

Based on production from sugarcane in Thailand, Groot and Borén (2010) reported the results of a cradle-to-gate LCA for PLLA and compared their results with the environmental profiles of petrochemical-based polymers retrieved from the European Plastics Association's database and representing the average of several production sites in Europe. On a weight-by-weight basis, PLLA resulted in significantly lower emissions of GHG and less use of material resources and nonrenewable energy compared to petrochemical-based polymers. The global warming potential (GWP) for PLLA was 500–800 kg CO_2e tonne^{-1}.

Vink et al. (2010) provided the latest cradle-to-polymer-factory-gate life cycle inventory data for Ingeo® (NatureWorks PLA) as produced for 2009; this followed on from earlier LCAs in 2003 and 2007. The gross nonrenewable energy use (for process and feedstock) from the cradle to the polymer factory gate was 42.2 MJ kg^{-1} Ingeo. The gross nonrenewable energy use for the lactic acid production segment was 20.57 MJ kg^{-1} Ingeo. This 20.57 MJ represents the total or gross energy used to produce and deliver the nonrenewable energy required (electricity, natural gas and steam) in the lactic acid production process, and the energy required to produce and deliver all kinds of operating supplies (water, acids, nutrients and compressed air) as well as the energy required for processing the air and water emissions generated by the lactic acid production facility. The gross GHG take-up (1.94 kg CO_2e kg^{-1} Ingeo of which 95% is built into the polymer backbone) and the gross GHG emissions (total 3.18 kg CO_2e kg^{-1} Ingeo) per production segment, resulted in a net GHG emission of 1.24 kg CO_2e kg^{-1} Ingeo.

A cradle-to-grave LCA of PLA bottles for drinking water compared to PET bottles of identical weight (Gironi and Piemonte, 2011) highlighted that the true advantage of the PLA bottles arose from the use of renewable resources, a factor that is not taken into account in LCAs. However, this benefit was “paid” in environmental terms by the higher impact on human health and ecosystem quality due to the use of pesticides, consumption of land and consumption of water for the production of raw material (corn) for PLA manufacture.

Stonyfield published a non-peer-reviewed LCA of yogurt cups made from PS and PLA based on existing literature and current inventory data (Kuczenski and Geyer, 2010). While PLA production used 22% less total energy and 8% less GHG emissions compared to PS production, it still needed improvement in electricity use and wastewater emissions (during corn production). Fertilizer use for corn was also considered in the study. Toxicity impacts of PLA were many times lower compared to PS, although noxious air emissions were larger for PLA. Other areas of comparison still being studied include water use and environmental assessment of PLA and PS recycling, neither of which is currently practiced in the United States. The independent review of PLA’s environmental impacts found that composting is not the best option for disposing of the cups because composting would release the carbon in the PLA back into the atmosphere as CO_2, where it would contribute to global warming.

A cradle-to-gate LCA study compared the Brazilian PHA production process with petrochemical-based plastics. The study encompassed the net CO_2 production and all major categories of the production cycles. As a conclusion, PHB from the “Brazilian process” turned out to be superior to PP and LDPE in all major LCA categories (Harding et al., 2007).

A cradle-to-gate LCA of PHB derived from corn grain (Kim and Dale, 2008) showed that PHB offered environmental advantages over petrochemical-based polymers in terms of nonrenewable energy consumption and GHG emissions. Most of the energy used in the corn wet milling and PHB fermentation and recovery processes was generated in a cogeneration power plant in which corn stover was burned to generate electricity and steam. PHB provided GHG credits and, thus, PHB use reduced GHG emissions compared to petrochemical-based polymers. However, corn cultivation is one of the environmentally sensitive areas in the PHB production system, and more sustainable practices in corn cultivation such as using no-tillage and winter cover crops could reduce the environmental impacts of PHB by up to 72%. It was suggested that improving process technologies, using cellulosic biomass to provide process energy and utilizing fermentation residues as fuel would further improve the environmental performance of the PHB production system.

A cradle-to-factory-gate LCA by Yu and Chen (2008) using the data of a simulated ethanol plant based on laboratory and pilot plant results indicated that 0.49 kg CO_2e was emitted from the production of 1 kg of PHA resin compared with 2–3 kg CO_2e for petrochemical-based counterparts. The fossil energy requirement per kg of PHA was 44 MJ lower than those of petrochemical-based counterparts (78–88 MJ kg^{-1} resin). About 62% of fossil energy was used for processing utilities and wastewater treatment, and the rest was required for raw materials in different life cycle stages.

Krüger et al. (2009) found that from a climate change point of view, the best end of life (EOL) option for any clamshell (PLA; PET and rPET) was landfill (assuming 0% degradation), followed by incineration with energy recovery and composting. From a nonrenewable energy point of view, the best choice was incineration with energy recovery.

Madival et al. (2009) assessed the environmental profile of PLA, PET and PS clamshell containers for strawberries using LCA methodology. It considered all the inputs such as fertilizers, pesticides, herbicides and seed corn required for the growing and harvesting of corn used for manufacturing PLA. For PET and PS, the extraction of crude oil and the entire cracking processes from crude oil through styrene, EG and TA were considered. The study considered different EOL scenarios in terms of landfill, incineration and recycling but not composting. Global warming, aquatic acidification, aquatic eutrophication, aquatic ecotoxicity, ozone depletion, nonrenewable energy and respiratory organics, land occupation and respiratory inorganics were the selected midpoint impact categories. PET showed the highest overall values for all the impact categories, mainly due to the higher weight of the containers. The main impacts to the environment were the resin production and the transportation stage of the resins and containers. The results were highly site specific since the strawberries were grown and packed on the west coast of the United States, and the resin converted there; however, resin was manufactured in other states.

A comparison of biobased materials (paper, PLA, bioPE and bioPET) as well as conventional ones (PP & LDPE) used data from 13 companies that produced raw materials, films and/or laminates (Hermann et al., 2010). The functional unit chosen was 1 m^2 of packaging film that was (mostly) laminated, printed film delivered on reels to food manufacturers where the laminate was cut, sealed and filled. The impact assessment for nonrenewable energy use, total energy use, global warming potential, depletion of abiotic resources, photooxidant formation, acidification, eutrophication, water use, and land use was presented. The available LCA studies and environmental assessments strongly supported the further development of biodegradable and biobased polymers, but careful monitoring of the various environmental impacts continues to be necessary both for decision makers in companies and those developing public policy. For some materials, the environmental benefits achieved were already substantial; in many other cases, the potentials are very promising and need to be exploited.

Tabone et al. (2010) presented a case study of 12 polymers: seven derived from petrochemicals, four derived from biological sources and one derived from both (bioPET as used in the PlantBottle™ where EG is generated from sugarcane ethanol instead of natural gas). The environmental impacts of each polymer's production were assessed using LCA methodology. Biopolymers exhibited relatively large environmental impacts from production and ranked in the middle of the LCA rankings. Polyolefins ranked 1, 2 and 3 in the LCA rankings, whereas complex polymers such as PET, PVC and PC were placed at the bottom of the rankings with bioPET ranked lowest. In spite of some uncertainties and information gaps, the body of work analyzed overwhelmingly indicated that biodegradable and biobased polymers offer important environmental benefits today and for the future. Of all the materials studied, starch polymers were considered to perform best in environmental terms under the current state of the art, with some differences among the various types of starch polymers. Compared to starch polymers, the environmental benefits seemed to be smaller for PLA (data were only available for energy and CO_2). For PHA, the achievable environmental advantage currently seemed to be very small compared to conventional polymers (data were only available for energy use). For both PLA and PHA, the production method, scale of production and type of waste management treatment can influence decisively the ultimate conclusion about the overall environmental balance.

Most LCAs have found that by replacing petrochemical-based plastics with biobased plastics made from renewable feedstocks, it is possible to reduce GHG emissions. However, most of these studies failed to count the carbon emissions that occur as farmers worldwide convert forest and grassland to new cropland to replace the corn (or sugarcane) diverted to bioplastics (so-called land-use change [LUC] emissions). Converting rainforests, peatlands, savannahs or grasslands to produce food-crop-based bioproducts creates a “carbon debt” by releasing 9–170 times more CO_2 than the annual GHG reductions from bioplastics displacing petrochemical-based plastics. Piemonte and Gironi (2011) compared the LCAs of LDPE and Mater-Bi starch-based shopping bags including LUC. The GHG savings from Mater-Bi would equalize and, therefore, pay back carbon emissions from LUC in about 174 years. It should be stressed that the theoretical models used to calculate the LUC emissions are still under development. If the raw materials needed for bioplastics production are taken from waste biomass or cultivated on fallow, marginal or degraded land where previously no conventional crops were grown, no indirect LUC occurs and the GHG balance can become favorable, leading to a real and instantaneous advantage of biobased plastics compared to petrochemical-based plastics.

As far as the environmental impacts of bioPE and bioPET are concerned, publicly available data are very scant to supports claims that they will reduce GHG emissions. Liptow and Tillman (2012) reported a comparative LCA of LDPE derived from sugarcane or crude oil. LDPE from sugarcane used significantly less fossil fuels and has the potential to significantly reduce emissions of GHGs but it uses more total primary energy and contributes more to acidification and eutrophication. If effects of LUC are ignored, the sugarcane route is the better one with respect to global warming and the use of nonrenewable resources.

Currently, PlantBottle™ is made using sugarcane ethanol from Brazil where most sugarcane is grown on degraded pastures located over 2000 km from the Amazon, so it has a lower impact on biodiversity; the sugarcane is predominantly rain fed and mechanically harvested. An unpublished LCA conducted by Imperial College in London and reviewed by the Institute for Energy and Environmental Research in Germany apparently indicated that the PlantBottle™ reduced carbon emissions by up to 25% and reduced fossil fuel consumption by 10% compared with petrochemical-based PET.

One of the main environmental benefits of bioPE is the sequestration of roughly 2 kg of CO_2 kg^{-1} of polyethylene produced, which comes from the CO_2 absorbed by the sugarcane while growing, minus the CO_2 emitted during the production process. There is also less water consumption because water is generated by the steam during the dehydration of ethanol to ethylene. Vinasse (the material that remains after the ethanol has been removed) is used as a fertilizer in the sugarcane fields as well as in thermophilic digesters to produce biogas (mainly CH_4). Another important by-product is bagasse and it is used to generate energy at the plant with the surplus energy being sold (Morschbacker, 2009).

3.5 FUTURE TRENDS

Numerous factors including political and legislative changes, as well as global demand for foods and energy resources, will influence the development and success of biobased packaging materials (Queiroz and Collares-Queiroz, 2009). However, there is no doubt that the use of biobased materials for food packaging will increase, partly as a result of improvements in mechanical and barrier properties, partly as a result of decreases in costs vis-à-vis petrochemical-based polymers, and partly as a result of their improved environmental profiles. Major supermarket chains are already leading the way by encouraging their suppliers to use biobased packaging materials and this trend is likely to accelerate.

Future biobased food packaging materials are likely to be blends of polymers and nanoclays (so-called bionanocomposites) in order to achieve the desired barrier and mechanical properties demanded by the food industry. Already, important research has been undertaken in this area with some small commercialization; the next decade will see significant production of bionanocomposites for food industry use.

Cost is undoubtedly a limitation to the widespread adoption of biobased packaging materials but as production capacity increases, costs will fall. One barrier to reducing costs is the increase in the production of biofuels that in many cases are competing for the same raw materials (sugarcane, corn and maize) as biobased packaging, putting upward pressure on raw material costs. If PHA is to be economically competitive with synthetic plastics, it must be produced on a far larger scale than any other aerobically produced microbial product. Also, since PHAs are intracellular products, the amount that can be produced per cell has physical limitations.

According to a 2010 report (Pira, 2010), global biobased plastic packaging demand is forecast to reach 0.884 Mt (million metric tonnes) by 2020. A 24.9% compound annual growth rate (CAGR) is expected from 2010–2015, slowing to 18.3% in the 5 years to 2020. Pira expects that the fast-growing GM and bioderived segments will account for a quarter of the total bioplastic packaging market demand by 2020. PHAs are forecast to achieve a CAGR of 41% and bioPE 83% over the period. At the same time, traditional biobased plastic packaging technologies based on starch, cellulose and polyesters are each forecast to show a decline in market share.

In 2010, Europe was the largest market for biobased plastic packaging with demand accounting for more than a 50% share of world tonnage. While North America and Asia are presently lagging behind, growth rates in these two regions are expected to outstrip Europe in the period to 2020. Rigid packaging presently has a 52% share of the biobased plastic segment but the report forecasts that flexible packaging, which currently accounts for the remaining 48%, will take a growing share of the biobased plastics segment up to 2020. Demand will likely be driven by the commercialization of bioPE and PHA and the wider availability and improved properties for BOPLA film.

An earlier report (Shen et al., 2009) indicated that the global capacity of biobased plastics (according to company announcements) will increase from 0.36 Mt in 2007 to 3.45 Mt in 2020. It was projected that the most important materials will be starch plastics (1.3 Mt), PLA (0.8 Mt), bioPE (0.6 Mt) and PHA (0.4 Mt). However, not all of these biobased plastics will be used for packaging; a significant proportion will be used for man-made fibers.

In contrast to fuels and energy, the much lower amount of renewable resources needed for the production of biobased polymers does not result in a significant impact on global food production. Using the figure from the Pira (2010) report, the market for biobased plastics will grow to 884,000 tonnes in 2020. The volume of corn needed for the production of this amount of biobased plastics would equal ~0.1% of the total 800 million tonnes of annual global corn (maize) harvest. Of course, other raw materials like sucrose (from sugarcane or beet) or wheat or rice starch are used and the global annual production is around 1700 million tonnes for sugarcane and over 700 million tonnes each for wheat and rice. When the long-term objective of making cellulosic materials available for monomers (e.g., lactic acid) and biobased plastics (e.g., PLA, PHA) is realized, no competition with food production will exist.

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4 Optical, Mechanical and Barrier Properties of Thermoplastic Polymers

4.1 INTRODUCTION

The range of optical, mechanical and barrier properties of plastics for food packaging is extremely wide, given the possible combinations of thermoplastic polymers, often coupled with laminations using paper or aluminum foil. It is necessary to be aware of just what properties are essential at the package development stage of any application. While the dangers of under-performance of food packaging are usually well understood, over-performance is equally to be avoided in light of the high costs of packaging materials and societal pressures to reduce the quantity of packaging materials used commercially.

In Sections 4.2 through 4.9, a brief overview of the major optical and mechanical properties of plastics is given. For further details on these aspects of plastic polymers the reader is referred to van Krevelen and te Nijenhuis (2009), Furches (2007), Shah (2007) and Mathur and Bhardwaj (2003). Then follows a major section on the barrier properties of plastics.

4.2 OPTICAL PROPERTIES

Optical properties are related to both the degree of crystallinity and the actual polymer structure (Carraher, 2010). There are a number of optical properties of importance with thermoplastic polymers including clarity, haze, color, transmittance, reflectance, gloss and refractive index. The clarity of a film indicates the degree of distortion of an object when viewed through the film, with "see-through" clarity referring to the ability of the film to resolve fine details of fairly distant images viewed through the film.

Many of the optical properties of a polymer are related to the refractive index, n, which is a measure of the ability of the polymer to refract or bend light as it passes through the polymer (Carraher, 2010). Since refractive index is dependent on density, it follows that where the crystalline and amorphous densities of polymers differ, there will be a difference in refractive index. Thus, thick polyethylene objects will be opaque since they cannot be quenched rapidly and the spherulites formed have a significantly higher density (about 1010 kg m^{-3}) than the amorphous region (840–850). In the case of PP, the difference is less marked (crystal density 940; amorphous density 850) and moldings are more translucent. Generally, the refractive index for many plastics is around 1.5.

Amorphous polymers free from fillers or other impurities are transparent unless chemical groups which absorb visible light radiation are present. Generally, crystalline polymers are translucent, but they will be transparent when the crystal structures such as spherulites are smaller than the wavelength of light. However, if the structures are greater in diameter than the wavelength of light, the light waves will be scattered if the crystal structures have a different refractive index to that of the amorphous regions. The clarity of crystalline plastics can be improved by quenching or by random copolymerization.

Light that is scattered on passing through a film or sheet of a material can produce a hazy or smoky field when objects are viewed through the material. *Haze* can be taken as a measure of the "milkiness" or "cloudiness" of an otherwise transparent polymer and is often the result of surface imperfections, particularly in the case of thin films. The appearance of haze with consequent loss of contrast is caused by light being scattered by the surface imperfections, or by inhomogeneities in the film due to voids, large crystallites, incompletely dissolved additives or cross-linked material. Internal haze does not arise with amorphous polymers; with crystalline polymers it increases with the degree of crystallinity and size of spherulites or other forms of crystal aggregates, as well as with the ratio of the density between the crystalline phase and the amorphous phase.

Methods for measuring haze are specified in ASTM D1003 and ISO 14782. Haze is defined in these standards as the percentage of transmitted light which, in passing through a specimen, deviates by more than 2.5° on average from an incident parallel beam by forward scattering from both surfaces and from within the specimen. Although haze measurements are made most commonly using a hazemeter, a spectrophotometer may be used; use of a spectrophotometer can provide valuable diagnostic data on the origin of the haze.

When light falls on a material, some is transmitted, some is reflected and some is absorbed. The transmittance is the ratio of the light passing through to the light incident on the material and the reflectance is the ratio of the reflected light to the incident light.

The *gloss* (strictly speaking specular gloss) of a film has been defined as the degree to which a surface simulates a perfect mirror in its capacity to reflect incident light. Thus, it is a function of the reflectance and the surface finish of a material. Where transmittance and reflectance do not add up to unity, then some of the light waves are absorbed; if this absorption does not occur uniformly over the visible spectrum, the material appears colored. Measurement of the gloss of plastic films and solid plastics, both opaque and transparent, is determined by standard tests (ASTM D523 and D2457) using a device (known as a glossmeter) which measures the percentage of light, incident at an angle (20°, 45° (most common) or 60°) to the surface of the film, that is reflected at the same angle. The fraction of the original light that is reflected is the gloss of the sample; if the specular reflectance is near zero, the surface is said to be matte. Surface roughness, irregularities and scratches all decrease gloss. Gloss is a complex attribute of a surface which cannot be completely measured by any single number.

4.3 TENSILE PROPERTIES

The four properties tensile and yield strength, elongation and Young's modulus are considered under a single heading because the same equipment is used for measuring each of them. The basic principles of tensile testing (tensile meaning capable of being drawn out or stretched) can be found in any introductory physics textbook. In most tensile tests the rate of crosshead travel is constant and changes in load or stress are monitored as the primary dependent variable.

The *stress* σ is defined as the force per unit cross-sectional area of a material. Thus, if the force is F newtons and the cross-sectional area is A square meters, then the stress is given by

$$\sigma = \frac{F}{A}\ \mathrm{Nm}^{-2}(\mathrm{Pa}) \tag{4.1}$$

The *strain* ε is defined as the fractional change in length of a material, that is, $\Delta L/L_o$, where L_o is the initial length and ΔL the change in length. It is expressed as a dimensionless ratio.

Tensile strength (or more accurately, ultimate tensile strength) is the maximum tensile strength which a material can sustain and is taken to be the maximum load exerted on the test specimen during the test, divided by the original cross section of the specimen.

Yield strength is the tensile stress at which the first sign of a nonelastic deformation occurs and is the load at this point (known as the yield point) divided by the original cross section of the specimen.

Elongation is usually measured at the point where the film breaks and is expressed as the percentage of change of the original length of the material between the grips of the testing machine. Its importance is as a measure of the film's ability to stretch, a large value for elongation indicating that the material will absorb a large amount of energy before breaking.

Yield strength is usually more important than ultimate tensile strength, especially during the passage of the film through packaging or printing equipment where a sudden "snatch" could cause a non-reversible distortion and thus, for example, out-of-register printing.

Both yield point and elongation are important properties during the unwinding of plastic films. There is the danger of uneven stretching of the film if the elongation is high, unless special handling techniques are used. Too low an elongation should also be avoided as any sudden unbalance in the unwind operation could lead to breaking of the film. Because a certain amount of tension is necessary during unwind, the possibility exists that films with low yield strength could be stressed beyond their yield point.

One problem which arises when considering the strength of thermoplastic polymers is the time and temperature dependence of the changes which occur under mechanical stress, particularly in the case of thermoplastics. This time dependence is well illustrated by the behavior of thermoplastics under tensile stress. This is measured by gripping the test material between fixed and moving clamps which are capable of separating at a range of speeds, the stress in the sample being measured continuously and recorded on a chart. At very slow speeds the molecules can readily disentangle and the measured tensile strength depends largely on the magnitude of the weakest intermolecular forces. At faster speeds, on the other hand, there is little time for either disentanglement or slipping and the breaking point will not happen until the largest intermolecular forces have been overcome.

Methods for testing tensile properties of thermoplastic films are described in ASTM D882 and ISO 527 (three parts). It is usual when carrying out a tensile strength determination to plot the stress against the strain, that is, the load against the elongation. Such a stress-strain curve can give a great deal of information. In general, the shape of such a curve will be of the form shown in Figure 4.1, although variations occur from plastic to plastic. For instance, brittle plastics will break at a much

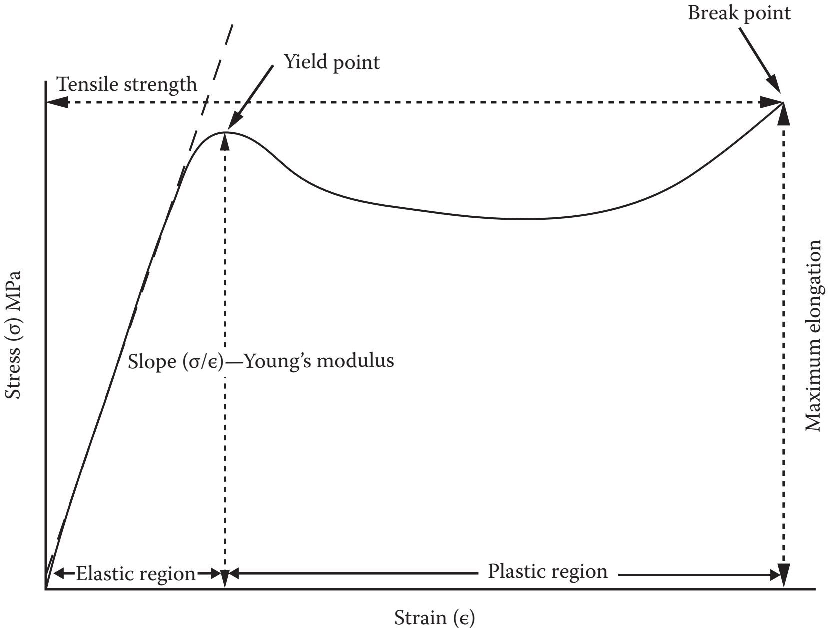

FIGURE 4.1 Typical stress-strain curve for thermoplastic polymers.

earlier stage of the curve, sometimes before the yield point has been reached. Stress has units of pressure while strain is dimensionless. The slope of the initial, linear portion of a stress-strain curve is called the Young's modulus E or the modulus of elasticity and has units of pressure (MPa). It is a measure of the force required to deform the film by a given amount and so is also a measure of the intrinsic stiffness of the film. The larger the value of E, the stiffer and more brittle the material. For example, E for LDPE is 250 MPa and for crystal grade PS it is 2500 MPa.

In industry, the Secant modulus of elasticity is a very common alternative test; it is defined as the slope of the line connecting the origin and a given point on the stress-strain curve or the ratio of nominal stress to corresponding strain at any specified point on the stress-strain curve expressed in force per unit area. It is easily determined automatically by a computer, whereas a true Young's modulus usually needs manual/graphical determination.

A great deal of information about the material can be obtained from the shape of its stress-strain curve. In addition to the numerical values for tensile strength, Young's modulus, elongation and so on, it is possible to obtain some idea of the toughness of the material by measuring the area under the curve. This area is a measure of the energy needed to break the test specimen and hence is directly related to toughness.

4.4 BURSTING STRENGTH

The bursting strength of a film is the resistance it offers to a steadily increasing pressure applied at right angles to its surface under certain defined conditions. The bursting strength is taken to be the pressure at the moment of failure of the film and is essentially a measure of the capacity of the film to absorb energy.

Methods for measuring bursting strength are usually based on those developed for paper (see ISO 2758) in which paper is submitted to increasing hydraulic pressure; it is applicable to paper having bursting strengths within the range 70–1400 kPa. The bursting strength tester, commonly called a Mullen tester, has clamps for holding the sample over a circular rubber diaphragm of 30.48 mm diameter and a pump that forces a liquid (usually glycerol) into a pressure chamber under the diaphragm. The measure of the total hydraulic pressure expanding the diaphragm at the time the sample ruptures is its bursting strength. Although the test is simple and rapid, its exact significance as an index of performance has been questioned.

4.5 IMPACT STRENGTH

The impact properties of polymeric materials are directly related to the overall toughness of the material, toughness being the ability of the polymer to absorb applied energy. The area under the stress-strain curve (described in the preceding section) is directly proportional to the toughness of the material. The impact strength of a film is a measure of its ability to withstand shock loading.

The standard methods for determining the Izod pendulum impact resistance of plastics are ASTM D256 and ISO 180. The pendulum impact test indicates the energy to break standard test specimens of specified size under stipulated parameters of specimen mounting, notching and pendulum velocity at impact. The results are expressed in energy lost per unit of thickness (J cm^{-1}) at the notch. Alternatively, the results may be reported as energy lost per unit cross-sectional area at the notch (J m^{-2}).

The standard method for determining the Izod pendulum impact resistance of plastic films is ASTM D3420. This method provides a means to determine parameters of plastic films at strain rates closer to some end-use applications than provided by low-speed uniaxial tensile tests. Dynamic tensile behavior of a film is important, particularly when the film is used as a packaging material. An arm held at a specific height (constant potential energy) is released; the arm hits the sample and breaks it. From the energy absorbed by the sample, its impact strength is determined. This test measures the difference between the potential energy of the pendulum at the maximum height of its free swing and the potential energy of the pendulum after rupture of the sample. This difference in energy is defined as impact strength and is useful in predicting the resistance of a material to breakage from dropping or other quick blows.

A test similar in scope, method and significance is the dart drop impact test (ASTM D1709 and ISO 7765) known as the free-falling dart method. The dart consists of a hemispherical head fitted with a shaft to which removable weights can be added. These methods cover the determination of the energy that causes plastic films to fail under specified conditions of impact of a free-falling dart. This energy is expressed in terms of the weight (mass) of the missile falling from a specified height which would result in 50% failure of specimens tested. These tests give an index of the film's dynamic strength and approximate what will occur when a package is dropped. The impact resistance of plastic film, while partly dependent on thickness, has no simple correlation with sample thickness.

Impact strength tests can also be carried out on the finished package. One such method is to fill the plastic bags with sand (or the actual food itself) and subject them to controlled drop tests. The results of such tests cannot usually be applied to any other size or shape of pack, even if the same film is used. However, it is a useful comparative test when several different films are available for packaging a particular product.

ASTM D4272 describes the determination of the total energy impact of plastic films by measuring the kinetic energy lost by a free-falling dart that passes through the film. This test method and ISO 7765 address the same subject matter, but differ in technical content; results cannot be directly compared between the two test methods. The ISO method calls for a direct readout of energy by using a load cell as part of the impactor head, while D4272 calls for a constant weight impactor and then measuring the time of travel through a given distance to get energy values.

Puncture resistance is a measure of the energy-absorbing ability of a film in resisting a protrusion and is very important in end-use performance of stretch wrap film. ASTM D5748 provides a means of measuring the puncture resistance performance of stretch wrap film under essentially biaxial deformation conditions, a biaxial stress being representative of the type of stress encountered by stretch wrap products in many end-use applications. The maximum force, force at break, penetration distance and energy to break are determined.

4.6 TEAR STRENGTH

The usual tests for measuring tear strength actually measure the energy required for tear propagation rather than for tear initiation, as it is difficult to start a tear in most plastics films. More specifically, what is measured is the energy absorbed by the test specimen in propagating a tear that has already been initiated by cutting a small nick in the sample with a blade.

Tear strength is an important property of packaging films and knowledge of resistance to both tear initiation and tear propagation is often helpful. Samples for testing should be cut from both machine and transverse directions as the tear strength can vary widely according to the direction of tear. Due to orientation during their manufacture, plastic films and sheeting frequently show marked anisotropy (the property of being directionally dependent) in their resistance to tearing.

One of the most common tests for measuring tear strength is the Elmendorf test which, like so many other film tests, was originally developed for paper testing. It measures the force required to propagate a tear or precut slit through a specified length of plastic film with a pendulum and is described in full in ASTM D1922 and ISO 6383. Tear strength is commonly reported as tearing force in millinewtons (mN) with specimen thickness also reported. Materials that can be tested according to this method include PVC and polyolefin films, but variable elongation and oblique tearing effects on the more extensible films may cause poor reproducibility of test results. This method may not be suitable for testing more rigid materials such as nylon and polyester films and rigid PVC. There is no direct linear relationship between tearing force and specimen thickness.

ASTM D1004 covers the determination of the tear resistance of flexible plastic film and sheeting at very low rates of loading (51 mm min^{-1}) and is designed to measure the force to initiate tearing. The maximum stress, usually found near the onset of tearing, is recorded as the tear resistance in newtons.

Another test measures the force necessary to propagate a tear in plastic film and is described in ASTM D1938 *Test Method for Tear-Propagation Resistance (Trouser Tear) of Plastic Film and Thin Sheeting by a Single-Tear Method*. Pre-slit strips of film are pulled at a constant rate of separation on a tensile testing machine. Whether or not the tear strength is acceptable depends on the particular application. For example, in plastic packs used to package sharp products such as frozen beans and French fries, rough handling may demand that tears do not run from small snags or punctures incurred during transit. On the other hand, applications relying on a tear tape to give easy access to the contents require ease of tear propagation in one direction.

4.7 STIFFNESS

Stiffness (or flexural rigidity) is the opposite of softness or limpness, all properties which find important applications in package use and sales appeal. Stiffness can be considered as the resistance of the film to distortion and, in particular, to bending. It depends on the thickness of the film as well as the inherent stiffness of the material. Young's modulus is one measure of the inherent stiffness of a single ply film.

There are also more direct methods of measuring stiffness, such as the use of the Handle-O-Meter stiffness tester that measures "handle" which is the combined effects of flexibility and surface friction of films. The data generated has been shown to correlate well with the actual performance of the material in production processes and finished product performance. The Handle-O-Meter has a flat plate to hold the sample over a slot, a penetrator beam that pivots on a cam and forces it into the slot and a strain gauge to sense the force (reported in grams) exerted against the beam by the sample. Stiff materials offer greater resistance to the motion of the beam as it moves into the slot.

A very simple method for measuring stiffness is the cantilever test, where one end of the film strip is clamped in a horizontal plane and the amount by which the film droops under its own weight is measured. Like several other properties already discussed, stiffness is usually different in the machine and transverse directions so that separate measurements must be made on strips cut in each of these directions. The main importance of stiffness is the influence it has on the performance of a film during its passage through a packaging machine; this is especially true for the feed section of such machines.

4.8 CREASE OR FLEX RESISTANCE

The resistance to repeated flexure or creasing is important in use and is measured by repeatedly folding the film backward and forward at a given rate. The number of cycles to failure is recorded as the flex resistance. Even if failure does not occur, certain properties of the film may be seriously impaired. For example, permeability may be increased, or tensile properties may be reduced or optical properties may be seriously affected. For this reason another way of testing crease or flex resistance is to subject the film to a given number of cycles in the test equipment and then compare the relevant properties with those of the uncreased film.

The ASTM F392 method for flex durability is valuable in determining the resistance of flexible packaging materials to flex-formed pinhole failures. It uses the Gelbo Flex Tester, an instrument designed to enable the prediction of end-use performance of materials which are likely to be affected by flexing, for example, formation of pinholes and breaks in the region of the creases. The Gelbo Flex Tester simulates the creasing and flexing action, which many films may be subjected to in use. Properties such as WVTR can then be measured on film samples before and after flexing on the Gelbo Flex Tester.

However, in common with many other test methods, some difficulty is often experienced in relating test results to actual end-use performance of the films in commercial packages.

4.9 COEFFICIENTS OF FRICTION

All surfaces are rough to a greater or lesser degree and they exert different forces on objects resting on them which act parallel to the surface and resist sliding motion. This force is called friction. The coefficients of friction or COF (both static and dynamic or kinetic) are a measure of the ease with which the surface of one material will slide over another; films which move easily over various surfaces have a low COF.

A simple method for measuring the COF uses the inclined plane, a common piece of equipment found in all elementary physics laboratories. However, more satisfactory methods are described by ASTM D1894 and ISO 8295; they are based on a similar principle but use a special foam-covered metal block as a sled. Typically, the film is wrapped around the sled which is then motor driven at 15 cm min^{-1} over a table covered with the material to be tested. The horizontal force on the sled is measured at intervals by a strain gauge and from this the static and dynamic COFs are determined. The methods permit the use of a stationary sled with a moving plane, or a moving sled with a stationary plane; both procedures yield the same COF values for a given sample.

The frictional properties of a film are important, both during its passage through printing and packaging machines and after being made up into a bag, sack or overwrap. In practice it is usual to speak of a film's slip properties rather than COF, one being the reciprocal of the other. The characteristic of good slip (i.e., no indication of periodic sticking) is indicated by a relatively low (0.2–0.5) COF μ, a dimensionless scalar value which describes the ratio of the force of friction between two bodies and the force pressing them together. High slip is normally required for a number of reasons: it eases the passage of the film through packaging equipment and facilitates the movement of finished packages over various surfaces as they are ejected from packaging machines. However, there are also occasions when low slip is a definite requirement. For example, woven plastic sacks and plastic wraps around frozen meat carcasses are often required to be stacked to heights of several meters; any tendency towards slip under these conditions can present a real danger.

4.10 BLOCKING

Blocking is the tendency of two adjacent layers of film in intimate contact with nearly complete exclusion of air to stick together as, for example, when films are stacked in sheets or compacted rolls. Temperature or pressure, or both, can induce or change the degree of adhesion of the surfaces. It can also make bags made from layflat film difficult to open. Blocking is also affected by static charges, surface treatment (such as printing pretreatment) and storage conditions. Anti-blocking additives are often added to the film to reduce the tendency to blocking; these act by diffusing to the surface and forming non-adherent layers.

In ASTM D3354 and ISO 11502, the degree of blocking is determined by the force required to separate the two layers of blocked film, when the force is applied perpendicularly to the surface of the film.

4.11 ORIENTATION AND SHRINKAGE

Although orientation itself is not of primary practical importance, the way in which it affects the physical and mechanical properties of a film is. Measurement of the shrink tension and orientation release stress of plastic film is described in ASTM D2838. Shrink tension affects the appearance and performance of a film in a shrink-packaging application. Orientation exerts a great influence on important physical characteristics such as tensile strength, stiffness, tear resistance and impact strength. Two procedures are described that permit the measurement of shrink forces at predetermined temperatures. One is designed to measure the maximum force exerted by a specimen that is totally restrained from shrinking as it is heated rapidly to a specific temperature. The other is designed to measure the maximum force exerted by a specimen that is permitted to shrink a predetermined amount prior to restraint while being heated rapidly to a specific temperature. Data from the first procedure are most useful for determining the degree and direction of orientation, orientation release stress and the maximum force that the film can exert at a given temperature. Data from the latter procedure are useful in estimating the force an item to be packaged will actually receive and in predicting the appearance of packaged items.

4.12 BARRIER PROPERTIES

4.12.1 INTRODUCTION

The barrier properties of plastics indicate their resistance to sorption and diffusion of substances such as gases and flavor and aroma compounds. The solution and transport behavior of low MW substances in plastics has become increasingly important in recent years with the widespread and expanding use of polymer films and rigid plastics for food packaging. The selection or development of plastics for food packaging applications with stringent design specifications relating to their solution and diffusion behavior requires knowledge and appreciation of the many factors which affect those phenomena.

Unfortunately, there are many examples of foods packaged with an apparent lack of proper consideration of the effects of the end-use environment on properties, or of limitations imposed on performance due to unfavorable solution or transport characteristics. Plasticization of polymers by sorption of ambient vapors or liquids resulting in a decrease in mechanical properties and the loss of components (e.g., CO_2, flavor compounds and so on) from a beverage in a plastic bottle are just two of many examples which could be cited.

The protection of foods from gas and vapor exchange with the environment depends on the integrity of packages (including their seals and closures) and on the permeability of the packaging materials themselves. There are two processes by which gases and vapors may pass through polymeric materials:

1. A pore effect, in which the gases and vapors flow through microscopic pores, pinholes and cracks in the materials.
2. A solubility-diffusion effect, in which the gases and vapors dissolve in the polymer at one surface, diffuse through the polymer by virtue of a concentration gradient and evaporate at the other surface of the polymer. This "solution-diffusion" process (also known as "activated diffusion") is described as true permeability.

When sufficiently thin, most polymers exhibit both forms of permeability. Porosity falls very sharply as the thickness of a polymer is increased, reaching virtually zero with many of the thicker types of commercially available materials. True permeability, however, varies inversely as the thickness of the material and hence cannot be effectively eliminated merely by increasing the material thickness.

Unlike metal and glass packages, plastics packages are permeable and the concept of permeability is normally associated with the quantitative evaluation of the barrier properties of a plastic. A plastic that is a good barrier has a low permeability. This section is concerned with aspects of the solution, diffusion and permeation of gases and vapors ("permeants") in effectively non-porous polymeric materials.

4.12.2 THEORY

The first recorded observation of the permeation of a gas through a membrane appears to be that of Thomas Graham in Scotland who, in 1829, described the permeation of CO_2 into a wet pig's bladder. In 1831, J.K. Mitchell, an American physician and the inventor of the toy rubber balloon, discovered that his balloons collapsed at different rates when they were filled with different gases. In 1855, the German physiologist Adolf Fick, who was concerned with measuring the transport of O_2 in blood, proposed his law of mass diffusion by analogy with Fourier's law for heat conduction, Ohm's law for electrical conduction and Newton's law for momentum transfer.

In 1866, Graham first postulated that the permeation process entailed solution of the gas in the upstream surface of the membrane, diffusion through by "colloidal diffusion" (likened to diffusion in liquids), followed by evaporation from the downstream membrane surface. This is the basis for the so called solution-diffusion model which is still used today in various forms and modifications. The subject was placed on a quantitative basis in 1879 by the Polish physicist Szygmunt von Wróblewski, who showed that the solubility of gases in rubber obeyed Henry's law (named after the English physician and chemist William Henry who, in 1803, showed that, at a given temperature, the amount of gas dissolved in a solution is directly proportional to the pressure of the gas above the solution) and combined this with Fick's law to obtain the now familiar expression relating permeation rate and the area and thickness of the membrane. In 1920, Harold Daynes in England showed that it was impossible to evaluate both diffusion and solubility coefficients by steady-state permeation experiments. He extended Wróblewski's equation to unsteady-state conditions and showed that both the diffusivities and solubilities of gases could be determined by measuring the increase in pressure with time. The "time lag" method of Daynes was further developed by Barrer in England from 1937, leading to much new information about the mechanism of gas permeability in polymers. For a detailed review on the history of gas transport in polymers the reader is referred to Stannett (1978).

Under steady-state conditions, a gas or vapor will diffuse through a polymer at a constant rate if a constant pressure difference is maintained across the polymer. The diffusive flux, J, of a permeant in a polymer can be defined as the amount passing through a plane (surface) of unit area normal to the direction of flow during unit time as follows:

$$J = \frac{Q}{At} \tag{4.2}$$

where Q is the total amount of permeant which has passed through area A during time t.

The relationship between the rate of permeation and the concentration gradient is one of direct proportionality and is embodied in Fick's first law:

$$J = -D\frac{\delta c}{\delta x} \tag{4.3}$$

where

J is the flux (or rate of transport) per unit area of permeant through the polymer
c is the concentration of the permeant
D is defined as the diffusion coefficient
$\delta c/\delta x$ is the concentration gradient of the permeant across a thickness δx

D reflects the speed at which the permeant diffuses through the polymer; it is a function of temperature and may be a function of concentration. Equation 4.3 can be used to calculate the steady-state rate of diffusion assuming that D is constant and the concentration is a function only of the geometric position inside the polymer.

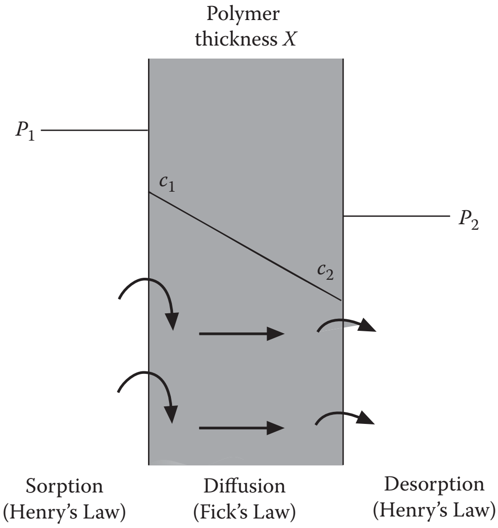

FIGURE 4.2 Permeability model for gas or vapor transfer through a polymer.

Consider a polymer X mm thick, of area A, exposed to a permeant at pressure p_1 on one side and at a lower pressure p_2 on the other as shown in Figure 4.2. The concentration of permeant in the first layer of the polymer is c_1 and in the last layer c_2.

If x and $(x + \delta x)$ represent two planes through the polymer at distances x and $(x + \delta x)$ from the high-pressure surface, and if the rate of permeation at x is J mL sec^{-1}, and at $(x + \delta x)$ is $J + (\delta J/\delta x)\delta x$, then the amount retained per unit volume of the polymer is $(\delta J/\delta x)$. This is equal to the rate of change of concentration with time:

$$\frac{\delta}{\delta x}(J) = -\frac{\delta c}{\delta t} \tag{4.4}$$

A negative sign is used because the concentration of permeant decreases across the material. Under steady-state conditions, $\delta c/\delta t = 0$ and J = constant. When the concentration gradient is zero (i.e., $c_1 = c_2$) there will be no permeation.

If Equation 4.3 is substituted into Equation 4.4, then

$$\frac{\delta}{\delta x}(J) = \frac{\delta}{\delta x}\left[-D\frac{\delta c}{\delta x}\right] = -\frac{\delta c}{\delta t} \tag{4.5}$$

Rearranging the terms

$$\frac{\delta c}{\delta t} = \frac{\delta}{\delta x}\left[D\frac{\delta c}{\delta x}\right] \tag{4.6}$$

Equation 4.7 is obtained

$$\frac{\delta c}{\delta t} = D\frac{\delta^2 c}{\delta x^2} \tag{4.7}$$

which is a simplified form of Fick's second law of diffusion and applies under circumstances where diffusion is limited to the x-direction and D is independent of concentration which is usually true in polymers above their T_g. It describes the unsteady or transient state for one dimensional diffusion. A wide range of values for D in polymers are reported from 10^{-19} to $10^{-9}\,\mathrm{m^2\,s^{-1}}$. By way of comparison, D in liquids is around $10^{-9}\,\mathrm{m^2\,s^{-1}}$ and in gases around $10^{-5}\,\mathrm{m^2\,s^{-1}}$.

4.12.3 STEADY-STATE DIFFUSION

When a steady-state of diffusion has been reached, J = constant and Equation 4.3 can be integrated across the total thickness of the polymer X and between the two concentrations, assuming D to be constant and independent of c:

$$JX = -D(c_2 - c_1) \tag{4.8}$$

and

$$J = \frac{D(c_2 - c_1)}{X} \tag{4.9}$$

This expression can be rewritten by substituting for J using Equation 4.2. This enables calculation of Q, the quantity of permeant diffusing through a polymer of area A in time t:

$$Q = \frac{D(c_2 - c_1)At}{X} \tag{4.10}$$

When the permeant is a gas, it is more convenient to measure the vapor pressure p which is at equilibrium with the polymer, rather than measure the actual concentration. At sufficiently low concentrations, Henry's law applies and c can be expressed as

$$c = Sp \tag{4.11}$$

where S is the solubility coefficient of the permeant in the polymer. S reflects the amount of permeant in the polymer. By combining Equations 4.10 and 4.11,

$$Q = \frac{DS(p_1 - p_2)At}{X} \tag{4.12}$$

The product DS is referred to as the *permeability coefficient* or *constant* and is represented by the symbol P:

$$P = DS \tag{4.13}$$

Thus, the permeability coefficient is the product of a kinetic term (D) which reflects the dynamics of the penetrant–polymer system and of a thermodynamic term (S) which depends on the penetrant–polymer interactions. P represents the ease with which a gas permeates through a polymer when subjected to a pressure gradient:

$$P = \frac{QX}{At(p_1 - p_2)} \tag{4.14}$$

or

$$\frac{Q}{t} = \frac{P}{X}A(\Delta p) \tag{4.15}$$

The term *P/X* is called the *permeance* and is represented by the symbol *R*. Permeance is not a property of the material but a performance evaluation indicator.

There are four assumptions made in the earlier simple treatment of permeation. First, diffusion is at steady-state. Second, the concentration–distance relationship through the polymer is linear. Third, diffusion takes place in one direction only (i.e., through the film with no net diffusion along or across it) and fourth, both *D* and *S* are independent of the concentration.

Like all simplifying assumptions, there are many instances when they are not valid and, in such cases, the predictions made are not subsequently borne out in practice. Although steady-state is usually attained in a few hours for small molecules such as O_2, larger molecules in barrier polymers (especially glassy polymers) can take a long time to reach steady-state, this time possibly exceeding the anticipated shelf life. Although *D* and *S* are independent of concentration for many gases such as O_2, N_2 and, to a certain extent, CO_2, this is not the case where considerable interaction between polymer and permeant takes place (e.g., water and hydrophilic films such as PAs, or many solvent vapors diffusing through polymer films).

Although the chemical structure of a polymer can be considered to be the predominant factor which controls the magnitude of *P*, it also varies with the morphology of the polymer and depends on many physical factors such as density, crystallinity and orientation (Pauly, 2005).

The permeability coefficient defined earlier is independent of thickness, because the thickness is already accounted for in the calculation of *P*. However, the total amount of protection afforded by unit area of a barrier material (i.e., the permeance *P/X*) approaches zero only asymptotically. Consequently, as polymer thickness *X* is increased beyond a certain value, it becomes uneconomical to increase it further to obtain lower permeability.

4.12.4 UNSTEADY-STATE PERMEATION

Because of the finite diffusion rate of the solute in the polymer, there is an interval before the steady-state is achieved. The situation which exists during this transient or unsteady-state period, where concentration varies with time, is described by Fick's second law (Equation 4.6), which is a derivative of the first law. Solutions have been found for various boundary conditions; a useful solution in the present context is for the case of a finite solid with a concentration-independent diffusion constant, where the polymer is initially free from gas and one surface is then exposed to gas at pressure p_1 giving a concentration in the surface layer of c_1.

With these boundary conditions it can be shown that

$$Q = \frac{Dc_1}{X}\left[t - \frac{X^2}{6D}\right] \tag{4.16}$$

$$= \frac{Dc_1 t}{X} - \frac{c_1 X}{6} \tag{4.17}$$

Thus, the amount of gas permeating through the polymer increases linearly with time once the steady-state has been reached, as indicated in Figure 4.3.

If the linear portion of the steady-state line AB is extrapolated back to $Q = 0$ where the intercept $t = \tau$, then from Equation 4.17

$$\frac{Dc_1\tau}{X} = \frac{c_1 X}{6} \tag{4.18}$$

or

$$D = \frac{X^2}{6\tau} \tag{4.19}$$

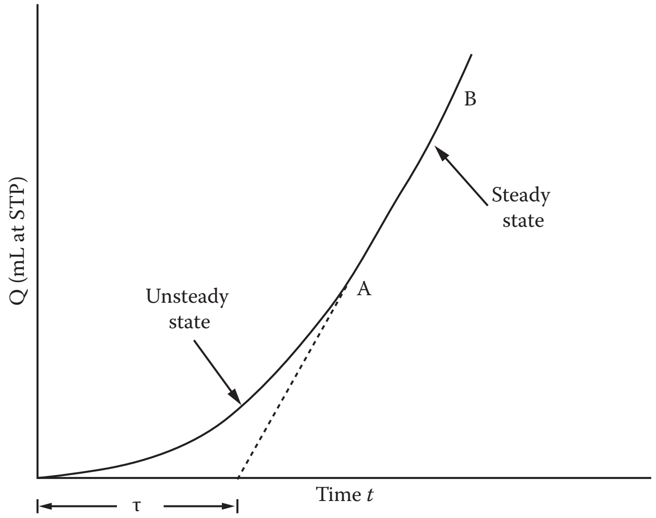

FIGURE 4.3 Typical permeation and time lag curve where Q is the amount of permeant that has permeated as a function of time t and τ is the time lag.

and

$$\tau = \frac{X^2}{6D} \tag{4.20}$$

The value τ is called the time lag and is the intercept on the time axis of the extrapolated steady-state portion of the curve in Figure 4.3. Thus, all three parameters of interest can be calculated from a single experiment. The permeability coefficient P is obtained by calculating the steady-state permeation rate Q/t (the slope of the asymptotic line in Figure 4.3) and substituting in Equation 4.12. The diffusion coefficient D is obtained from the time lag τ (Equation 4.16) and the solubility coefficient S is calculated as P/D.

Under ordinary conditions for a constant D, the steady-state of flow is reached after a period amounting to about 2.7τ. Failure to continue a transmission experiment to obtain the real steady-state of flow, together with inaccuracy in determination of the thickness X (which is squared in Equation 4.18), constitute major sources of error in the subsequent estimation of D.

4.12.5 PERMEATION THROUGH PORES

The presence of pores in a plastic food package is generally considered undesirable and pores or channel leaks are sometimes found in defective seals as a result of faulty heat sealing of plastic films. Numerous micropores are often present in very thin homogeneous films but incorporation of such films into a laminate package generally cancels microporosity. Pores, microholes and cracks not only allow mass transfer between the interior of a package and the ambient environment, but also permit microbe penetration into the package, with some bacteria penetrating holes as small as 0.4 μm in diameter. Microscopic defects are common in metallized films, even although the metallic coating is generally considered impermeable to small molecules such as gases, water vapor, flavors and also light due to its opacity. These pinholes are created in the metallic layer during manufacture due to the presence of antiblock and dust particles or aluminum aggregates, as well as during the packing and/or transportation of packaged foods. Hanika et al. (2003) developed a numerical model to simulate defects on single films and layered structures and revealed a complex interaction between film thickness, defect area and defect spacing on permeability. Many small defects lead to a higher permeability than a small number of large defects, for the same whole area of defects. The better the gas barrier properties of the packaging material, the more significant is the relative increase in permeability due to leaks.

Unlike permeation, transport of gases through pores involves diffusion but not adsorption and desorption. The diffusion of O_2 and CO_2 through air is 8.5 and 1.5 million times greater, respectively, than through LDPE films. Thus, even a small hole has the potential to significantly affect the package atmosphere, the effect being greater on the O_2 concentration than the CO_2 concentration inside the package.

Perforations are small holes deliberately made in the packaging material to provide means for increased gas transfer and essentially have a negligible length-to-diameter ratio.

Microperforated films are commonly used in the modified atmosphere packaging (MAP) of high respiration fresh food products such as minimally processed fruits and vegetables. The perforations range from laser-made micropores typically between 40 and 200 μm in diameter to mechanically perforated macropores which can be up to 20 mm diameter, but are typically 10 mm. Techavises and Hikida (2008) measured the effective permeability of a perforation for temperatures from 5°C to 25°C, perforation diameters from 2 to 15 mm and film thicknesses of 0.012 and 0.025 mm. The temperature and film thickness had no significant effect on the effective permeability which, for most conditions, did not differ between gas types (O_2, CO_2, N_2 and water vapor). They developed an empirical equation of the effective permeability of a macroperforation in a thin film as a function of perforation diameter. Mahajan et al. (2008) analyzed the WVTR for different perforation dimensions (diameter: 9, 13 and 17 mm; length: 10, 20 and 30 mm) and storage temperatures (4°C, 10°C and 16°C). Diameter was the variable with the greatest influence on WVTR, followed by tube length and temperature. The WVTR of perforation-mediated packages increased with increasing temperature and tube diameter and decreased with increasing tube length. A mathematical model to describe the changes in WVTR as a function of perforation diameter, length, porosity and storage temperature was developed and validated successfully at 7°C.

González et al. (2008) derived an empirical equation from experimental data relating the area of a microperforation with the transmission rate of O_2 and CO_2. These predicted rates were very close to those obtained with the modified Fick's equation in which the total diffusive pass length of a perforation was considered as the sum of the perforation length and a correction factor (approximately 0.5 times the diameter of the perforation). This equation can be used for a wide range of conditions: diameters between 40 μm and 10 mm, and thicknesses between 30 μm and 1.5 mm.

Rennie and Tavoularis (2009) developed a space-and-time dependent mathematical model describing perforation-mediated modified atmosphere packages for respiring commodities. The model was based primarily on fundamental laws, with empirical relations used only when no other approach could be devised or when there was a significant advantage from using an empirical approach. The model permits the determination of the gas mixture velocity in the commodity layer and in the headspace, perforation and surrounding ambient storage area. Solubility of CO_2 within the commodity was included in the model, together with commodity temperature and gas mixture temperature.

Recently, OTR and CDTR values at 5°C for OPP films of varying thickness and microperforated PP film of 30 μm thickness were reported (Lucera et al., 2011) and are presented in Table 4.1. As expected, the OTR and CDTR values of microperforated films decreased as the number of perforations decreased, while the barrier properties of the unperforated films increased with their thickness. Such data are very useful in the design of packaging for respiring produce (see Chapter 18).

4.12.6 PERMEABILITY COEFFICIENT UNITS

D has dimensions of length^2 time^{-1} and is usually expressed as cm^2 s^{-1}. The dimensions used for *P* and *S* are much more varied and a source of much confusion. Consideration of Equation 4.14 shows the dimensions of *P* to be

$$P = \frac{\text{(quantity of permeant under stated conditions)(thickness)}}{\text{(area)(time)(pressure drop across polymer)}} \tag{4.21}$$

TABLE 4.1
OTR and CDTR of Unperforated OPP and Perforated PP Films at 5°C

	mL m^{-2} d^{-1}	
Film	**OTR**	**CDTR**
OPP 20 µm	1,015	2,700
OPP 40 µm	457	1,100
OPP 80 µm	249	606
PP 50[a]	23,296	18,995
PP 20[a]	9,318	7,330
PP 12[a]	6,809	3,978
PP 9[a]	4,838	3,046
PP 7[a]	3,673	2,562

Source: Lucera, A. et al., *J. Food Eng*., 102, 122, 2011.

[a] Number of 70 µm diameter perforations per package surface area of 500 cm^2; PP films were 30 µm thick.

The quantity of permeant can be expressed in mass, mole or volume units. For gases, volume is preferred, expressed as the amount permeating under conditions of standard temperature and pressure (STP), which corresponds to the standard temperature of 273.15 K and standard pressure of 1.01325×10^5 Pa. The standard ambient temperature and pressure (SATP) are set at $T = 298.15$ K and $p = 10^5$ Pa = 0.9678 atm. Data in handbooks is still mostly expressed with $p = 1$ atm as standard pressure. For practical purposes, the difference between these two conventions is insignificant compared to the variability of the materials themselves.

Over 30 different units for P appear in the scientific, commercial and patent literature. An attempt to rationalize these units from a practical point of view was made by Huglin and Zakaria (1983), but has proved unsuccessful. The adoption of a single unit for P called the *barrer* (B) after the New Zealander Richard Maling Barrer (1910–1996), a pioneer in the membrane field with wide ranging and seminal contributions in the area of formation of membrane materials and gas transport through membranes, was proposed by Alter (1962) and subsequently adopted by the ASTM; it is defined as 10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} (cm Hg)$^{-1}$. Although it has not found widespread use in the packaging industry, it is widely used in the contact lens industry and is one of the so-called Practical Units mentioned by the *Journal of Membrane Science* (*Journal of Membrane Science* recommended units for key parameters, 2011). A unit which is identical in every respect, except that the exponential term is 10^{-11}, occurs frequently in the scientific literature and standard reference texts such as the *Polymer Handbook* (Pauly, 2005).

A very logical suggestion by Yasuda (1975) to use cm^2 s^{-1} as the unit of P has regrettably gained little acceptance, as has that to use attoseconds (1 *as* = 1×10^{-18} s). Under the SI system, the units of P are kg m m^{-2} s^{-1} Pa^{-1} and permeability data in scientific publications are commonly expressed in these units with an exponential term of 10^{-18} (e.g., Joo et al., 2011).

It is helpful to understand the background for the plethora of units which are now used around the world for the permeability coefficient. The traditional definition of a barrier polymer in the United States required an O_2 permeability coefficient of less than 1 mL mil 100 in.$^{-2}$ d^{-1} atm^{-1} at room temperature. This definition was based partly on function and partly on conforming to the old commercial unit of permeability in the United States that was created so that the O_2 permeability of Saran™ Wrap (PVdC copolymer from Dow Chemical Company) would have a numerical value of 1. This unit could be converted to the metric unit nmol m^{-2} s^{-1} GPa^{-1} by multiplying by 2 in the case of O_2 (DeLassus, 2002). Both units had the added advantage of being free of exponential terms. Since then, a large number of units have been used with, for example, time being given in s, h or d, and thickness in mm, cm, m and in.

In this book, the unit *barrer* (*B*) will be used for the permeability coefficient *P*:

$$\frac{10^{-10}(\text{mL at STP})\,\text{cm}}{\text{cm}^2\,\text{s}\,(\text{cm Hg})}$$

Note that the exponential term 10^{-10} is an integral part of this unit and is absent when the value of *P* is given in *barrer*. In the case of high barrier (i.e., low permeability) films, the use of the unit *centiBarrer* (*cB*) is convenient to reduce the number of zeros after the decimal point (Pye et al., 1976).

While mL is a unit of volume, (mL at STP) is not a unit of volume but a unit to express the number of molecules. That is, (mL at STP) represents the molar quantity of gas rather than a true volume and is the quantity of gas that would take up 1 mL at STP as calculated via the ideal gas law. The selection of mL at STP as the unit to express the amount of gas rather than, for instance, grams of gas, is truly arbitrary. Consequently, there is no reason to consider that the use of (mL at STP) for the amount of gas and [(mL at STP) cm cm^{-2} s (cm $Hg)^{-1}$] for gas permeability is preferred over numerous other composite units.

One g mole of an ideal gas occupies 22.4 L at 0°C and 1 atm pressure. The mass of 1 mol of a substance is its atomic weight in g, for example, 1 mol of O_2 is 32 g. The volume of O_2 (at STP) can be converted to moles by dividing by 22,414 and then to mass by multiplying by 32; for CO_2 the multiplying number is 44. The volume occupied by 1 mol of an ideal gas at STP is $22414 \times 10^{-6}\,m^3\,mol^{-1}$.

It is important to note that the term milliliter (mL) is equivalent to and interchangeable with the term cubic centimeter (abbreviated cc or cm^3). A micron (abbreviated μm) or micrometer is 10^{-6} meters or 10^{-4} centimeters and a mil when used to express thickness is one-thousandth of an inch which is equivalent to 25.4 μm or 2.54×10^{-3} cm. The term gauge is sometimes used in the United States to indicate the thickness of plastic films; its units are one hundred thousandths of an inch, that is, 100 gauge is 1×10^{-3} in. or one "thou" which is one mil.

Factors for converting permeability coefficients from various units to the standard units used throughout this book (*barrer*) are given in Table 4.2 and broadly representative permeability coefficients for a number of polymers to several gases and water vapor are given in Table 4.3.

Difficulty and uncertainty are sometimes experienced in interpreting the permeability coefficients from tables and converting them into different units. The following examples are designed to demonstrate the use of the data in Tables 4.2 and 4.3.

Example 4.1

What is the permeability coefficient *P* of polystyrene to CO_2 at 25°C expressed in *barrer* and in basic units?

Taking the upper range value from Table 4.3

$$\begin{aligned} P &= 10.5\ \textit{barrer} \\ &= 10.5 \times 10^{-10}\left[\text{mL(STP)cmcm}^{-2}\,\text{s}^{-1}(\text{cmHg})^{-1}\right] \\ &= 1.05 \times 10^{-9}\left[\text{mL(STP) cm cm}^{-2}\,\text{s}^{-1}(\text{cmHg})^{-1}\right] \end{aligned}$$

TABLE 4.2
Factors for Converting *P* from Various Units into *Barrer*

Unit	Multiplication Factor to Obtain *P* (*barrer*)
[mL(STP) m m^{-2} s^{-1} Pa^{-1}]	1.33×10^{1}
[mL(STP) cm cm^{-2} s^{-1} Pa^{-1}]	1.33×10^{2}
[mL(STP) cm cm^{-2} s^{-1} bar^{-1}]	1.33×10^{-2}
[mL(STP) cm cm^{-2} s^{-1} atm^{-1}]	1.33×10^{-3}
[mL(STP) cm m^{-2} d^{-1} atm^{-1}]	1.52×10^{-12}
[mL(STP) cm m^{-2} d^{-1} bar^{-1}]	1.54×10^{-12}
[mL(STP) mm cm^{-2} s^{-1} (cm Hg)$^{-1}$]	1.00×10^{-1}
[mL(STP) mm cm^{-2} s^{-1} atm^{-1}]	1.33×10^{-2}
[mL(STP) mm m^{-2} d^{-1} atm^{-1}]	1.52×10^{-12}
[mL(STP) mm m^{-2} d^{-1} kPa^{-1}]	1.54×10^{-11}
[mL(STP) µm m^{-2} d^{-1} atm^{-1}]	1.54×10^{-11}
[mL(STP) µm m^{-2} d^{-1} kPa^{-1}]	1.54×10^{-13}
[mL(STP) µm m^{-2} d^{-1} bar^{-1}]	1.54×10^{-15}
[mL(STP) mil 100 in^{-2} d^{-1} atm^{-1}]	6.00×10^{-13}
[mL(STP) mm 100 in^{-2} d^{-1} atm^{-1}]	1.53×10^{-14}
[mL(STP) mil m^{-2} d^{-1} atm^{-1}]	3.86×10^{-14}
[in^{3}(STP) mil 100 in^{-2} d^{-1} atm^{-1}]	9.82×10^{-13}
[m^{3}(STP) m m^{-2} s^{-1} Pa^{-1}]	1.33×10^{7}
[kg m m^{-2} s^{-1} Pa^{-1}] for O_2	9.34×10^{6}
[kg m m^{-2} s^{-1} Pa^{-1}] for CO_2	6.79×10^{6}
[kg m m^{-2} s^{-1} Pa^{-1}] for N_2	10.67×10^{6}
[kg m m^{-2} s^{-1} Pa^{-1}] for H_2O	16.60×10^{6}

Example 4.2

What is the permeability coefficient of polypropylene to O_2 in *barrer*, given that it is 1.53×10^{12} [in.^{3}(STP) mil 100 in.$^{-2}$ day^{-1} atm^{-1}]?

From Table 4.2

Conversion factor is 9.82×10^{-13}

Therefore,

$$P = (1.53 \times 10^{12}) \times (9.82 \times 10^{-13})$$

$$= 1.5 \textit{ barrer}$$

which is within the range specified in Table 4.3.

TABLE 4.3
Broadly Representative Permeability Coefficients of Various Polymers and Permeants at 25°C and 0% RH Unless Indicated Otherwise

	P (*Barrer*)				
Polymer	**O_2**	**CO_2**	**N_2**	**SO_2**	**H_2O (90% RH)**
Linear low density polyethylene	1.3–3.0	13	1.5		
Low density polyethylene	3.0–6.7	13–28	0.6–1.9	20	80
High density polyethylene	0.6–1.1	1.7–4.5	0.14–0.33	5.7	13
Poly(ethylene-co-vinyl acetate)[a]	3.0–4.2	13.1–17.3			29
Polypropylene	0.9–2.3	9.2	0.44	0.7	57
Poly(vinyl chloride) film	0.005–0.12	0.03–1.0	0.04	0.12	156–275
Polystyrene film (oriented)	1.1–2.7	8.8–10.5	0.29–0.78	22	11–1,800
Polyacrylonitrile	0.00024	0.006			2.2
Nylon-6 (0% RH)	0.012–0.038	0.04–0.16	0.01	2.2[b]	700
Nylon-MXD6	0.001–0.003	0.0093			
Poly(ethylene terephthalate)					
(amorphous)	0.055–0.075	0.21–0.30	0.005		
(40% crystalline)	0.018–0.030	0.12–0.16	0.006		130–183
Poly(ethylene naphthalate)	0.0075	0.022			
Polycarbonate film	1.5	6.4			
PVdC copolymer	0.0006	0.0022–0.0036	0.0009		1.4–4.5
EVOH copolymer					
32% ethylene	0.00012	0.00036	0.000012		
44% ethylene	0.00048	0.0014	0.00005		
PCTF	0.03–0.50	0.05–1.25	0.01–0.13		0.3–36
Cellulose acetate	0.4–0.8	2.4–18	0.2–0.5		1,500–10,600
Regenerated cellulose (cellophane)	0.0021	0.0047	0.0032		1,900
Poly(lactic acid)(98% L)	0.11–0.56	1.88	4.99		3,000

[a] 12%.

[b] Nylon-11.

Example 4.3

What is the permeability coefficient of HDPE to SO_2 in [mL(STP) mil m^{-2} day^{-1} atm^{-1}]?

From Table 4.3

$$\begin{aligned} P &= 5.7\ barrer \\ &= 5.7 \times \left\{10^{-10}\left[\mathrm{mL(STP)cm\,cm^{-2}\,s^{-1}\,(cmHg^{-1})}\right]\right\} \end{aligned}$$

The conversion factor from Table 4.2 = 3.86 × 10^{-14}. This must be divided into the permeability coefficient obtained from Table 4.3.

$$\begin{aligned} P &= \frac{5.7\times10^{-10}}{3.86\times10^{-14}} \\ &= 1.48\times10^{4}\left[\mathrm{mL(STP)mil\,m^{-2}\,day^{-1}\,atm^{-1}}\right] \end{aligned}$$

Example 4.4

What is the permeability coefficient of PVdC copolymer to O_2 in *barrer*, given that it is 6.42×10^{-20} [kg m m^{-2} s^{-1} Pa^{-1}]?

From Table 4.2

Conversion factor is 9.34×10^6

$$\begin{aligned} P &= 6.42\times10^{-20}\times(9.34\times10^{6}) \\ &= 6.42\times10^{-13}\left[\mathrm{mL(STP)cm\,cm^{-2}\,s^{-1}\,cmHg^{-1}}\right] \end{aligned}$$

Therefore,

$$\begin{aligned} &= 0.006\times10^{-10}\left[\mathrm{mL(STP)cm\,cm^{-2}\,s^{-1}\,cmHg^{-1}}\right] \\ &= 0.006\ \textit{barrer}\ (=0.6\ \textit{cB}) \end{aligned}$$

which corresponds to the value in Table 4.3.

Example 4.5

What is the permeability coefficient of PLA to CO_2 in *barrer*, given that it is 7.35×10^{-17} [kg m m^{-2} s^{-1} Pa^{-1}]?

From Table 4.2

Conversion factor is 6.79×10^6

Therefore

$$\begin{aligned} P &= 7.35\times10^{-17}\times6.79\times10^{6} \\ &= 4.99\times10^{-10} \\ &= 4.99\ \textit{barrer} \end{aligned}$$

Example 4.6

What is the permeability coefficient of LDPE to water vapor in *barrer*, given that it is 0.349×10^{-2} g mm m^{-2} d^{-1} $(\text{mm Hg})^{-1}$?

As there is no conversion factor in Table 4.1, the conversion must be done from first principles:

$$\begin{aligned} P &= 0.349\times10^{-2}\,\frac{\mathrm{g}\,\cancel{\mathrm{mm}}}{\cancel{\mathrm{m}}^{\cancel{2}}\ \cancel{\mathrm{d}}\ \cancel{\mathrm{mmHg}}}\times\frac{\mathrm{cm}}{10\,\cancel{\mathrm{mm}}}\times\frac{\cancel{\mathrm{d}}}{60\times60\times24\,\mathrm{s}}\times\frac{\cancel{\mathrm{m}}^{\cancel{2}}}{100\times100\,\mathrm{cm}^2}\times\frac{10\,\cancel{\mathrm{mmHg}}}{\mathrm{cmHg}} \\ &= 4.04\times10^{-11}\,\mathrm{mL(STP)cm\,cm^{-2}\,s^{-1}(cmHg^{-1})} \\ &= 0.404\times10^{-10}\,\mathrm{mL(STP)cm\,cm^{-2}\,s^{-1}(cmHg^{-1})} \\ &= 0.404\,\textit{barrer} \end{aligned}$$

4.12.7 POLYMER/PERMEANT RELATIONSHIPS

For noncondensable gases, the permeability ratio of two gases is relatively constant and independent of polymer type. Table 4.4 shows average values for a range of different polymers and these are useful as a general guide. When a value for one gas is known, then values for another can be

TABLE 4.4
Relative Values of Permeability Parameters

Gas	*P*	*D*	*S*
N_2 (=1)	1	1	1
CO	1.2	1.1	1.1
CH_4	3.4	0.7	4.9
O_2	3.8	1.7	2.2
He	15	60	0.25
H_2	22.5	30	0.75
CO_2	24	1	24
H_2O	550	5	110

Source: van Krevelen D.W. and te Nijenhuis K. 2009. *Properties of Polymers*, 4th edn., Elsevier, Oxford, England, pp. 655–702. With permission.

TABLE 4.5
Diffusion, Solubility and Permeability Coefficients for Low Density Polyethylene Film at 25°C to CO_2, O_2 and N_2

	$D \times 10^6$ cm^2 s^{-1}	$S \times 10^4$ mL(STP) mL^{-1} (cm Hg)$^{-1}$	*P* (*barrer*)
CO_2	0.37	33.87	12.6
O_2	0.46	6.29	2.9
N_2	0.32	3.04	0.97

Source: Adapted from Pauly, S., Permeability and diffusion data, in: *Polymer Handbook*, 4th edn., Brandrup, J., Immergut, E.H., and Grulke, E.A. (Eds), Wiley-Interscience, New York, Section VI-543, 2005.

estimated using the corresponding values from Table 4.4. These relative values are also valid to a lesser degree for the *D* and *S* values. It can be seen that O_2 permeates about four times as fast as N_2 and CO_2 permeates about six times as fast as O_2 and 24 times as fast as N_2. Table 4.5 gives actual diffusion, solubility and permeability coefficients for LDPE and in this specific case CO_2 permeates about four times as fast as O_2 and almost 13 times as fast as N_2, illustrating that the values in Table 4.4 are generalizations.

It may be thought strange that CO_2, the largest of the three gas molecules, has the highest permeability coefficient. In fact, it has a low diffusion coefficient as would be expected from its relative size, but its permeability coefficient is the highest because its solubility coefficient *S* is much greater than that for the other gases as illustrated in Table 4.5 for LDPE.

Of particular interest in MAP is the effect of multiple gas transfer through polymers. Although CO_2 does not affect O_2 and N_2 transfer through PAs, it has a plasticizing effect on O_2 and N_2 transfer through LDPE. Lewis et al. (2003) reported that the solubility and diffusion of N_2 in amorphous and biaxially oriented films of PET were markedly affected by the presence of O_2 and CO_2 with differences in detail for amorphous and biaxially oriented films. N_2 solubility in PET decreased with an increase in CO_2 or O_2 concentration because of a competitive effect for occupying sites in the polymer. N_2 diffusivity increased with an increase in CO_2 or O_2 concentration because O_2 sorption decreased the tortuosity of the polymeric matrix. CO_2 exerted a plasticizing effect on the polymer although CO_2 diffusivity was little affected by N_2 and O_2 in the mixture, whereas CO_2 solubility increased with their concentration in the mixture.

The separation of gas mixtures by dense polymeric membrane processes is one of the fastest growing branches of separation technology, with such separation relying on the different permeability values of gases in different membranes and relative to each other. In food packaging, the permeability ratio β (referred to as the *permselectivity*) is the ratio of P for CO_2 to that for O_2 and is of particular interest in MAP applications. The permselectivity ratios are not constant for a given polymer but increase as the temperature is lowered. For example, β for LDPE has been reported to decrease from 5.08 at 0°C to 3.45 at 20°C and β for PVC from 6.0 at 5°C to 4.0 at 40°C. By way of comparison, β in air is 0.76 and in water 23.33.

Factors which can affect the permeability coefficients of a polymer may be divided into those associated with the polymer itself and those affecting the diffusion coefficient D and the solubility coefficient S.

4.12.8 VARIABLES OF THE POLYMER

Not unexpectedly, the barrier properties of films depend on the specific molecular structures of the polymers involved. A structure that provides a good barrier to gases may provide a poor water vapor barrier. For example, highly polar polymers such as those containing hydroxyl groups (PAs and EVOH copolymers) are excellent gas barriers but poor water vapor barriers. Furthermore, their effectiveness as gas barriers is reduced when the polymer is plasticized by water. In contrast, nonpolar hydrocarbon polymers such as polyethylene have excellent water vapor barrier but poor gas barrier properties, the latter property improving as the density of the polyethylene increases. The magnitude of such effects is illustrated in Table 4.6.

Diffusion of a dissolved permeant in a polymer is viewed as a series of activated jumps from one vaguely defined cavity within the polymer matrix to another. Qualitatively, any agent that increases the number or size of cavities in a polymer or renders chain segments more mobile increases the rate of diffusion. A low value of D can result from either static or dynamic effects. Static effects include molecular packing in the amorphous phase, orientation and the amount of crystallinity. Molecular packing affects the way permeant molecules move through the free volume or vacancies in the polymer.

TABLE 4.6
Effects of Water Vapor on Oxygen Permeability Coefficients at 20°C

	***P* (barrer)**	
Polymer	**0% RH**	**100% RH**
EVOH (32% ethylene)	0.00005	0.006
Nylon-6	0.0076	0.043
Nylon-MXD6	0.0009	0.004
PET	0.023	0.023
LDPE	2.38	2.38

When there is a small amount of free volume, movement is limited. Symmetrical monomers lead to good packing and hence lower diffusion rates.

Orientation often leads to lower permeability as it can increase packing density which lowers *D*. However, mere stretching does not always lead to orientation of the molecular chains and may in fact lead to void formation which increases permeability. Increased crystallinity can reduce permeability because the crystal regions are impenetrable in most semicrystalline polymers and movement must occur around the crystallites resulting in a lower *D*.

Therefore, to be a good all-round barrier material, the polymer must possess the following properties:

1. Some degree of polarity such as is found in nitrile, chloride, fluoride, acrylic or ester groups.
2. High chain stiffness.
3. Inertness to the permeant. Many polymers, particularly those containing polar groups, can absorb moisture from the atmosphere or from liquids in contact with the polymer. This has the effect of swelling or plasticizing the polymer and reducing the barrier properties as Table 4.6 shows.
4. Close chain-to-chain packing ability brought about by molecular symmetry or order, crystallinity or orientation. Linear polymers with a simple molecular structure lead to good chain packing and lower permeant permeability than polymers whose backbone contains bulky side groups leading to poor packing ability. The higher the degree of crystallinity, the lower the permeability because the crystalline regions are relatively impermeable compared with the amorphous regions.

   It is difficult to generalize the effect of orientation on the permeability of polymers; permeability in some polymers is unaffected by orientation while in others increases or decreases are observed. Table 4.7 shows the effect of orientation on the O_2 permeability of three polymers. Orientation of amorphous polymers decreases permeation by about 10 to 15%, while in crystalline polymers reductions of over 50% can be observed. The permeability of an amorphous polymer below or not far above its T_g depends on the degree of orientation of the molecular segments; it is normally reduced compared to that at high temperatures, although sometimes some small strains increase the permeability.

TABLE 4.7
Effects of Orientation on Oxygen Permeability Coefficients at 23°C

Polymer	Degree of Orientation (%)	*P* (*barrer*)
Polypropylene	0	0.89
	300	0.48
Polystyrene	0	2.52
	300	1.80
Poly(ethylene terephthalate)	0	0.06
	300	0.03

Source: Adapted from DeLassus, P., Barrier Polymers, in: *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn., Vol. 3, Kroschwitz J.I. (Ed), John Wiley & Sons, Inc., New York, pp. 375–407, 2002.

TABLE 4.8
Effects of Functional Groups on Oxygen Permeability Coefficients

Nature of *R* in (–CH_2–CHR–)$_n$	***P* (*barrer*)**
–OH	0.0006
–CN	0.00024
–Cl	0.048
–F	0.09
–$COOCH_3$	0.10
–CH_3	0.90
–C_6H_5	2.5
–H	2.9

Source: Adapted from Ashley, R.J., Permeability and plastics packaging, in: *Polymer Permeability*, Comyn, J. (Ed), Elsevier Applied Science, Essex, England, (Reprinted 1994), pp. 269–308, 1985.

5. Some bonding or attraction between chains. Cross-linking of polymer chains restricts their mobility and thus decreases their permeability, due mainly to the decrease in the diffusion coefficient. For example, in the case of polyethylene, one cross-link about every 30 monomer units leads to a halving of the diffusion coefficient. The effect of cross-linking is more pronounced for large molecular sized permeants.
6. High T_g. Below T_g, the segments have little mobility and there is also a reduction in free volume. Thus not only are there less voids, but, in addition, a diffusing molecule will have a much more tortuous path through the polymer. Therefore, if a polymer has a high T_g, then it is likely that its temperature of use will be below its T_g and it will consequently have improved barrier properties.

The sorption of moisture by polymers lowers their T_g and causes them to soften at lower temperatures. In certain polymers, the water acts as an internal lubricant, decreasing the energy barrier for chain segment movements. For example, the T_g values of EVOH copolymers and PAs are greatly reduced by only about 1% of water. Strong hydrogen bonds in PAs act in a similar way to cross-links in raising T_g, while small amounts of water break these bonds and cause abnormally large decreases in T_g. Table 4.8 shows the effect which different functional groups have on the O_2 permeability coefficient.

4.12.9 FACTORS AFFECTING THE DIFFUSION AND SOLUBILITY COEFFICIENTS

4.12.9.1 Pressure

In the case of the permanent gases, *P* is independent of the pressure of the diffusing gas. This is also true in many instances for other gases and vapors, provided there is no marked interaction between the polymer and the diffusing material. However, where there is strong interaction, *P* is found to be pressure dependent and, in general, it increases as the pressure increases. This is due to an increase in *D* promoted by the plasticizing effect of the sorbed permeant and an increase in *S* due to the shape of the sorption isotherm.

The past 20 years has seen the increasing commercialization of high pressure processing (HPP) as a method of increasing the shelf life of foods and beverages without the use of chemical preservatives or excessive heat treatments. Foods are normally subjected for periods of a few seconds up to several minutes to hydrostatic pressures above 150 MPa. The effects of

HPP on the barrier properties of mono- and multi-layer food packaging materials have been extensively studied and were recently reviewed (Guillard et al., 2010; Juliano et al., 2010). Most researchers have found that the barrier properties are not significantly modified by HPP. Although HPP causes a decrease in free volume which prevents diffusion in the polymeric matrix during the treatment, this effect disappears as the pressure is released. However, multilayer and composite structures can undergo severe deformation leading to wrinkles, delamination and even holes with a resultant increase in permeability (Galotto et al., 2010). Juliano et al. (2010) usefully summarized the results of reported studies including the OTRs and WVTRs before and after HPP.

Bull et al. (2010) found that the barrier properties of vapor-deposited oxide and nylon containing films were compromised by the combination of high pressure (600 MPa) and high temperature (~110°C) which would be reasonably expected to be required to render food commercially sterile by high pressure thermal (HPT) processing. However, the barrier properties of aluminum foil and films containing PVdC-methyl acrylate copolymer were not significantly affected by HPT processing. All materials suffered cosmetic deformation of the outer surface to some degree and mechanisms for these changes were proposed.

4.12.9.2 Sorption

The term sorption is generally used to describe the initial penetration and dispersal of permeant molecules into the polymer matrix and includes both adsorption (limited to the surface of the polymer) and absorption (penetration into, and sometimes even through, the polymer) as well as cluster formation. Sorption behavior has been classified on the basis of the relative strengths of the interactions between the permeant molecules and the polymer or between the permeant molecules themselves within the polymer.

The simplest type of sorption (known as Type I) arises when both polymer/permeant and permeant/permeant interactions are weak relative to polymer/polymer interactions; that is, when ideally dilute solution behavior occurs and Henry's law is obeyed. S is independent of sorbed concentration at a given temperature and therefore the sorption isotherm shows a linear dependence of concentration c versus vapor pressure p:

$$c = Sp \tag{4.22}$$

This type of behavior is observed when permanent gases are sorbed by rubbery polymers at low (<1 atm) pressure and arises from the very low solubility (<0.2%) of the permanent gases in these polymers.

The partition coefficient K is a fundamental physicochemical parameter describing the equilibrium distribution of a solute between two contacting phases (solid and vapor phase or solid and liquid phase or two solid phases in contact):

$$K = \frac{c_\mathrm{f}}{c_\mathrm{p}} \tag{4.23}$$

where c_f and c_p are the solute equilibrium concentrations in the two phases (Baner and Piringer, 2008). The partition coefficient describing solute partitioning between air and polymer is often referred to as a solubility coefficient S and can be expressed in terms of the molal activity coefficient for polymers using Equation 4.11:

$$S = \frac{c}{p} \tag{4.24}$$

where p is the solute partial pressure.

The term *scalping* is used to refer to the uptake of components of the food such as flavor, aroma and pigments by plastic packaging. There have been many studies on scalping and recent reviews (Sajilata et al., 2007; Caner, 2011) provide a good summary. Sorption properties are largely determined by the characteristics of the package, the properties of the flavor molecules, food matrix composition and environmental conditions. The chemical composition, chain stiffness, morphology, polarity and crystallinity of the polymer influence flavor absorption as much as the chemical composition, concentration and polarity of the flavor compounds, as well as the presence of other chemical constituents. External factors such as duration of storage, RH, temperature and the presence of other food components can also affect the solubility of aroma compounds in packaged foods.

As well as loss of aroma, sorption of organic molecules can also affect the mechanical properties of polymer films such as a reduction in seal and tensile strengths, and an increase, O_2 permeability by two to four times. Organic molecules act as plasticizing agents, inducing an increase in the polymer free volume and the new holes that are formed allow transfer of O_2.

Polyesters such as PET, PEN and PC have a more polar character than the polyolefins and therefore show less affinity to the common flavor compounds; that is, they absorb fewer flavor compounds. An extensive review (Linssen et al., 2003) concluded that although packaging and flavor interactions exist, they do not influence food quality to the extent that they cause insuperable problems in practical situations. This is evident from the fact that packaging materials in which polyolefins are in contact with juices are widely used commercially.

The impact of HPT treatments (pasteurization at 800 MPa and 40°C, and sterilization at 800 MPa and 115°C) on scalping of four aroma compounds (2-hexanone, ethyl butanoate, ethyl hexanoate, *d*-limonene) was assessed for LDPE and PLA by Mauricio-Iglesias et al. (2011). While both materials appeared suitable for pasteurization, LDPE showed a significant increase in the uptake of aroma compounds during sterilization. For scalping in PLA, temperature was a critical factor, especially if the temperature of the treatment exceeded T_g which was the case during sterilization; as a consequence scalping increased notably.

4.12.9.3 Temperature

The temperature dependence of S over relatively small ranges of temperature can be represented by an Arrhenius-type relationship:

$$S = S_o \exp\left(-\frac{\Delta H_s}{RT}\right) \tag{4.25}$$

where ΔH_s is the heat of sorption. For the permanent gases, ΔH_s is small and positive and therefore S increases slightly with temperature. For easily condensable vapors, ΔH_s is negative due to the contribution of the heat of condensation, and thus S decreases with increasing temperature.

The temperature dependence of D can also be represented by an Arrhenius-type relationship as in the following:

$$D = D_o \exp -\frac{E_d}{RT} \tag{4.26}$$

where E_d is the activation energy for the diffusion process. E_d is always positive and D increases with increasing temperature.

From the two previous equations, it follows that

$$P = P_o \exp\left(\frac{-E_p}{RT}\right) \tag{4.27}$$

$$= (D_oS_o)\exp[-(E_d + \Delta H_s)/RT] \quad (4.28)$$

where

E_p (=$E_d + \Delta H_s$) is the apparent activation energy for permeation
E_p, E_d and ΔH_s are expressed in kJ mol^{-1}
$R = 8.314$ J mol^{-1} K^{-1} while T is the absolute temperature in Kelvin

It follows that the P of a specific polymer–permeant system may increase or decrease with increases in temperature depending on the relative effect of temperature on S and D. Generally, S increases with increasing temperature for gases and decreases for vapors and D increases with temperature for both gases and vapors. For this reason, P of different polymers determined at one temperature may not be in the same relative order at other temperatures.

Example 4.7

The permeability coefficient P of a PET bottle to CO_2 at 20°C is 0.12 *barrer*. Calculate the value of P at 40°C given that $E_p = 32$ kJ mol^{-1} and $R = 8.314$ J K^{-1} mol^{-1}.

Equation 4.27 needs to be written for each temperature condition.

$$P_{20} = P_o\exp(-E_p/RT_{20})$$

$$P_{40} = P_o\exp(-E_p/RT_{40})$$

On dividing the second equation by the first

$$P_{40} = P_{20}\exp(-E_p/R[1/T_{40} - 1/T_{20}]) \quad (4.29)$$

Converting temperatures from °C to K

$$1/T_{40} = 1/(273+40) = 1/313 = 0.003195$$

$$1/T_{20} = 1/(273+20) = 1/293 = 0.003413$$

On substituting into Equation 4.29

$$\begin{aligned} P_{40} &= 0.12\exp(-32{,}000/8.314[0.003195 - 0.003413]) \\ &= 0.12\exp(-3848.93 \times -0.000218) \\ &= 0.12\exp(0.8391) \\ &= 0.278 \textit{ barrer} \end{aligned}$$

That is, P is 2.3 times greater at 40°C than at 20°C. This result has significant implications for the shelf life of carbonated beverages in warm climates. However, the aforementioned calculation is based on some gross simplifications. As DeLassus (2002) has pointed out, for the case of a PET soft drink bottle, the principal mechanism for loss of CO_2 is by sorption in the bottle walls as 5 atm of CO_2 equilibrates with the polymer. For an average wall thickness of 37 µm, many months are required to lose enough CO_2 (15% of initial volume) to become unacceptable.

A computer model for predicting the performance of plastic packaging under a broad range of environmental conditions was introduced commercially in 2002 and is widely used by the packaging industry (www.containerscience.com). Known as M-RULE® after founder and President

Dr. Mark Rule, it is a fundamental model based on the prediction of the diffusion and solubility of gases from first principles. It takes into account all the factors that affect permeation, including concentration-dependent diffusion, temperature, crystallinity, orientation, stress and stress relaxation. The model simultaneously calculates the migration of O_2, N_2, CO_2 and H_2O and continually revises the diffusivities and solubilities of each of these permeants as a function of the aforementioned factors. It is applicable to all the major barrier technology options including plasma coatings, multilayers, blends and nanocomposites and allows the user to assess the impact of package design, filling, storage and distribution conditions on product shelf life.

4.12.10 TRANSMISSION RATE

The earlier treatment of steady-state diffusion assumed that both D and S are independent of concentration but in practice deviations do occur. Equation 4.14 does not hold for heterogeneous materials such as coated or laminated films, or when there is interaction such as that occurs between hydrophilic materials (e.g., EVOH copolymers and PAs) and water vapor. The property is then defined as the transmission rate (TR) of the material, where

$$\mathrm{TR} = \frac{Q}{At} \tag{4.30}$$

where

Q is the amount of permeant passing through the polymer
A is the area
t is the time

Permeabilities of polymers to water vapor, gases and organic compounds are often presented in this way, especially in the commercial world. As a guide, it is possible to assume that if the thickness of a barrier layer is doubled, the TR of a permeant is halved. In the case of water, the term WVTR (water vapor transmission rate) is in common usage. For gases, the general term GTR (gas transmission rate) is used as well as the specific terms OTR or O_2TR (oxygen transmission rate) or O_2GTR (oxygen gas transmission rate according to ASTM standards) and CDTR or CO_2TR (carbon dioxide transmission rate) where appropriate.

TR is related to P as follows:

$$P = \frac{Q}{At}\frac{X}{\Delta p} = \mathrm{TR}\frac{X}{\Delta p} \tag{4.31}$$

Because the TR includes neither pressure of the permeant nor thickness of the polymer in its dimensions, it is necessary to know either the pressure or the concentration of permeant and the thickness of the polymer, under the conditions of measurement. Furthermore, since the TR is not a real constant which is characteristic for a polymer, it should only be used as a means of comparing orders of magnitude. In this book, the units of (g m^{-2} d^{-1}) will be used for WVTR and (mL m^{-2} d^{-1}) for GTRs. Such data for a variety of polymer films are given in Table 4.9.

To assist in the calculation of the driving force for water vapor transmission, Table 4.10 gives the saturation vapor pressure of water at various temperatures. WVTR expressed in g 100 in^{-2} d^{-1} (a common unit in the United States) is 1/15 of the value of WVTR expressed in g m^{-2} d^{-1}.

The data sheets from most suppliers of plastic films give the WVTRs determined at 38°C/90% RH. While this is relevant for products sold in tropical conditions, it is not particularly helpful for products sold in temperate conditions where 25°C/75% RH is more appropriate. The water

TABLE 4.9
Oxygen Transmission Rate (OTR) and Water Vapor Transmission Rate (WVTR) of Some Plastic Films

	OTR	WVTR	
Polymer (25 μm Thick)	**(23°C/0% RH) mL m^{-2} day^{-1}**	**(38°C/90% RH) g m^{-2} day^{-1}**	**(25°C/75% RH) g m^{-2} day^{-1}**
Low density polyethylene	7400	12.50	4.00
High density polyethylene	1600	3.70	1.45
Polypropylene (cast)	3040	8.20	3.30
Polypropylene (oriented)	1550	5.00	1.35
Polypropylene (acrylic-coated)	1200	4.60	1.80
Polypropylene (oriented and metallized)	35	1.00	
Poly(vinyl chloride) (rigid)	120	32.00	12.00
Poly(vinyl chloride) (oriented)	27	17.50	7.00
Poly(vinyl chloride) (plasticized)	190–3100	85.00	32.70
PVdC/PVC copolymer	1.25–14.5	0.6–3.20	0.25
Poly(ethylene terephthalate)	55	20.00	7.00
Poly(ethylene terephthalate) (PVdC/PVC copolymer-coated)	8.00	8.50	3.40
Poly(ethylene terephthalate) (metallized)	0.65	1.00	0.40
Polyamide (nylon) 6	40	280	80–110
Polyamide (nylon) 6 (oriented)	18	130	28
Polyamide (nylon) 6,6	35	90	15–30
EVOH copolymer (32% ethylene)	0.2	80.0	32.0
Cellulose film MXXT/A (PVdC/PVC copolymer coated)	8.75	8.60	3.40

Source: Mathlouthi, M., Packaging/packaging of solids, in: *Encyclopedia of Food Sciences and Nutrition*, 2nd edn., Vol. 7, Caballero, B., Trugo, L.C., and Finglas, P.M. (Eds), Academic Press, London, England, p. 4314, 2003. With permission.

vapor pressure at 38°C/90% RH (4.47 cm Hg) is 2.5 times that at 25°C/75% RH (1.78 cm Hg) and therefore shelf life calculations based on a WVTR determined at the higher temperature and humidity will underestimate actual shelf life under temperate conditions by approximately 2.5 times.

Example 4.8

Calculate the permeability coefficient P of an OPP film to O_2 at 23°C given that the OTR through a 2.5×10^{-2} mm thick film with air on one side and inert gas on the other is (from Table 4.9) 1550 mL m^{-2} day^{-1}.

Because air contains approximately 21% O_2, the O_2 partial pressure difference across the film is 0.21 atm = 16 cm Hg.

$$P = \frac{\text{OTR}}{\Delta p} \times \text{thickness}$$

$$= \frac{1550\,\text{mL m}^{-2}\ \text{day}^{-1}}{16\,(\text{cm Hg})} \times 2.5 \times 10^{-2}\ \text{mm}$$

TABLE 4.10
Saturation Vapor Pressure of Water at Various Temperatures

Temperature (°C)	cm Hg	Temperature (°C)	cm Hg	Temperature (°C)	cm Hg
−18	0.096	16	1.363	37	4.707
−10	0.215	17	1.453	38	4.969
−5	0.316	18	1.548	39	5.244
−2	0.396	19	1.648	40	5.532
−1	0.426	20	1.754	41	5.834
0	0.458	21	1.864	42	6.150
1	0.493	22	1.983	43	6.480
2	0.529	23	2.107	44	6.826
3	0.569	24	2.238	45	7.188
4	0.610	25	2.376	46	7.565
5	0.654	26	2.521	47	7.960
6	0.701	27	2.674	48	8.371
7	0.751	28	2.835	49	8.802
8	0.805	29	3.004	50	9.251
9	0.861	30	3.182	55	11.804
10	0.921	31	3.370	60	14.038
11	0.984	32	3.666	65	18.754
12	1.052	33	3.773	70	23.37
13	1.123	34	3.990	80	35.51
14	1.199	35	4.218	90	52.6
15	1.287	36	4.456	100	76.0

These units must be converted into the appropriate ones for P as follows:

$$\begin{aligned} P &= \frac{1550\,\text{mL}\times 2.5\times 10^{-2}\ \cancel{\text{mm}}}{\cancel{\text{m}}^{2}\ \cancel{\text{day}}\times 16(\text{cm}\,\text{Hg})}\times\frac{\cancel{\text{day}}}{(24)\,(3600)\text{s}}\times\frac{\text{m}^2}{(100\,\text{cm})^2}\times\frac{\text{cm}}{10\,\text{mm}} \\ &= 2.8\times 10^{-10}[\text{mL cm cm}^{-2}\ \text{s}^{-1}\ (\text{cm}\,\text{Hg})^{-1}] \\ &= 2.8\ \textit{barrer} \end{aligned}$$

Adjusting to STP

$$P = 2.8\times\frac{273}{296} = 2.6\ \textit{barrer}$$

For films where the transmission rate is given at a different (reference) thickness X_{ref}, the transmission rate at the actual thickness X_{act} can be calculated as follows:

$$\text{TR}_{\text{act}} = \text{TR}_{\text{ref}}\cdot\frac{X_{\text{ref}}}{X_{\text{act}}} \tag{4.32}$$

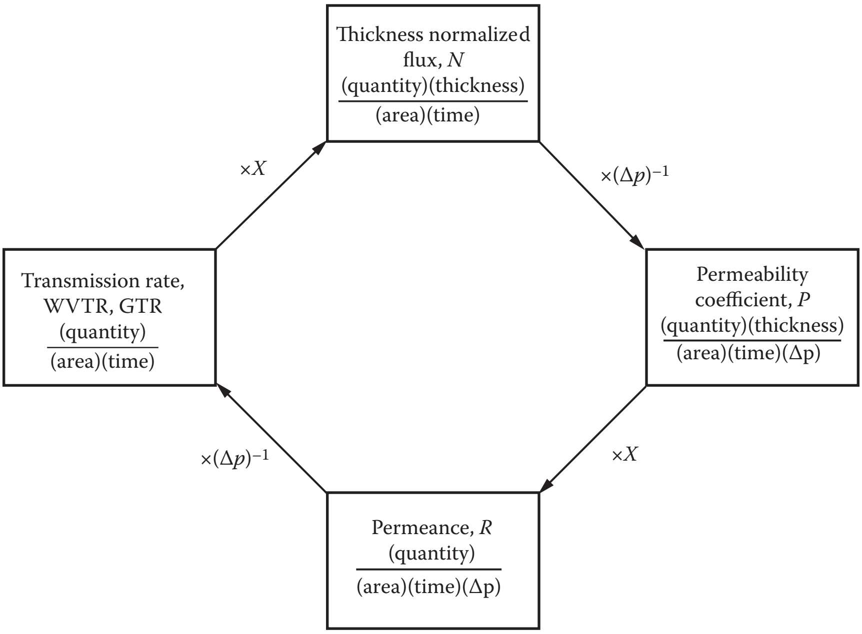

FIGURE 4.4 Relationship between transmission rate TR, thickness normalized flux *N*, permeance *R* and permeability coefficient *P*. (Hernandez, R.J., Food packaging materials, barrier properties and selection, in: *Handbook of Food Engineering Practice*, Valentas, K.J., Rotstein, E., and Singh, R.P. (Eds), CRC Press, Boca Raton, FL, pp. 291–360, 1997.)

Example 4.9

What is the OTR for 25 μm OPP at 5°C given that it is 1015 mL m^{-2} d^{-1} for 20 μm OPP?

$$\mathrm{TR_{act}} = \mathrm{TR_{ref}} \cdot \frac{X_{\mathrm{ref}}}{X_{\mathrm{act}}} 1015 \cdot \frac{20}{25} = 812\ \mathrm{mL\ m^{-2}\ d^{-1}}$$

Sometimes the WVTR is given in units of g mm m^{-2} d^{-1} in which case it should be (but is seldom) referred to as the thickness normalized flux *N*. The relationship between transmission rate TR, thickness normalized flux *N*, permeance *R* and permeability coefficient *P* is shown in Figure 4.4.

Example 4.10

Joo et al. (2011) reported the WVTR of 290 μm thick OPLA at 37.8°C and 100% RH as 36.7 g m^{-2} d^{-1}. What is the permeability coefficient in *barrer*?

From Table 4.10, the saturated vapor pressure of water at 37.8°C is 4.9167 cm Hg.

$$P = \frac{36.7\ \cancel{\mathrm{g}} \times 290\ \cancel{\mathrm{\mu m}}}{\mathrm{m^2}\ \cancel{\mathrm{d}}(4.9167\ \cancel{\mathrm{cmHg}})} \times \frac{\mathrm{kg}}{1000\ \cancel{\mathrm{g}}} \times \frac{1 \times 10^{-6}\ \mathrm{m}}{\cancel{\mathrm{\mu m}}} \times \frac{\cancel{\mathrm{d}}}{86{,}400\ \mathrm{s}} \times \frac{7.5 \times 10^{-4}\ \cancel{\mathrm{cmHg}}}{\mathrm{Pa}}$$

$$= 1.88 \times 10^{-14}\ \mathrm{kg\ m\,m^{-2}\ s^{-1}\ Pa^{-1}}$$

From Table 4.2, the conversion factor to *barrer* is 16.60 × 10^6

Therefore,

$$\begin{aligned} P &= (1.88 \times 10^{-14}) \times (16.60 \times 10^{6}) \\ &= 3.12 \times 10^{-7} \\ &= 3120 \times 10^{-10} \\ &= 3120 \textit{ barrer} \end{aligned}$$

Of considerable interest in many food packaging applications is the TR of various organic compounds such as flavors, aromas, odors and solvents through polymers. This is particularly so where the package contents have to be protected against contamination from foreign odors or where there is a requirement to ensure that volatile flavoring compounds are not lost from the food. The significant off-flavors found in some food products may result from the packaging material itself or may permeate through the packaging material from the outside environment. In other situations, foods may contain highly desirable but volatile flavor compounds whose loss from the packaged food would detract from its quality. In both situations, suitable tests must be undertaken to select materials which have the desired odor barrier properties.

Flavor and aroma losses from foods to package components occur by solution (sorption), with the rate being governed by the magnitude of the diffusion coefficient, followed by permeation if enough time elapses. However, the majority of such problems involve scalping, the term for sorption of fugitive molecules into the package contact surfaces which was discussed earlier in Section 4.12.9.2. In these situations, permeation is usually of no consequence. Scalping has been of particular concern in the packaging of beverages and fruit juices (see Section 21.6.2).

The permeation of organic vapors through polymer films is much more complicated than that of gases, due to the pressure-dependent S and the concentration-dependent D. The values of D calculated by different techniques and for films of different thicknesses may differ by more than an order of magnitude. As well, the rearrangement of polymer molecules in the presence of the permeant may proceed relatively slowly, so that the apparent D is a function of both permeant concentration and time.

While it can be assumed that the S and D of permeants in polymers are independent of concentration when dealing with non-interactive permeants such as the common gases, this assumption may not be valid in the case of organic vapors. For example, once an apparent steady-state rate of diffusion had been obtained, continued exposure to the organic penetrant can result in concentration-dependent phenomena such as long-term chain relaxation, swelling of the polymer matrix and additional sorption of permeant.

The permeability of organic vapors is often expressed in the so-called Modified Zobel Unit (MZU) which is defined as (10^{-20} kg m m^{-2} s Pa^{-1}). For example, Miller and Krochta (1998) reported P for *d*-limonene in PVdC copolymer film at 55°C as 18,000 MZU (±5000) while that in EVOH was 0.9 MZU (±0.3). Although extensive studies have been made on the permeability, solubility and diffusivity of various organic vapors in LDPE, much less data are available for other polymers. Since the solvent action of organic vapors varies from polymer to polymer, the permeability cannot be compared in a similar fashion as it can for permanent gases and water vapor. The state of aroma compounds (liquid or vapor), as well as physicochemical properties such as MW, structure, hydrophobicity and polarity have an effect on the affinity for a polymeric matrix (sorption) and also on the transfer kinetics (diffusion).

Mercea (2008) reviewed most of the literature on the kinetics of low MW organic compounds (migrants) in polyethylenes and polypropylenes and compiled diffusion data (D values) at 23°C in a very large but valuable table. The D of a given migrant depends on the molecular type and morphology/structure, density and crystallinity of the polymer as well as temperature. He noted that there are a series of problems involved in comparing and interpreting experimentally determined Ds in polymers. These result from the complex physical and chemical interactions between the migrants and the host polymer matrix that can have a significant influence on the magnitude of D. Problems are also generated by the dependence of the morphological character of the polymer matrix on its physical and chemical, as well as manufacturing, history. D may also be influenced by the experimental setup used. Thus, the sometimes large spread of D values reported for one and the same migrant in the same polymer should not be considered as unusual or incorrect.

4.12.11 MIGRATION

Migration is the release of substances initially present in the packaging material into the food. Plastics contain numerous low MW substances that can migrate including monomers, oligomers and various additives such as plasticizers and antioxidants. These substances diffuse through the material until they reach the inside surface of the package where they are partially transferred to the headspace and/or dissolved in the food. This may result in a loss of food quality due to flavor or color changes, or it may make the food toxic without perceptibly altering the organoleptic properties of the food. It is for this latter reason that regulations have been promulgated which establish maximum migration limits for substances found in plastics which are used to package food. Migration is considered in detail in Section 22.1.2.

4.12.12 PERMEABILITY OF MULTILAYER MATERIALS

Many foods require more protection than a single material can provide to give the product its intended shelf life. Where increased barriers to gases and/or moisture vapor are necessary, it is more economical to incorporate a thin layer of barrier material than to simply increase the thickness of a monolayer. In most cases, increasing the monolayer thickness would be impractical as it would require too much material. For example, to equal the O_2 barrier of a 25 μm film of a high barrier material such as PVdC copolymer would require 62,500 μm of PP or 4,375 μm of PETG or 1,250 μm of PET or 1,250 μm of rigid PVC or 250 μm of nylon-6.

Multilayer materials can be considered as a number of membranes in series. Consider the case of three layers in series as shown schematically in Figure 4.5. The total thickness $X_T = X_1 + X_2 + X_3$. Assuming steady-state flux, the rate of permeation through each layer must be constant, that is,

$$Q_T = Q_1 = Q_2 = Q_3 = Q_O \tag{4.33}$$

likewise, the areas will also be constant so that

$$\mathrm{A_T = A_1 = A_2 = A_3} \tag{4.34}$$

Recall Equation 4.15

$$\frac{Q}{t} = \frac{P}{X} A(\Delta p) \tag{4.15}$$

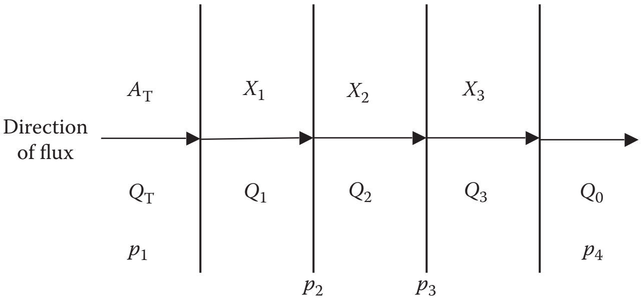

FIGURE 4.5 Schematic representation of permeation through three materials in series.

Then, on substituting

$$\frac{Q_T}{t} = \frac{P_1}{X_1} A_1(p_1 - p_2) = \frac{P_2}{X_2} A_2(p_2 - p_3) = \frac{P_3}{X_3} A_3(p_3 - p_4) \tag{4.35}$$

By rearranging Equation 4.35 and writing it for the case of permeation through the multilayer material

$$\frac{Q_T X_T}{t A_T P_T} = (p_1 - p_4) = \Delta p_i \tag{4.36}$$

now, because

$$(p_1 - p_4) = (p_1 - p_2) + (p_2 - p_3) + (p_3 - p_4) \tag{4.37}$$

therefore,

$$\frac{Q_T X_T}{t A_T P_T} = \frac{Q_T}{t A_T}\left[\frac{X_1}{P_1} + \frac{X_2}{P_2} + \frac{X_3}{P_3}\right] \tag{4.38}$$

and

$$\frac{X_T}{P_T} = \frac{X_1}{P_1} + \frac{X_2}{P_2} + \frac{X_3}{P_3} \tag{4.39}$$

or

$$P_T = \frac{X_T}{(X_1/P_1) + (X_2/P_2) + (X_3/P_3)} \tag{4.40}$$

Thus, if the individual thicknesses and permeability coefficients are known for each layer and provided that the permeability coefficients are independent of pressure, then Equation 4.40 can be used to calculate the permeability coefficient for any multilayer material. If they are not independent of pressure, then differing permeability coefficients will be obtained depending on the positioning of the layers.

The standard methods discussed next for gas permeability measurements through polymeric materials all specify dry gas. However, in practice, packaging films are almost always used in humid conditions and for materials such as EVOH copolymers and PAs, the O_2 permeability is dependent on the humidity. In such cases, Equation 4.40 cannot be used directly since P_2 (the permeability coefficient of the center layer) will depend on the average partial pressure at the center.

Example 4.11

Calculate the total O_2 permeability at 30°C of a multilayer film with the following structure:

	Polymer	***P* (*barrer*)**	**Thickness (cm)**
Layer 1	LDPE	5.5	5.0×10^{-3}
Layer 2	Nylon-6	0.018	2.0×10^{-3}
Layer 3	LDPE	5.5	5.0×10^{-3}

On substituting into Equation 4.39

$$\frac{0.005+0.002+0.005}{P_{\mathrm{T}}}=\frac{0.005}{5.5}+\frac{0.002}{0.018}+\frac{0.005}{5.5}$$

and

$$\frac{0.012}{P_{\mathrm{T}}}=9.091\times10^{-4}+1.111\times10^{-1}+9.091\times10^{-4}$$

Solving for P_{T}

$$\begin{aligned}P&=1.129\times10^{-3}/0.012\\&=0.094\ \mathit{barrer}\end{aligned}$$

Note that in this example, the nylon barrier layer is providing virtually all of the resistance to transmission. Given that the accuracy of P is seldom better than ±5%, the contribution of the supporting layers in this example could have been ignored without significantly affecting the final result.

Recently, a simple mathematical model to predict the O_2 transport properties of multilayer films was proposed (Mastromatteo and Del Nobile, 2011). The results obtained suggested that despite the approximations involved in deriving the model, its ability to predict the P of the multilayer film was quite satisfactory.

An equation for predicting the average partial pressure at the center of a multilayer material containing a water sensitive center layer can be derived as follows: Consider again the case of three layers in series as shown schematically in Figure 4.5, but this time assume that the O_2 permeability of the center layer is humidity dependent and that the direction of water vapor flux is from the outside in.

Since the partial pressure of water vapor will not be constant across the multilayer, Equation 4.30 must be modified to include a term for the partial pressure difference and the thickness:

$$\mathrm{WVTR}=\frac{Q}{AtX}\Delta p \tag{4.41}$$

Now, because the area A and time t will be the same for all three layers, the equilibrium WVTR between the outside and center layers can be expressed as the following:

$$\frac{Q_1}{X_1}(p_1-p_2)=\frac{Q_2}{X_2}(p_2-p_3) \tag{4.42}$$

Similarly, the equilibrium WVTR between the center and the inside layer will be

$$\frac{Q_2}{X_2}(p_2-p_3)=\frac{Q_3}{X_3}(p_3-p_4) \tag{4.43}$$

The average partial pressure of the center layer (p_c) will be

$$p_c=\frac{p_2+p_3}{2} \tag{4.44}$$

Simultaneous linear solution of Equations 4.42 and 4.43 for p_2 and p_3 and substitution in Equation 4.44 yields

$$p_c = \frac{p_1\left[\frac{X_2}{Q_2} + 2\frac{X_3}{Q_3}\right] + p_4\left[\frac{X_2}{Q_2} + 2\frac{X_1}{Q_1}\right]}{2\left[\frac{X_3}{Q_3} + \frac{X_2}{Q_2} + \frac{X_1}{Q_1}\right]}$$

$$= \text{average partial pressure of the center layer} \tag{4.45}$$

From knowledge of p_c, the permeability coefficient P_c of the center layer can be determined experimentally at this partial pressure and Equation 4.40 used to calculate the overall permeability of the multilayer material.

4.12.13 MEASUREMENT OF PERMEABILITY

4.12.13.1 Gas Permeability

There are many methods for measuring gas permeability; the four major methods will be considered here. For a complete understanding of the principles behind permeability measurements, it is important that the meaning of two terms which are constantly used—total and partial pressure of gases in a mixture—is clearly appreciated.

In a constant volume, the total pressure exerted by the gases present is the sum of the partial pressures of each of the gases, a discovery made by English scientist John Dalton in 1801 and known as Dalton’s law. The partial pressure of any one of the constituent gases is the pressure which would result if that particular gas occupied the same volume by itself. That is, each of the gases of a gas mixture behaves independently of the others.

The rate of permeation of a specific gas through a polymeric material is a function of the partial pressure differential of that gas across the material and not of the total pressure difference between the two sides.

4.12.13.1.1 Pressure Increase Method

The ASTM manometric method for measuring gas transmission rates and permeabilities of flat films is designated D1434. It is sometimes referred to an isochoric or constant volume method. Test gas (normally at 1 atm) is introduced on one side of the flat film or sheet which is supported with a filter paper and sealed with an O-ring. The pressure in the receiving chamber is measured with an open-ended mercury manometer. Provided that the pressure on the high-pressure side remains much larger than that on the low-pressure side, the pressure difference remains essentially constant. Through equations relating the geometry of the cell with the rate of pressure rise in the manometer, the gas transmission rate can be calculated.

4.12.13.1.2 Volume Increase Method

In the ASTM standard volumetric method (also designated D1434), the change in volume (at constant pressure), due to the permeation of gas through the film, is measured. Variable volume permeation cells are used for rapid measurement of relatively high steady-state permeation rates. Although the volume increase method is generally simpler to implement, it is less sensitive than the pressure increase method. Volumetric methods are used relatively infrequently compared with the use of the pressure increase or concentration increase methods. A simple whole bag method based on a constant pressure/volume increase method has been described (Moyls, 2004).

Interlaboratory testing has revealed that permeances measured by the D1434 procedures exhibit a strong dependence on the procedure being used, as well as on the laboratory performing the testing.

Agreement with other methods is sometimes poor and may be material-dependent. The materials being tested often affect the between-laboratory precision. The causes of these variations are not known at this time and it is suggested that this method not be used for referee purposes.

4.12.13.1.3 Concentration Increase Method

In ASTM D3985 *Standard Test Method for Oxygen Gas Transmission Rate through Plastic Film and Sheeting Using a Coulometric Sensor* (also known as the quasi-isostatic coulometric method since the total pressure on both sides is approximately equal), a partial pressure difference across the film with respect to the test gas is created without a difference in total pressure, thus obviating the need for rigid support of the film. A partial pressure difference is maintained by sweeping one side continuously with the test gas and maintaining an inert gas on the other side into which the test gas diffuses. The concentration of the diffusing gas can be measured by chemical analysis, gas chromatography, thermal conductivity or special electrodes. A variation of this method (ASTM F1307 *Standard Test Method for Oxygen Transmission Rate through Dry Packages Using a Coulometric Sensor*) can be used to determine the O_2 transmission rate through dry packages. Both these methods operate at 0% RH.

ASTM F1927 *Standard Test Method for Determination of Oxygen Gas Transmission Rate, Permeability and Permeance at Controlled Relative Humidity through Barrier Materials Using a Coulometric Detector* covers a procedure for determination of the rate of transmission of O_2 at steady-state, at a given temperature and RH, through film, sheeting, laminates, coextrusions or plastic-coated papers. The ASTM recommended unit of O_2GTR is cm^3 (STP) m^{-2} d^{-1} at 1 atm pressure differential; O_2GTR in SI units of mol m^{-2} s^{-1} is obtained by multiplying the value in metric units by 5.165×10^{-10}. To obtain the O_2GTR for air on one side (the situation commonly encountered with food packages), the value should be multiplied by 0.21 since air contains 21% O_2. Sometimes, the unit is incorrectly reported as cm^3 (STP) m^{-2} d^{-1} atm^{-1} which can create confusion unless it is made clear that the value is for a pressure differential of 1 atm. Once the correction for air on one side has been made, the term atm should no longer be used. The corresponding standard for CO_2 is ASTM F2476.

Instruments are in widespread commercial use for the measurement of O_2 and CO_2 transmission rates by the isostatic methods, an advantage being that the permeability of not only flat film but also containers, bottles, pouches, tubes and so on can be determined, thus permitting the assessment of possible adverse effects from machine processing, printing and distribution. The use of these instruments is included in ASTM D3985, F1307 and F1927. The AOIR (ambient O_2 ingress method) is a modified version of the quasi-isostatic method and can be used to test actual packages over a wide range of temperature and humidity conditions, including chill and freezing temperatures (Larsen, 2004). Recently, a permeability testing device using fluorescence-based optical O_2 sensing was developed as a potential new instrument for measuring the O_2 permeability of packaging films (Siro et al., 2010).

4.12.13.1.4 Detector Film Method

A method for measuring permeabilities of films, which requires little equipment and is both rapid and accurate, was developed by Holland et al. (1980). The basis of the method is a plastic detector film impregnated with a reagent that is sensitive to the gas being measured. The film has an absorption spectrum that changes as the gas or vapor is absorbed and is thus suitable for spectrophotometric monitoring. The detector film is sealed between two pieces of test film in a simple cell so that the permeation rate of the penetrant gas or vapor can be readily measured.

The detector film can measure much less than the minimum detectable quantity of O_2 determined by most other methods, and therefore permits the use of either smaller film samples or more rapid permeability determinations.

The O_2 detector consists of a cast film of ethyl cellulose containing dimethylanthracene (DMA) and erythrosine. On absorbing blue light, the erythrosine can activate O_2 dissolved in the ethyl cellulose to form singlet O_2, a reactive form of O_2. Singlet O_2 (which has a lifetime of only a few microseconds in the film) diffuses to a neighboring DMA molecule and reacts with it. Thus, the disappearance of DMA (monitored in the UV) is a measure of the O_2 consumed. Since the ethyl cellulose detector is highly permeable to O_2, it is capable of measuring very low rates of O_2 permeation.

4.12.13.2 Water Vapor Permeability

The standard method to determine WVTRs (see ASTM E96) is to place a quantity of desiccant in an aluminum dish, which is covered with a sheet of the material being tested and sealed in position with wax. The dish is then placed in a closely controlled atmosphere (typically either 25°C ± 0.5°C and 75% ± 2% RH for temperate conditions, or 38°C ± 0.5°C and 90% ± 2% RH for tropical conditions) and the increase in weight noted as a function of time. If the points are plotted out, then they should fall more or less on a straight line because Δp is constant throughout the test. From Equation 4.30

$$\text{WVTR} = \frac{Q}{At} \tag{4.46}$$

$$= \frac{\text{slope}}{\text{area}} \tag{4.47}$$

$$= \frac{\text{g H}_2\text{O}}{\text{m}^2\ \text{day}} \tag{4.48}$$

To convert WVTR into permeance (P/X), it should be divided by the driving force Δp.

These methods have several disadvantages, including the length of time needed to make a determination (between 2 and 14 days) and the lower limit of the useful range (about 1 g m^{-2} day^{-1} for a typical packaging film). A further disadvantage is that, depending on the desiccant, Δp may not remain constant during the test period. In the case of anhydrous $CaCl_2$, the partial pressure of water vapor in the dish remains below 2% of the vapor pressure of water at the test temperature during the test, whereas in the case of silica gel, the partial pressure of water sorbed on it increases with coverage.

WVTR tests on flat sheets of film sealed across aluminum dishes do not always correlate closely with actual performance of the film when made up into complete packages. Therefore, it is often preferable to carry out WVTR tests where the desiccant is contained in a finished package which has been closed and sealed in the conventional manner. Details of the test procedures can be found in ASTM D3079.

In recent years, more rapid methods have been developed. Most of these depend on detecting small changes in the RH of the atmosphere on the dry side of the film. Typically, test cells consist of two sections separated by the material under test. The lower section contains water to give a saturated atmosphere, while the upper section contains a humidity sensor which is dried by purging with dry air. The movement of water vapor through the film raises the RH of the air surrounding the humidity sensor and the time for a given rise can be recorded; from this, the WVTR is calculated. Commercial instruments are available to determine WVTRs using either a pressure-modulated infrared detector or a mechanically modulated infrared detector. ASTM F1249 *Standard Test Method for Water Vapor Transmission Rate through Plastic Film and Sheeting Using a Modulated Infrared Sensor* describes the procedures.

A detector film to measure transmission rates of water vapor was developed by Holland and Santangelo (1982). It consists of transparent cellulose film which becomes bright blue when soaked in $CoCl_2$ solution and dried over $CaCl_2$ but rapidly turns pink on exposure to high humidities. A humidity cabinet is used to provide the partial pressure gradient across the test film, which is sealed in the same way and in a cell of similar design to that used to measure O_2 permeability (see Section 4.12.13.1.4). The change in absorbance of the detector film is measured at 690 nm, and from this the quantity of water absorbed by the detector film, and hence the WVTR of the test film, can be calculated.

4.12.13.3 Permeability of Organic Compounds

Although the permeabilities of the permanent gases and of water vapor through many packaging materials are well known, there is limited data for the permeation of organic compounds. It was shown earlier in this chapter that, for gases, P is independent of concentration. Thus, permeability measurements made at high concentrations can be reliably extrapolated to predict permeation rates where there are low concentration gradients across the barrier. However, in the case of many organic compound/plastic package combinations, P is strongly dependent on concentration. This effect occurs because the organic compound interacts with and swells the polymer, increasing the permeation rate.

Measuring the transport rates of organic compounds in plastics is more complicated than those of either water vapor or noncondensable gases, and elaborate equipment and sensitive analytical devices are required to obtain reliable results. As with permeability studies of the permanent gases, procedures to study organic vapor permeability include the isostatic and quasi-isostatic methods. Three main methods are used: integral permeation, differential permeation and sorption methods; these have been described by Dury-Brun et al. (2007). Commercial equipment based on these different methods is marketed to measure permeation of aroma compounds or sorption into and through packaging films. Inverse gas chromatography (IGC) and fourier transform infrared spectroscopy (FTIR) to measure transfer of aroma compounds through packaging films have been used since 1997.

Measurement of the transport phenomena of volatile compounds has been reviewed by Cayot et al. (2008). The authors pointed out that D values varying by several orders of magnitude can be found if different experimental permeation systems are used to determine them. The D for limonene in PP was found to vary from 3.7 to $2330 \times 10^{-16}\,\mathrm{m^2\,s^{-1}}$ at the same temperature and RH but with different concentrations in the vapor phase. In HDPE films, variations from 370 to $1700 \times 10^{-16}\,\mathrm{m^2\,s^{-1}}$ have been reported for the D for limonene. Such variations in D can be explained by differences in experimental conditions, which are sometimes not indicated or not controlled, and also by the limits of the methods which are not always known.

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5 Processing and Converting of Thermoplastic Polymers

5.1 EXTRUSION

5.1.1 MONOLAYER EXTRUSION

Extrusion can be defined as continuously forcing a molten material through a shaping device. It requires the development of pressure in order to force the melt through a die because the viscosity of most plastic melts is high. Extrusion is one of the most important plastics processing methods in use today. Most plastic materials are processed in extruders and commonly pass through two or more extruders on their way from the chemical reactor to the finished product. Manufacturers of plastic resins supply the product in the form of cylindrical, spherical or cubic pellets 2–3 mm in diameter. The manufacturers of packaging materials remelt these pellets and extrude specific profiles such as film, sheet or tubing, or as a molten tube of resin (parison) for blow molding or into molds, as in injection molding. Film has been arbitrarily defined by the ASTM as sheeting having a nominal thickness not greater than 0.25 mm (250 µm or 0.010 in.). The first screw extruder designed specifically for thermoplastic materials appears to have been made by Paul Troesterin in Germany in 1935.

The heart of the extruder is the Archimedean screw that revolves within a close-fitting, heated barrel. It is capable of pumping a material under a set of operating conditions at a specific rate, depending on the resistance at the delivery end against which the extruder is required to pump. The extruder resembles a mincer into which granules are fed, heated and compressed until they fuse into a melt that is forced through a slot or circular die.

The standard single-screw extruder (Figure 5.1) receives solid polymer in the form of powder, beads, flakes or granules through a hopper to a throat at one end of the barrel and delivers it to the compression zone of the screw. In this section, the diminishing depth of thread causes a volume compression and an increase in the shearing action of the material. It melts and is converted into a homogeneous mass by contact with the heated walls of the barrel and by the heat generated by friction. Generally, external heating is only required at the start of the run, since the frictional or exothermal heating is sufficient for steady-state operation. After the compression zone, the melt passes through the metering zone where the flow is stabilized before being pumped through the die that determines its final form. The output from the die is known as the *extrudate*.

The screw is the most important component of the extruder and different designs are used for extruding different polymers. Extruder screws are characterized by their length to diameter ratios (commonly abbreviated to *L*/*D* ratios) and their compression ratios—the ratio of the volume of one flight of the screw at the in-feed end to the volume of one flight at the die end. *L*/*D* ratios commonly used for single-screw extruders are between about 15:1 and 30:1, while compression ratios can vary from 2:1 to 4:1.

There are basically two processes by which the extruded thermoplastic can be converted into film: the flat film process and the tubular process. The first process is illustrated in Figure 5.1, while the latter process is illustrated in Figure 5.2.

In flat film (also known as cast film or slit die) extrusion, the molten polymer is extruded through a slit die into a quenching water bath or onto a chilled roller that is highly polished and plated and imparts a smooth and virtually flawless surface to the film. In both cases, rapid cooling of the

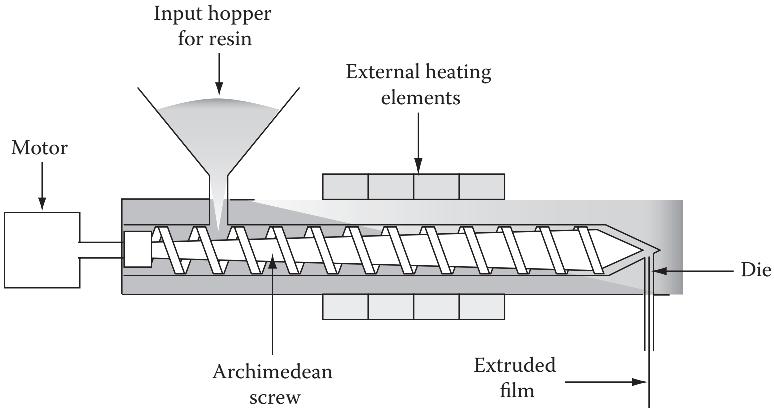

FIGURE 5.1 Single screw extruder.

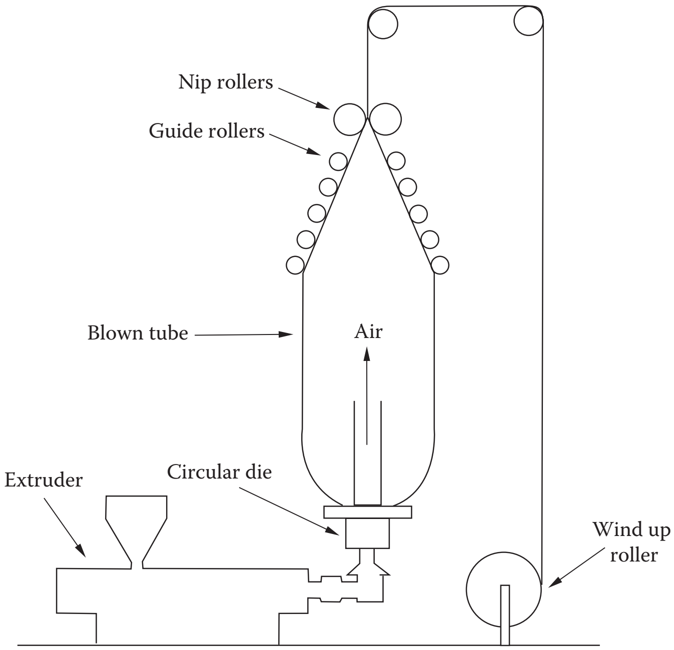

FIGURE 5.2 Blown tubular film extrusion.

extruded film is most important. The ratio of the haul-off rate to the natural extrusion rate is referred to as the draw-down ratio. Draw-down ratios between 20:1 and 40:1 are typical.

In the tubular (or blown film) process, a thin tube is extruded (usually in a vertically upward direction but sometimes in a horizontal or downward direction), and by blowing air through the center of the tubular die, the tube is inflated into a thin bubble and cooled, after which it is flattened and wound up. The ratio of bubble diameter to die diameter is known as the blow-up ratio (BUR) and most blown films used in packaging are made with a BUR of 2:1–4:1. Typical film thicknesses are 0.007–0.125 mm. Unless carefully controlled, blown film extrusion can produce defects such as variations in film thickness, surface defects, low tensile and impact strength, haze, blocking and wrinkling. The properties of the film depend strongly on the polymer used and the processing conditions. The higher the density, the lower the flexibility and the greater the brittleness. The higher the MW, the greater the tensile strength and resistance to film brittleness at low temperatures, but the lower the transparency.

Advantages of tubular film are that the mechanical properties are generally better, and the process is easier and more flexible to operate. The cost for making wide tubular film is much lower than for wide cast film, due to the cost of precision grinding long chill rolls. Advantages of the flat film process include less thickness variation, very high outputs and superior optical properties. This latter advantage is a consequence of the quicker cooling that can be achieved in the flat film process where cooling is by conduction, compared with the tubular film process where cooling is by convection. Slower cooling permits the formation of more and larger crystals in the film, leading to haze that arises from the scattering of light between the crystal interfaces.

5.1.2 COEXTRUSION

Coextrusion consists of coupling two or more extruders feeding different resins to a single die head to simultaneously extrude two or more different polymers that fuse at the point of film formation into a single web. Such a process is known as coextrusion and permits the production of a single web that has, for example, barrier properties not possessed by any one of the component polymers. A two-component slit die is capable of producing a two- or three-layer film from two materials, while a three-component die (such as the one shown in Figure 5.3) can produce a five-layer film from three materials. Today, seven- and nine-layer films and sheet are being produced for food packaging applications. Typical structures include

HIPS-Tie-Barrier-Tie-HIPS (PP and HDPE may replace HIPS depending on the application)
PP-Tie-Barrier-Tie-Regrind-PP (six-layer asymmetrical with one regrind layer)
PP-Regrind-Tie-Barrier-Tie-Regrind-PP (seven-layer symmetrical with two regrind layers)
LDPE-Tie-Regrind-Tie-Barrier-Tie-GPPS (seven-layer asymmetrical with one regrind layer)
PP-Tie-Barrier-Tie-Regrind-Tie-Barrier-Tie-PP (nine-layer with two barrier layers and one regrind layer)

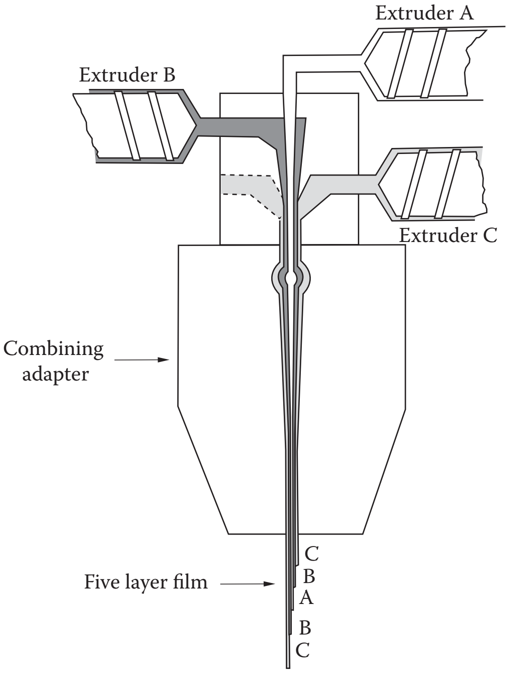

FIGURE 5.3 Three-component slit die.

The use of two barrier layers in the nine-layer structure decreases the potential loss of barrier due to pinholes or flaws in the barrier layer, the rationale being that there is a negligible probability of two adjacent holes in separate barrier layers. The tie or adhesive layers used in the aforementioned structures vary depending on the nature of the layers that they are required to bind, and different tie layers may, therefore, be used in the same structure. The technology behind tie layers is complex and maintained as proprietary by coextrusion manufacturers. However, EVA copolymers (25%–50% VA) are used extensively; the higher VA copolymers are more soluble and display greater initial bonding force (tack), better adhesion to polar surfaces and better low temperature performance. Modified PE–PP copolymers (usually containing acrylates for increased adhesion) are also used (Brown, 1992). Polymers are chosen for individual layers to achieve special combinations of properties, for example, mechanical strength and stiffness, gas and water vapor barrier, oil and grease barrier, heat seal, hot tack, adhesion, optics, formability, machinability and economics. Individual layers may be pure polymers or blends, sometimes with regrind or recycled scrap.

The main advantages of coextruded films over conventionally produced laminates (which they have displaced in many applications) are lower cost, less tendency toward delamination and a greater flexibility in obtaining a wide range of properties. The major disadvantage lies in the difficulty of utilizing the scrap produced during the extrusion process. Coextruded films can also be laminated to other films such as OPP and to paper and foil. Coextrusion has the ability to produce thinner layers than lamination, a distinct advantage when expensive barrier layers are used.

Rigid sheet makes use of resins such as HIPS, HDPE and PP for the bulk layers to provide package strength and rigidity, while flexible films make more use of LDPE and LLDPE resins as well as PP. For barrier layers, both types use EVOH and PVdC copolymers. The largest use of coextruded sheet is in thermoformed semirigid, high barrier containers for shelf stable products—so-called retortable trays and pouches. Flexible packaging finds use in stand-up pouches and a host of other applications for packaging flesh foods, frozen foods, cheese and snack foods. Films make greater use of BON as, apart from its gas barrier properties, it has excellent puncture, tear and abrasion resistance.

5.2 CALENDERING

Calendering produces an unoriented cast sheet with uniform gauge at high throughput. It is a complementary process to film and sheet extrusion, and involves the formation of continuous sheets of controlled thickness by squeezing a heated plastic material between two or more horizontal rollers. Although calenders were originally developed for processing rubber, they are now widely used for producing flexible PVC sheet and film.

Calenders consist of from two to five rollers that can be steam heated or water cooled. The thickness of the final film or sheet depends on the gap between the last pair of rollers. The surface finish of the material is determined by the last roller and can be glossy, matt or embossed. On leaving the calender, the material is cooled by passing over cooling rollers and it is then reeled up.

In addition to the wide variety of PVC films and sheets that are processed by calendering, such materials as ethylene–propylene copolymers, EVA copolymers and rubber-modified PS have been fabricated into sheet stock on calenders.

Calendering usually produces film with a better uniformity of gauge compared with that obtained by extrusion. Several factors contribute to this, including the precision engineering of the calender rollers. In extrusion, the gauge depends more on the BUR in the case of tubular film, or the drawdown ratio in the case of flat film.

5.3 COATING AND LAMINATING

Coating and laminating are two of the most widely used processes for transforming flexible films and sheets into products having properties useful in food packaging. Coating is the process of applying one or more layers of a fluid or melt to the surface of a material, while laminating is the bonding of two or more webs (Brown, 1992). A laminate is defined as any combination of distinctly different plastic film materials or plastic plus nonplastic materials (typically paper and aluminum foil), where each major web is generally thicker than 6 μm, regardless of the method of manufacture. There is no upper limit to the possible number of webs, but two is the obvious minimum and one of these must be thermoplastic.

Two major techniques are employed in the fabrication of laminates: adhesive lamination and extrusion coating. However, before coating and laminating films, it is necessary to treat the surface to ensure good adhesion; four treatments are used commercially.

5.3.1 SURFACE TREATMENT

5.3.1.1 Surface Energy

The surface energy of a packaging film is a critical film property when printing, coating or laminating packaging films. Surface tension γ has the dimension of force per unit length (mN m^{-1} which is equivalent to dyn cm^{-1}), or of energy per unit area (mJ m^{-2}). The two are equivalent but when referring to energy per unit area, the more general term surface energy is used as it applies to both solids and liquids. Surface tension is responsible for the shape of liquid droplets. For a liquid, the surface tension and the surface energy are identical. For example, water has a surface energy of 72 mJ m^{-2} and a surface tension of 72 mN m^{-1}.

The main objective of any surface treatment method is to increase the surface energy of the film surface to improve wet-out and adhesion of coatings, inks and adhesives used in converting the film into packaging. Wet-out refers to how completely a coating or adhesive flows and covers a surface to maximize the contact area and the attractive forces between the adhesive or coating and the film surface. Typical polymers used for packaging films have a surface energy without surface treatment of from 29 to 45 mN m^{-1}. A typical rule of thumb to insure good wet-out and adhesion to a substrate is that the surface energy of the substrate should be 7–10 mN m^{-1} higher than the surface tension of the coating being applied. For example, water has a surface tension of 72 mN m^{-1} compared to the surface tension of ethanol which is 22 mN m^{-1}. The surface energy of a PET film is ~42 mN m^{-1}, thus allowing the ethanol to easily wet out the surface of the film. However, the water, which is 50 mN m^{-1} higher than the ethanol, will bead up (form a sphere, which is the smallest surface area for a given volume) and not wet out the film. There are several different ways of surface treating a film to increase the surface energy and, thus, improve wet-out and adhesion of coatings, inks and adhesives, including corona discharge, flame treatment, priming and chemical etching.

5.3.1.2 Corona Treatment

Corona treatment involves the application of a high voltage (10–40 kV) low frequency (10–20 kHz) discharge across a fixed air gap between an electrode (treater bar) and an earthed conductive roller that carries the film. The air between the two surfaces ionizes and consists of positively charged ions, electrons and excited or metastable species of O_2 and N_2, as well as other forms of radiation. In addition, metastable O_2 species react with O_2 molecules to generate ozone, a powerful oxidizing agent. Particle energies are about 10–20 eV, which is high enough to break C–C and C–H bonds (2.54 and 3.79 eV, respectively) and generate free radicals in the polymer-surface region. A continuous arc discharge (corona) is generated at the surface of the film.

A corona generator is usually mounted in-line and prior to the extrusion coating head; the degree of treatment is regulated by rheostat adjustment of the power fed to the discharge electrode. Treatment will decay over time and is adversely effected by high humidity conditions. In continuous operation, the corona discharge appears to be a random series of faint sparks in a blue–purple glow (UV radiation).

The corona treatment cleans, oxidizes and activates the surface by converting it from a nonpolar to a polar state by bombarding it with ozone, O_2 and free radicals of O_2. This increases the surface energy and results in the substrate surface being more compatible with a freshly oxidized polyethylene surface, thus promoting adhesion between the two.

Pretreating substrates with corona discharge is a widely used method for polyolefin films. Corona treatment has been found to increase the O_2 content and carbon–oxygen functionalities on LDPE (Hirvikorpi et al., 2010a).

Corona-treated films should be used immediately for further applications such as extrusion coating or printing because of the diminishing effect of the improved properties with time (Ozdemir et al., 1999). Ozone is a by-product of the corona discharge method, and provision must be made for its removal for health and safety reasons. Corona treatment is often done during film manufacturing and can be done again in-line with a secondary converting process such as printing to "bump" or increase the film surface energy. For printing and laminating, it is common to increase the surface energy of an LDPE film from 34 mN m^{-1} to close to 50 mN m^{-1}.

5.3.1.3 Flame Treatment

In flame treatment, the polymer surface is passed through a flame (1000°C–2800°C < 1 s) generated by the combustion of a hydrocarbon (HC) (typically natural gas). The film passes directly through the flame tips that have formed an O_2-rich plasma. This produces an oxidized layer on the surface by a mechanism similar to that of corona discharge but it is more difficult to control; if the heat penetrates too far into the film, it degrades and becomes weak. This treatment method is said to produce high surface energy levels and longer lasting treatment levels than corona discharge.

5.3.1.4 Priming

In this method, primer treatments are applied in very thin coatings to the substrate. Optimum primer coating weight is usually in the order of a few milligrams per square meter. The primers seem to function by being of such a chemical nature that the oxidized, extruded polyethylene surface adheres strongly to them, and the primer, in turn, adheres strongly to the substrate. If the primer coating is too thick, loss of adhesion results since the primers have low cohesive strength. Primers consisting of polymers such as styrene–butadiene latexes are often applied to paper to prevent coatings from penetrating too deeply into the substrate (Brown, 1992).

5.3.1.5 Chemical Treatment

Treating polymer surfaces with chemicals can alter the surface chemistry to improve the surface energy by providing active chemical bonds or groups on the polymer surface.

Chemical treatment of a film typically involves cleaning, etching and rinsing steps. The cleaning removes any surface contaminants. The etching involves the use of acid, base or oxidizing agents such as nitric acid or potassium chromate to chemically change the polymer surface. Finally, the film is rinsed clean of the etching chemicals and dried. This process is usually done following film manufacturing, which significantly adds to the final cost of the film. This treatment method is often slow and creates waste disposal issues as the chemicals used are problematic in terms of handling and environment.

5.3.2 COATING PROCESSES

There are two types of coating processes: in one, an excess coating is applied to the web and the surplus removed, while in the other, a predetermined amount is applied to the web using rollers or other equipment. Nitrocellulose and PVdC copolymer are the most common surface coatings used, but synthetic resins, acrylics and many other formulations are used for varnishing, barrier formation and/or heat sealing.

Extrusion coating was first practiced on a commercial scale in the production of LDPE-coated paperboard for milk cartons in the mid-1950s as a replacement for wax-coated board (Robertson, 2002). Compared to wax, LDPE is superior with greater strength, seal integrity and resistance to cracking and flaking off. It also provides greater resistance to moisture, thus protecting the paperboard substrate from the damaging effects of water for much longer periods of time.

Today, almost all applications for wax-coated paperboard have been replaced by polyolefin-coated paper and board.

In theory, there is no reason why any thermoplastic that is normally processed by extrusion techniques cannot be coated onto paper or other substrates. In practice, most extrusion coating technology that has been developed utilizes the lower-density polyethylenes, although PP, PAs and PET are also used. For example, PET-coated paperboard is used in dual ovenable trays, where a 38 µm PET coating is put on 500–625 µm paperboard.

Extrusion coating with polyethylene has several advantages over adhesive lamination of a prefabricated polyethylene film to paper. First, thin films of polyethylene are difficult to handle and maintain flat, and handling them requires very low tensions that are difficult to control at high speeds. Second, extrusion coating temperatures are sufficiently high so that good mechanical bonds are obtained by resin penetration into the porous paper substrate. The same adhesion level can be obtained only by the use of adhesives when free films are laminated to paper, thus making extrusion coating less expensive.

The development of adhesion between polyethylene and various substrates is an aspect of extrusion coating that has received a great deal of attention. Substrates, whether polymer films, paperboard, aluminum foil or RCF, require some type of surface pretreatment to obtain an adequate level of adhesion of the extruded polyethylene.

5.3.3 LAMINATING PROCESSES

Methods that combine two or more webs by bonding them together are called laminating processes. Bonding is usually accomplished by thermal or chemical means with adhesives and curing systems. After the adhesive is adequately dried or cured, the coated web is combined with an uncoated web through the application of heat and/or pressure in a nip. A wide range of materials may be laminated to each other, and the process continued if required until the laminate has the desired protective properties.

Thermal laminating is the joining of two webs with an adhesive that is first applied to and cooled and dried on one of the webs. The webs are heated before pressing them together in the nip of two rollers that provide the force needed to establish the intimate contact required for the bond (Brown, 1992). The adhesives most commonly used are polyolefins such as EVA, and the webs that are most commonly laminated this way include plastic films, and aluminum foil joined with heat-seal-coated film or paper.

Wet bond laminating uses solvent or aqueous-based adhesives and can only be used when one or more of the webs are permeable to the water or other solvent used, thus allowing it to escape. Wet bonding is not generally successful with plastic films, even when laminating them to paper. Usually aqueous adhesives such as casein, sodium silicate, starch, PVA latex, rubber latex or dextrin are used.

Dry bonding is considerably more versatile in that any two materials can be laminated once an adhesive system has been developed. Either aqueous or solvent-based adhesives are used, and they are dried or cured, if necessary by the application of heat, prior to laminating. Adequate drying of the solvent is particularly important where the solvents cannot be absorbed into the film as excess solvent is a major cause of delamination and may permeate into the package and affect the food. However, the use of organic solvent-based adhesives has been largely phased out because of legislation limiting the release of VOCs (volatile organic compounds) into the atmosphere.

Solventless laminating consists of bonding together two webs by curing in the absence of solvents. It has now become the dominant laminating method in commercial use because of legislation limiting the release of VOCs. A reactive chemical system (either a single- or two-component system) is used to cure the adhesive. Because the adhesive layer is formed by curing (polymerization), it releases neither solvents nor water, although small amounts of CO_2 may be emitted. Single-component urethanes are the most widely used; polyester isocyanates are also used.

Extrusion laminating is a specialized use of extrusion coating, where a hot extruded film is trapped between two other webs and cooled. This process is used mainly for producing a triple laminate of such materials as paper, aluminum foil, RCF and PET with LDPE, where the latter material is extruded and acts as the bonding agent between the two substrates. As in the case of extrusion coating, this process is applicable to any thermoplastic material, but the technology has been highly developed mainly for polyethylene and associated copolymers, including ionomers.

5.4 BLENDING

Generally, multilayer structures (either coextrusions or laminates) have been used to improve the barrier properties of plastic packaging. They utilize complex and expensive technology and the final product is not easily recyclable. These structures, which have at least three layers, comprise a barrier material as the middle layer and PET or PP as the outer and inner layers. Polymer blending is a low-cost alternative route to multilayer extrusion and has attracted increasing attention over the last two decades in packaging applications to enhance properties, improve processing or lower cost. Some of the attributes that can be achieved by blending in addition to improving the barrier properties include tailoring surface properties such as COF, adding color, promoting adhesion, improving stability and obtaining easy-opening features (Morris, 2009). Achieving a consistent quality blend with the desired properties requires proper attention to both process and product design.

The properties of a polymer blend are influenced by specific interactions between the molecules (thermodynamics, which determines whether the blend forms a miscible single phase or immiscible multiple phases) and their response to deformation (rheology) (Morris, 2009). The term compatibility is used to describe the degree to which polymers interact.

A *masterbatch* is a highly concentrated blend of an additive with a carrier resin that should be compatible and miscible in the resin into which it is being blended. Film manufacturers commonly blend a masterbatch into the resin at the extruder feed hopper when making film or sheet. In more sophisticated (and expensive) compounding devices such as twin-screw extruders, ingredients can be added at various stages along the extruder.

Blends of PET and aromatic polyamides such as nylon-MXD6 are of interest in food packaging because of their potential for combining the low O_2 and CO_2 permeability of PAs with the good toughness, clarity and economics of polyester, although these blends suffer from low optical clarity and the generation of an undesirable yellow color during processing. Incompatibility of the constituent polymers makes it difficult to achieve the optimum barrier structure of PET/PA blends, and to overcome this problem, small amounts of an ionomer are added.

A new, alternative technology is smart blending (Zumbrunnen, 2009). Smart denotes an ability to control in situ fine-scale structure development in polymer blends and composites. Thus, even at a fixed composition, the structure and composition of extrusions can be optimized to obtain a balanced combination of physical properties or impart functionality. Extrusions have been produced with more than 10,000 layers and layer thicknesses less than 200 nm. This is an advantage because it is often preferable to have large numbers of thin layers *in lieu* of just a few thick layers. Figure 5.4 shows the essential elements of a smart blender system.

Smart blending machines operate on the principle of chaotic advection, a recent subfield of fluid mechanics. The term *advection* denotes movement, and chaotic advection refers to the chaotic (i.e., nonperiodic) motion of a particle in a fluid that can occur even where the flow field is simple and periodic. Chaotic advection provides a template for forming structured plastic materials in situ because minor and major polymer components in a melt are stretched and folded recursively about one another so that a layered polymer blend morphology first arises. Initially, large polymer melt streams are organized into multilayers *in lieu* of being broken down into droplets as in conventional mixing.

A desired structure type can be obtained from a smart blender (shown schematically in Figure 5.4) by extruding the structured melt through a conventional die. By this processing method, a wide

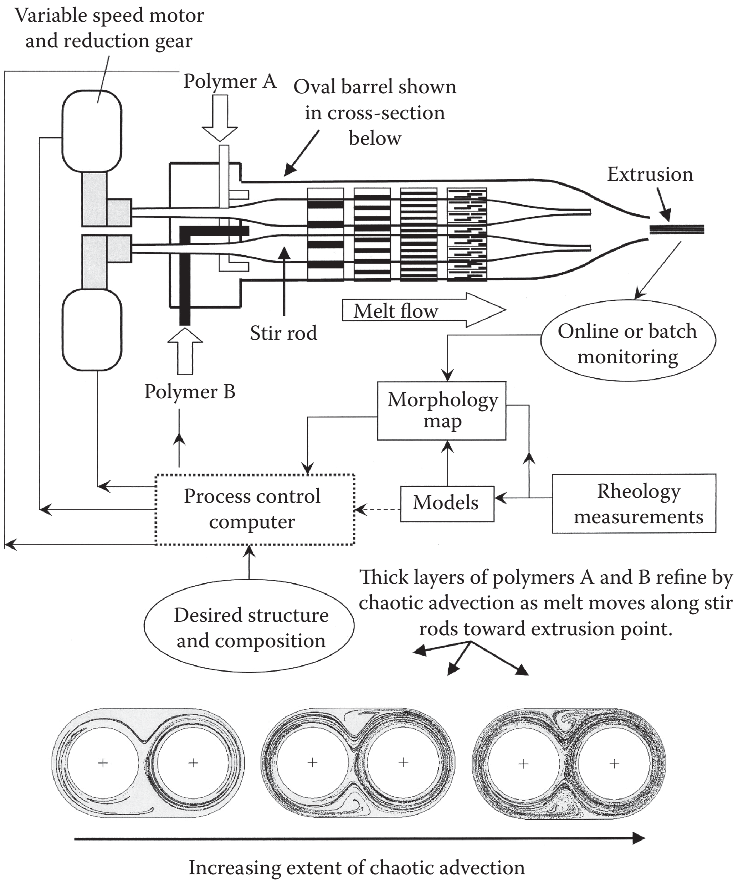

FIGURE 5.4 Schematic diagram of a smart blender system used to produce cast film and computational simulations of layer formation for increasing extents of chaotic advection. (From Zumbrunnen, D.A., Smart blending technology, in: *The Wiley Encyclopedia of Packaging Technology*, 3rd edn., Yam K.L. (Ed.), John Wiley & Sons, New York, pp. 1120–1124, 2009.)

variety of structural types are attainable even where overall composition is held constant. Because the structure of a composite material greatly influences additive diffusion, this processing method provides a means for producing packaging films with tailored release rates of active compounds (Jin et al., 2009).

5.5 VAPOR DEPOSITION

Physical vapor deposition (PVD) is a general term used to describe any of a variety of methods to deposit thin films by the condensation of a vaporized form of the material onto various surfaces. The coating method involves purely physical processes such as high temperature vacuum evaporation rather than a chemical reaction at the surface to be coated. *Chemical vapor deposition* (CVD) is a chemical process used to improve the barrier performance of polymer films and is also widely used in the semiconductor industry to produce thin films. There are a number of forms of CVD and they differ in the way by which chemical reactions are initiated (e.g., activation process) and the process conditions. Although some CVD processes can operate at atmospheric pressure, the use of low pressure/high vacuum is more common because reduced pressures tend to reduce unwanted gas-phase reactions and improve film uniformity. *Plasma-enhanced* CVD (PECVD) utilizes plasma to enhance chemical reaction rates of the precursors and permits deposition at lower temperatures.

Often a combination of PVD and CVD processes is used in the same or connected processing chambers. Details of the major deposition processes used in the manufacture of food packaging materials are discussed subsequently.

Many small holes in a barrier layer result in a much higher permeation than a few large holes of same total area. The barrier performance of coated polymers depends on coating thickness, substrate roughness and coating density.

5.5.1 PHYSICAL VAPOR DEPOSITION

PVD is a physical method of forming a thin film characterized by a bulk material being transported to the substrate's surface in vapor form, where it condenses. Vacuum metallization is the most common PVD process and produces coatings by thermal evaporation of metals in a vacuum. The vacuum allows vapor particles to travel directly to the target object (substrate), where they condense back to a solid state. Regenerated cellulose films were first metallized in the 1930s and used as decorative tinsel. Since the 1960s, metallized films have found a diverse range of applications in food packaging, initially in a purely decorative role, but since 1975 as important barrier materials as well as microwave-heatable susceptors (see Chapter 14). These films have the appearance of thin metal foil but are tougher than foil and usually have a more highly reflective surface. The end result of metallizing plastic films is a decorative, functional, durable and less expensive material than that made from solid metal. Aluminum usually gives the most highly reflective surface and is the most common material used for metallization, but other metals such as nickel and chromium have also been used to a limited extent.

When a metal is heated under vacuum, it evaporates and condenses on the cold polymer film that is unwound near the metal vapor source. The metal must be heated to a high enough temperature to effect vaporization, and for aluminum this involves temperatures in the range of 1500°C–1800°C. The coating is much thinner than a metal foil could be made and is typically 20 nm (0.02 µm) thick. While OPP and PET are the most common films used for metallization, PAs, PE and cast PP are also used. The coating reduces the permeability of the film to light, water and gases, but other properties of the film such as toughness and the ability to be heat sealed remain.

Three basic heat sources are used in vacuum metallization (Bakish, 2009). In *resistance heating*, aluminum wire is fed onto a block of metal (usually tantalum) that is heated by holding it in a carbon crucible or boat across which a high current is arced. A pool of melted metal forms in the boat cavity and evaporates into a cloud above the source. In *induction heating*, a high current passes through heating coils causing an induced magnetic field inside the coils where the crucible is located. The rapidly reversing polarity of the magnetic field causes the molecules to vibrate and heat up (Bishop and Mount, 2010). Although a popular heating source in the past, induction heating has been abandoned by many metallizers in favor of resistance heating (Bakish, 2009). In *electron beam heating*, the source is heated by an electron beam with an energy of up to 15 keV, care being taken to ensure that no secondary electrons impinge on the polymeric web. Electron beam heating allows tight control of the evaporation rate and although more expensive, it is notably simpler and much more versatile as it can be used to evaporate many different materials.

Vaporization of the aluminum causes minute particles to be ejected from the surface in all directions. Since the distance traveled by evaporated aluminum molecules before encountering air molecules and being deflected is very short, a high vacuum (3 kPa) must be maintained in the metallization chamber. This high vacuum is also required to prevent oxidation of the metals being vaporized. If the vacuum is not sufficiently high, the coatings are dull instead of being highly reflective, due to oxide contamination of the metal.

Metallization can be either a batch or a continuous process. The batch process involves the unwinding and then rewinding of the film in a vacuum chamber as shown in Figure 5.5. The continuous process consists of passing the film through vacuum-sealed slits with unwinding and rewinding being performed outside the vacuum chamber. Speeds in excess of 615 m min^{-1} are common (Mount, 2008).

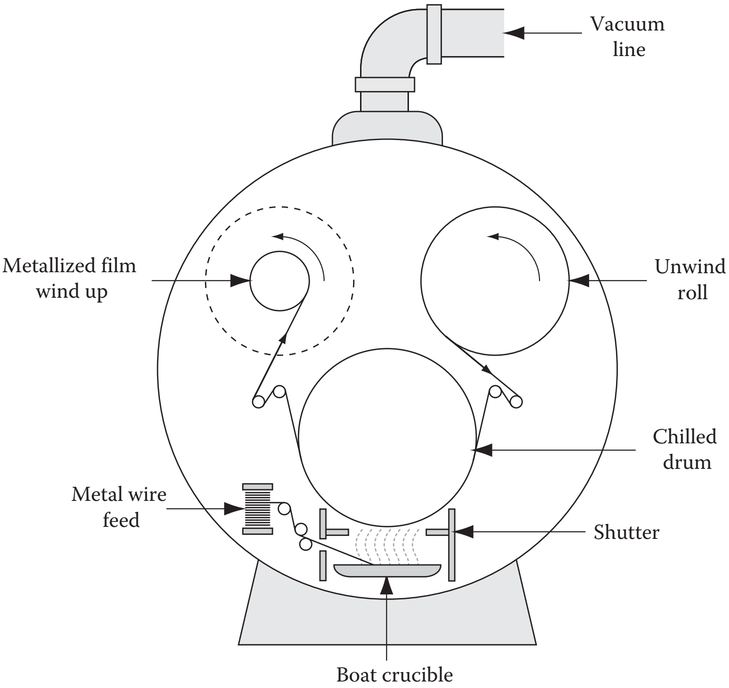

FIGURE 5.5 Schematic cross section of a batch vacuum metallizer.

Certain films have to be degassed prior to vacuum metallization because they contain moisture or other volatile constituents such as plasticizers, residual solvents or monomers. These may cause difficulties during the metallization process, since their continued out-gassing interferes with the adhesion of the aluminum, giving dull and incompletely anchored coatings. Films that require degassing include RCFs (which contain water and glycol) and PAs. Given that degassing may also remove other desirable constituents of the film, it is often preferable to seal the surface of the film with a lacquer. If colored metallic effects are required, the film can be self-colored or a colored lacquer applied after metallizing.

In order to increase the barrier properties of metallized film, more metal must be deposited on the film's surface; this can lead to adhesion problems and even flaking if the metallized layer becomes too thick. With thin films, the thickness of the coating that can be applied may have to be considerably less than the typical thickness because the heat of condensation of thicker layers would cause melting of the film. These thinner coatings tend to be full of pinholes and may even be transparent to transmitted light to some degree. The metallization process has a strong and complex effect on the development of barrier and adhesive properties of metallized films (Mount, 2008).

Many films have been successfully metallized, including PP, unplasticized PVC, PVdC copolymer, RCF, PS, PET and PAs. Paper can also be metallized if it is first given a coating of lacquer to ensure good adhesion, with most metallized paper being used for labels. Metallized films are not often used by themselves; usually they are laminated with other materials to improve machinability. Although metallized films match the aesthetics of foil, they do not, and cannot, ever have the same functional barrier properties inherent in foil. Table 5.1 illustrates the magnitude of the improvement in barrier properties that can be expected from metallization of plastic films.

Sputtering is a PVD technique in which the bulk material is released into the vacuum by bombardment from an ion source. The material coalesces onto the substrate surface, thus forming a thin film. It is not in widespread use.

TABLE 5.1
Percentage Decrease in Water Vapor and Gas Barrier Properties of Aluminum Metallized Films[a]

Material	Water Vapor (%)	Oxygen Barrier (%)
Polyester	98.5	99.0
PVdC copolymer-coated PET	95.5	91.1
Cast polypropylene	93.4	98.7
Biaxially oriented polypropylene	75	98.7
Low density polyethylene	95.3	99.2

[a] Thickness of aluminum layer 5×10^{-6} cm.

5.5.2 CHEMICAL VAPOR DEPOSITION

CVD is a chemical process in which a solid thin film of material is deposited from the vapor phase by the decomposition of chemicals on the surface of a substrate. It is used to produce high-purity, high-performance solid materials. Low pressure CVD is widely used in the electronics industry for the deposition of silicon oxide and other materials; the process is performed in tube furnaces and requires rather high temperatures. PECVD utilizes plasma to enhance chemical reaction rates of the precursors, allowing deposition at lower temperatures. It is the method most commonly used to coat plastics packaging materials. Combustion chemical vapor deposition (CCVD) is a proprietary process that utilizes an open-atmosphere, flame-based technique for depositing high-quality thin films. Atomic layer chemical vapor deposition (ALCVD) involves depositing successive layers of different substances to produce layered, crystalline films.

5.5.2.1 Plasma-Enhanced Chemical Vapor Deposition

PECVD is a process that utilizes plasma to enhance chemical reaction rates of the precursors allowing deposition at lower temperatures. It is used to deposit thin films from a gas state (vapor) to a solid state on a substrate. Chemical reactions are involved in the process, which occur after the creation of a plasma (any gas in which a significant percentage of the atoms or molecules are ionized) of the reacting gases. The plasma is generally created by RF (AC) or DC discharge between two electrodes in which the space between is filled with the reacting gases. The plasma is formed in the reaction chamber and contains reactive ions and radicals. Two important applications of PECVD in food packaging involve coating with silicon oxide and amorphous carbon.

5.5.2.1.1 Silicon Oxide

Thin, glass-like SiO_x films ($x = 1.5–1.8$) were originally industrialized in 1969 and have been produced by PVD of SiO_x since the mid-1980s, and by PECVD of gaseous organosilane and O_2 since the early 1990s, on PET, PP and PA. The thickness of the SiO_x coating is within the range of 50–300 nm versus 20 nm for aluminum-metallized coatings (Hill, 2009). The OTR drops from 120 mL m^{-2} day^{-1} for uncoated, 12 μm thick PET, to an optimal value equal to 21 mL m^{-2} day^{-1} when the SiO_x coating thickness is increased in the range from ~50 to 100 nm, after which it starts to gradually increase (Leterrier, 2003). They are sometimes referred to as QLF or quartz-like films, or GLF for good layer or glass-like films. Films coated with AlO_x or MgO_x are also produced but in limited quantities.

The PECVD process uses a mixture of helium, O_2 and silicon compounds with plasma at low pressures. Different silicon sources can be used such as gaseous silane (SiH_4) or evaporated liquids such as hexamethyldisiloxane (HMDSO), hexamethydisilazane (HMDSN) or tetraethoxysilane (TEOS). The decomposition of these latter materials also produces carbon and some of this can be

TABLE 5.2
Barrier Properties of SiO_x and HC Plasma Films

Film/Coating	Oxygen Permeability Barrier	WVTR × 10^{-2} (g mm m^{-2} day^{-1})
PET	0.015–0.075	0.5–2
PP	0.76–1.52	0.2–0.4
PA	0.0015–0.015	0.5–10
PET/SiO_x	0.00009–0.0009	0.24–6
PP/SiO_x	0.0003–0.006	0.2–2
PA/SiO_x	0.0003	1
PET/HC plasma	0.00018–0.00036	
PP/HC plasma	0.015	

Source: Lange, J. and Wyser, Y., *Packag. Technol. Sci.*, 16, 149, 2003. With permission.

advantageously included in the coating to improve barrier performance (Bishop and Mount, 2010). The layer composition is mainly influenced by the admixture of O_2 to change the layer properties from $SiO_xC_yH_z$-like, where the barrier improvement is negligible, to inorganic SiO_x films for which a barrier improvement factor (BIF—the ratio of the TR of a coated plastic to a noncoated plastic) of more than 65 for one-sided and more than 1000 for two-sided coatings has been observed (Deilmann et al., 2008). A strong correlation between layer composition and barrier property was observed with good barrier films having a stoichiometry of $SiO_{1.7}$. The E_A of O_2 permeation through plasma-polymerized $SiO_{1.7}$-coated PET films was increased by more than 20 kJ mol^{-1}, and for good barriers, a value of $E_p = 53.7$ kJ mol^{-1} was achieved.

SiO_x films are transparent, retortable and microwavable and provide barriers comparable to those obtained by metallization as shown in Table 5.2. The main drawbacks of these films are the limited flex and crack resistance of the SiO_x layer and the relatively high production costs (Lange and Wyser, 2003).

Several companies have developed SiO_x coatings for the inside of PET bottles using microwave PECVD methods. Interestingly, all of these commercially successful coatings are applied to the inside of bottles, while several unsuccessful coating technologies have tried to coat the outside of bottles. Intrinsic brittleness of SiO_x films requires rather complicated conversion processes in order to withstand mechanical stress and stretching on a PET bottle surface. Recently, Toyo Seikan Kaisha in Japan commercialized a PET bottle with a cushioning layer between the PET and the SiO_x layer. Known as SiBARD (SiO_x barrier-layer development), the PET bottle has two thin film layers: a highly flexible and adhesive organic silicon film covered by a SiO_x film layer. These colorless and transparent containers are recyclable to the same degree as conventional PET bottles.

Recently, promising results have been achieved by electron cyclotron resonance (ECR) plasma deposition of gradient layers from O_2/HMDSN gas mixtures on three-dimensional containers made of PP at industrially relevant plasma treatment times (Schneider and Walker, 2010).

5.5.2.1.2 Amorphous Carbon

It is also possible with PECVD to deposit HC films (sometimes referred to as amorphous carbon) on different substrates using, for example, acetylene in a plasma. An ion beam deposition system was first used to deposit thin films of carbon with many diamond-like properties in 1971. There are many noncrystalline carbons, known as amorphous carbons, and an amorphous carbon with a high fraction of diamond-like (sp^3) bonds is named diamond-like carbon (DLC). Unlike diamond, DLC can be deposited at room temperature. Furthermore, its properties can be tuned by changing the sp^3 content, the organization of the sp^2 sites and the hydrogen content (Casiraghi et al., 2007).

A DLC coating to improve the gas barrier properties of PET bottles was developed by Kirin Brewery in Japan in 1997. It subsequently succeeded in making high gas barrier DLC-coated PET bottles industrially for the first time (Shirakura et al., 2006). Since a DLC coating provides increased thermal stability, the E_p values for DLC-coated PET bottles ranged from 50% to 70% of those for uncoated bottles.

The coating is applied on the interior of the bottle at a thickness of about 200 nm and has a high clarity but a slight amber tint. PET bottles with an HC coating have similar properties and barrier resistance to those with a SiO_x coating but with a higher mechanical resistance. An HC coating on the inside of PET bottles reduces the O_2 permeability by a factor of up to 10 (Lange and Wyser, 2003).

Kirin's DLC coating process applies the deposition of a very thin DLC film to the inner surface of PET bottles by generating a coupled plasma between inner and outer electrodes. The inner electrode is grounded while the outer electrode is connected to the power supply. A bottle is placed in a vacuum chamber that functions as the outer electrode (Figure 5.6). RF power of 13.56 MHz is then applied to the outer electrode to generate a low temperature plasma state while C_2H_2 (acetylene) gas is injected into the bottle. The ions and radicals react to deposit on the inner surface of the bottle in a negative self-bias potential over the outer electrode. The advantages of using a DLC film for PET bottles are primarily derived from its flexible nature along with its high gas barrier property and chemical inertness. The DLC coating obtained is basically composed of a three dimensional amorphous carbon and hydrogen network. The adhesion and fracture behavior of DLC and polymers has been discussed by Asakawa et al. (2011).

DLC films containing a certain amount of H_2 can provide the following advantages to PET bottles (Shirakura et al., 2006):

1. *Gas barrier properties:* blocks O_2 and CO_2 passing through bottles
2. *Flavor barrier:* blocks migration and sorption between bottles and products
3. *UV barrier:* increases absorbance of UV rays
4. *Chemical inertness:* chemical stability with no interaction with contents
5. *Recyclability:* no obstacle to the recycling process for PET resin
6. *Others:* maintains existing benefits of PET bottles economically

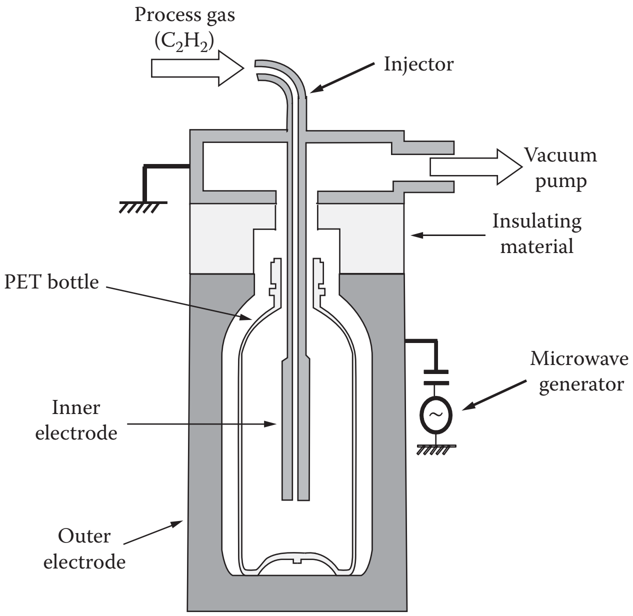

FIGURE 5.6 RF-plasma reactor used to create a DLC coating on the inside of PET bottles. (From Suzuki, T. and Kodama, H., *Diam. Relat. Mater.*, 18, 990, 2009.)

Sidel in France has developed another type of DLC-coating technology: Actis™ (amorphous carbon treatment on internal surface). It also uses C_2H_2 gas as a source of carbon coating. In the Sidel process, the bottle is placed neck up inside the reactor and the pumping system creates a vacuum of 5 kPa outside the bottle. At the same time, the inside of the bottle is pumped down to around 0.01 kPa. This pressure difference between inside and outside prevents the bottle from collapsing. An open-ended tube is introduced inside the bottle to inject the C_2H_2 gas. A 2.45 GHz microwave discharge is ignited for 1–3 s at a power of 200–500 W. This excites the gas into a plasma, which deposits a layer of transparent, hydrogenated amorphous carbon (a-C:H) about 150 nm thick on the inside of the bottle. Using C_2H_2 gives a faster deposition rate than other gases such as CH_4 or C_2H_4.

Sidel claims that Actis™ increases the CO_2 barrier of PET bottles by up to seven times (Boutroy et al., 2006). The OTR is reduced from 0.04 mL day^{-1} per bottle for a plain PET bottle to 0.0008 mL day^{-1} per bottle for a 100 nm a-C:H-coated bottle, a BIF of 50. The majority of the decrease in OTR occurs when the thickness reaches 40 nm and greater thickness does not decrease it proportionately. The thickness is chosen depending on the application. For example, beer needs the highest O_2 barrier and, therefore, the thickest coating of 150 nm. Juice and carbonated soft drinks need a medium gas barrier and a thickness between 40 and 60 nm gives good performances. Although Boutroy et al. (2006) did not report any CDTRs, an uncoated container had 10 weeks' shelf life and a coated container had 44–45 week shelf life for soft drinks; for beer, a non-coated container had just 4 weeks and a coated container 38 weeks shelf life based on CO_2 loss at 21°C.

Although the DLC film is sufficiently transparent, it does, however, retain a brown tint. A more transparent film can be obtained by reducing the coating thickness at the expense of higher permeability. DLC-coated PET bottles can be recycled in traditional PET recycling streams as the coating represents less than 0.04% of total PET bottle weight. However, it can be difficult to recycle DLC-coated PET bottles back into transparent bottles because of the brownish color, which does fade considerably during PET washing operations. Yamamoto et al. (2005) successfully synthesized transparent and colorless DLC films on PET substrates from CH_4 and H_2 gases by the RF-CVD method. They also investigated the relationship between OTR and optical transparency and showed that the optical transparency gradually improved with decreasing RF power and increasing deposition pressure, the films deposited at 15 W and 40 Pa being almost completely transparent; however, the OTR increased. Suzuki and Kodama (2009) synthesized DLC films under atmospheric pressure (AP-DLC) at room temperature. The growth rate increased as a function of C_2H_2 concentration and the maximum deposition rate was ~2000 times larger than that by low-pressure plasma CVD. The gas barrier properties of AP-DLC films were 5–10 times larger than those of uncoated PET substrates.

From a technical perspective, a DLC film less than 10 nm thickness is expected to achieve sufficient barrier improvement for PET bottles. This thin structure would exhibit much more colorless clarity than the current structure with a slightly tinted color, which limits the applications of the current DLC products to some specific product categories (Yamamoto et al., 2005). The current vacuum process is another drawback in the present market, because the achievement of high vacuum requires considerable capital investment, long process times (decreased throughput) and a large space due to pumps and other systems. Atmospheric plasma treatment could solve this problem.

DLC and SiO_x have become the major materials used to coat plastic packaging materials. SiO_x coating has a longer history than DLC coating for the gas barrier improvement of transparent plastics, and has been studied since the early 1980s. However, the intrinsic brittleness of SiO_x films requires rather complicated conversion processes to withstand mechanical stress and stretching on the PET bottle surface. Although the SiO_x coating has an advantage with its transparency, the process window for PECVD is so small that it makes it difficult to guarantee a reliable process, while the a-C:H coating has a very large process window (Boutroy et al., 2006).

5.5.2.2 Combustion Chemical Vapor Deposition

CCVD is a proprietary process developed by nGimat in the United States that utilizes an open-atmosphere, flame-based technique for depositing high-quality thin films. In the process, precursors (metal-bearing chemicals used to coat an object) are first dissolved in a solution that typically is a combustible fuel. This solution is then atomized to form microscopic droplets that are carried by an O_2 stream to the flame where they are combusted. A substrate (the material being coated) is coated by simply drawing it in front of the flame. The heat from the flame provides the energy required to vaporize the droplets and for the precursors to react and deposit on the substrate. The advantages of the CCVD process over traditional CVD/PVD techniques include the production of highly tailored and complex material solutions that cannot be achieved commercially with CVD/PVD processes, and the elimination of energy-intensive, highly specialized and expensive equipment such as vacuum chambers and reaction furnaces. This technique also has the potential to deposit UV barrier coatings and antimicrobial coatings, but to date there has been limited coating of food packaging materials using CCVD.

5.5.3 ATOMIC LAYER CHEMICAL VAPOR DEPOSITION

Atomic layer chemical vapor deposition (ALCVD), now more generally called atomic layer deposition (ALD), involves the depositing of successive layers of different substances to produce layered, crystalline films. It was invented in 1974 by Dr. Tuomo Suntola at the University of Helsinki in Finland. Prior to 2000, the term atomic layer epitaxy (ALE) was in common use when referring to this technique. The crystal lattice structure achieved by ALD is thin and uniform, and has found widespread use in the semiconductor industry. ALD on polymers was not performed until recently when low-temperature ALD became available, because polymers decompose at the temperatures required for many ALD systems (George, 2010).

Compared to basic CVD, in ALD, chemical reactants are pulsed alternatively in a reacting chamber and then chemisorbed onto the surface of the substrate in order to form the monolayer. Typically, one of the precursors will adsorb onto the substrate surface until it saturates the surface; further growth cannot occur until the second precursor is introduced. Thus, the film thickness is controlled by the number of precursor cycles rather than the deposition time as is the case for conventional CVD processes.

ALD is a surface-controlled, layer-by-layer, thin-film deposition process based on self-terminating gas–solid reactions. It is uniquely suited to produce high-performance gas barrier coatings on porous materials as it allows the preparation of dense and pinhole-free inorganic films that are uniform in thickness, even deep inside pores, trenches and cavities of various dimensions (Hirvikorpi et al., 2010b). Each atomic layer formed in the sequential process is a result of saturated surface-controlled chemical reactions. Commonly, in the growth of binary compounds such as metal oxides, a reaction cycle consists of two reaction steps. In the first step, the metal compound precursor is allowed to react with the surface, and in the second step, it reacts with the O_2 precursor. Between the steps a purge is applied to remove excess precursor and reaction by-products. The self-controlled growth mode of ALD results in several advantages. The thickness of the films can be controlled in a straightforward manner by controlling the number of reaction cycles, thereby enabling the controlled growth of ultrathin layers. The precursors form stoichiometric films with large area uniformity and conformality, even on complex surfaces with deformities (Kääriäinen et al., 2011).

Hirvikorpi et al. (2010a) studied the influence of corona pretreatment on the O_2 and water vapor barrier performance of polymer-coated paperboards additionally coated at 100°C with Al_2O_3 and SiO_2 by ALD. The positive effect of the corona pretreatment of the polymer-coated boards on the barrier properties after the ALD deposition was more significant with the LDPE-coated paperboard and with thin deposited layers, that is, the short ALD process. SiO_2 performed similarly to Al_2O_3 with the LDPE-coated board when it comes to the O_2 barrier, while performance of SiO_2 with the PLA-coated board was more moderate. However, the effect of corona pretreatment was negligible or even negative on the water vapor barrier, especially with the PLA-coated board. Clearly, the ALD film growth and the effect of corona pretreatment on different substrates need further investigation.

The cost of ALD is largely tied to the cost of the reactants and the equipment. Most ALD is performed with vacuum pumps that act to move the reactants and products through the reactor and maintain a clean environment in the reactor. These vacuum pumps would not be needed if ALD could be performed at above atmospheric pressure, where the reactant and product gases could be pushed through the reactor. Except for the greater gas usage and the lower gas diffusion rates at higher pressure, atmospheric pressure ALD should be commercially viable and has been demonstrated (George, 2010).

The main advantages of ALD are the extreme degree of conformality and uniformity that can be obtained, regardless of the orientation or shape of the substrate. As a CVD method, ALD is favorable over the physical methods such as sputtering that can be detrimental to the polymer surface. As a consequence, ALD layers provide excellent results when used as barrier layers where the diffusion of water vapor or O_2 must be minimized (Kääriäinen et al., 2011). For PEN substrates Groner et al. (2006) reported that a 5 nm Al_2O_3 ALD film had an OTR lower than 5×10^{-3} mL m^{-2} day^{-1} at 23°C and 50% RH, and a 26 nm Al_2O_3 ALD film had a WVTR of ~1×10^{-3} g m^{-2} day^{-1}. According to Kääriäinen et al. (2011), a 10 nm oxide layer decreased the OTR by a factor of 10 compared to uncoated material, and the use of an ALD layer allowed the polymer thickness on flexible packaging materials to be reduced. The water vapor barrier performance of the ALD film was optimum at ~100 nm thickness. Once the ALD layer was 40 nm thick, WVTRs and OTRs were no longer dependent on polymer layer thickness.

At present, conventional batch ALD processes suffer from slow throughput and the difficulty of applying a batch process to continuous webs. However, continuous and roll-to-roll processing is now being developed and, once commercialized, ALD is likely to become an important process for improving barrier properties of plastics and plastic-coated paperboards.

5.6 NANOCOMPOSITES

In 1986, researchers at Toyota in Japan revealed that polymerization of caprolactam in the presence of montmorillonite (MMT) clay resulted in a remarkable enhancement in several properties. Since then, research on polymer–clay nanocomposites (PCNs) has proliferated and there has been commercialization in many areas including food packaging. Today, an increasingly popular way to improve the barrier properties of plastic packaging at an economical cost is to incorporate nanoparticles into the polymer to form PCNs. A nanometer (nm) is one-billionth of a meter (1×10^{-9} m) and nanotechnology generally refers to materials with at least one dimension in the 1–100 nm range. The term nanocomposite refers to composite materials containing typically low additions of some kind of nanoparticles. In food packaging, nanocomposites usually refer to materials containing, typically, 1–7 wt% of modified nanoclays.

5.6.1 NANOCLAYS

Silicate minerals make up the largest and most important class of rock-forming minerals, constituting ~90% of the Earth's crust. They are classified based on the structure of their silicate group. Silicate minerals all contain silicon and O_2. Phyllosilicates, or sheet silicates, form parallel sheets of silicate tetrahedra with Si_2O_5 or a 2:5 ratio. Layered silicates are commonly referred to as clays.

The leading clay used in nanocomposites is MMT, a member of the smectite group with the chemical formula $(Na,Ca)_{0.33}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$. It is a layered alumino-silicate clay consisting of platelets with an inner layer of aluminum hydroxide octahedral sheet sandwiched between two layers of silicon oxide tetrahedral sheets. It exists in its natural state as agglomerated bundles consisting of 1000s of platelets held together by van der Waal forces. These platelets are typically 1 nm thick and 70–2000 nm across, giving an aspect ratio of up to 2000:1. These clay platelets are separated from each other by 1 nm gaps known as galleries, which are usually occupied by cations, normally alkali and alkaline-earth cations such as Na^+ and K^+ (Nguyen and Baird, 2006). The platelets must be separated after surface treatment through processes that are termed intercalation and exfoliation.

Pristine clays are hydrophilic, while most polymers are hydrophobic and, thus, except for a few hydrophilic polymers, most polymers are not compatible (miscible) with pristine clays. To form PCNs, the immiscibility between the polymer and the hydrophilic clay must be overcome by either modifying the polymer or, more frequently and easily, by modifying the clay (Zhang et al., 2008). A recent review (Rao and Geckler, 2011) gave a general description of the preparation of polymer nanoparticles, and a detailed description of the crucial parameters involved in techniques designed to obtain the desired properties.

There are four different methods to give the clay organophilic properties:

1. Ion exchange with organic cations (typically cationic surfactants). The exchange of metal ions with cationic surfactants, such as bulky alkylammonium ions, increases the spacing between the layers and reduces the surface energy of the filler. Consequently, these modified fillers, also called organoclays, are more compatible with polymers and form polymer-layered silicate (PLS) nanocomposites.
2. Covalent bond formation through a grafting reaction.
3. Direct adsorption of molecules.
4. A combination of two of the aforementioned methods.

In food packaging applications, it is imperative that the applied modifications should be harmless, comply with migration regulations and make use of approved food contact substances as valid modifiers. Unfortunately, for many technologies and producers, this is not the case. For example, ammonium salts are commonly employed to enhance the properties of engineering polymers in structural applications as organophilic chemical modifiers, but they are not approved for food contact applications in the EU. For food packaging applications, only approved food contact materials and additives should be used, and they should do so below their corresponding threshold migration levels. This limits the implementation of PCNs in food packaging (Sanchez-Garcia and Lagarón, 2009).

5.6.2 INTERCALATION AND EXFOLIATION

In general, the degree of dispersion of the clay platelets into the polymer matrix determines the structure of nanocomposites. Two key words are used in this context: *intercalate*, which means to insert between or among existing elements or layers, and *exfoliate*, which means to split into thin flakes. Thus, depending on the interaction between the clay and the polymer matrix, two main idealized types of polymer–clay morphologies can be obtained: namely, intercalated and exfoliated (Ray and Easteal, 2007):

1. *Intercalated structure*: Here, extended polymer chains are intercalated (inserted) between the silicate layers, which form a multilayer structure of alternating polymeric and inorganic layers.
2. *Exfoliated structure*: These are obtained when the individual silicate layers are completely separated from each other (delaminated) and dispersed randomly in the continuous polymer matrix.

These structures are schematically presented in Figure 5.7. Usually, exfoliated nanocomposites are preferred because they provide the best property improvements.

However, complete exfoliation of all the individual platelets is very difficult to achieve and most nanocomposites contain regions of both intercalated and exfoliated structures. If the polymer cannot intercalate between the silicate sheets, a microcomposite is obtained.

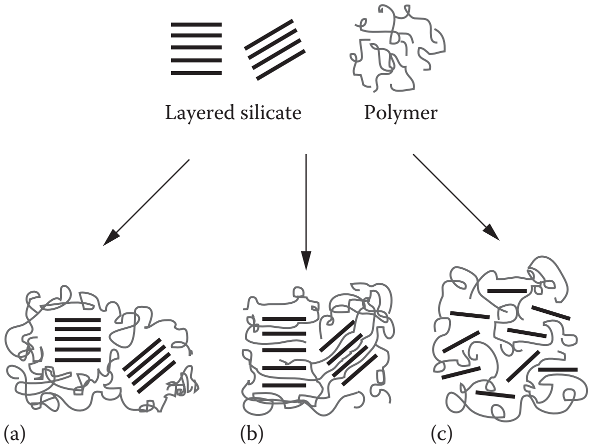

FIGURE 5.7 Illustration of different types of composites that can arise from the interaction between layered silicates and polymers. (a) Phase separated (microcomposite), (b) intercalated (nanocomposite) and (c) exfoliated (nanocomposite). (From Alexandre, M. and Dubois, P., *Mater. Sci. Eng.*, 28, 1, 2000.)

5.6.3 SYNTHESIS OF PCNs

A comprehensive review of the academic and industrial aspects of the preparation, characterization, materials properties, crystallization behavior, melt rheology and processing of PCNs was given by Ray and Okamoto (2003), with a special emphasis on biodegradable polymers. Pavlidou and Papaspyrides (2008) reviewed recent advances in the field of PCNs.

The three most common methods to synthesize PCNs are intercalation of a suitable monomer and subsequent in situ polymerization, intercalation of polymer from solution and polymer melt intercalation (Ray and Easteal, 2007):

1. In situ *intercalative polymerization*: The layered silicates are allowed to swell by absorption of a liquid monomer, or a monomer solution. The monomer migrates into the galleries of the layered silicate, so that polymerization can occur within the intercalated sheets. Polymerization can be initiated either by heat or radiation, by diffusion of a suitable initiator or by an organic initiator.
2. *Intercalation of polymer from solution*: This approach is similar to that used in the in situ intercalative polymerization method. First, the organoclay is swollen in a nonpolar solvent, for example, toluene. Then the polymer, dissolved in the same solvent, is added to the solution and intercalates between the clay layers. The final step is removal of the solvent by evaporation, usually under vacuum.
3. *Polymer melt intercalation*: The layered silicate is mixed with the polymer matrix in the molten state; no solvent is required.

For most technologically important polymers, both in situ polymerization and intercalation from solution are limited because neither a suitable monomer nor a compatible polymer–silicate solvent system is always available. Furthermore, they are not always compatible with current polymer processing techniques. Melt processing allows PCNs to be formulated directly using ordinary compounding devices such as extruders or mixers, without the necessary involvement of resin production. It therefore shifts PCN production downstream, giving end-use manufacturers many degrees of freedom with regard to final product specifications. At the same time, melt processing is environmentally sound since no solvents are required. For these reasons, the direct melt intercalation method has become the most common method of preparing PCNs (Ratto et al., 2009).

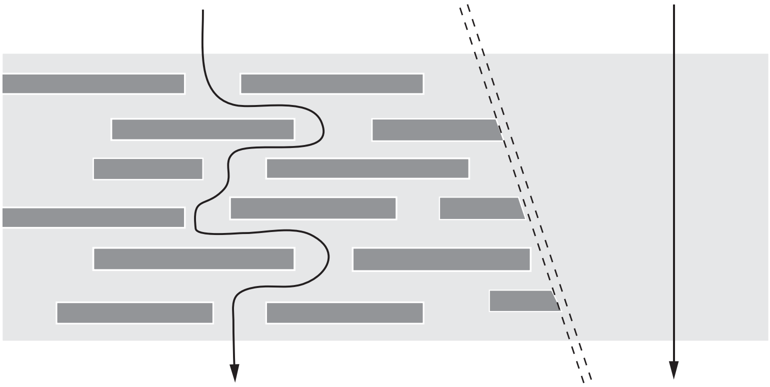

FIGURE 5.8 Nanolayered clay platelets force low MW components to follow a tortuous path through a polymer, thus improving its barrier properties.

5.6.4 BARRIER PROPERTIES

Generally, PCNs show an improvement in barrier properties. Although the enhancement in barrier properties of PCNs is well known, the dependence on factors such as the relative orientation and dispersion of the clay (whether intercalated, exfoliated or some intermediate stage) is not well understood. The clays or impermeable nanoparticles increase the barrier properties by creating a maze or tortuous path that retards the progress of the permeating molecules through the PCN by creating a longer diffusive path that the penetrants must travel as shown in Figure 5.8.

The barrier properties of a PA-12/organo-modified MMT nanocomposite were shown by Alexandre et al. (2010) to depend not only on the degree of exfoliation of the clay particles, but also on the interactions of diffusing molecules with the clay/matrix interface, leading to percolation paths. While a reduction in permeability for N_2 was mainly due to an increase in tortuosity, for water and toluene the permeation kinetics revealed many concomitant phenomena responsible for the permeation behavior. Despite the tortuosity effect, the toluene permeability of the nanocomposite increased with increasing levels of clay. The plasticization effect of water and toluene in the matrix involved a concentration-dependent diffusion coefficient. They suggested a new approach for relative permeability modeling, not only based on the geometrical parameters such as aspect ratio and orientation, but also including phenomenological parameters deduced from structural characterization and permeation kinetics.

5.6.5 APPLICATIONS

An increasing number of investigations have shown that PCNs have a lower permeability than that of the corresponding virgin polymer. PET is one of the most widely studied polymers in nanocomposite applications. Decreases in O_2 permeability of about 55% in melt-mixed nanocomposites of PET with 5 wt% nanoclay have been reported. In other examples, a PA-6 with 2 wt% nanoclay could achieve three times the O_2 barrier of unfilled PA-6, while 4 wt% nanoclay conferred a sixfold improvement, retaining most of its existing favorable characteristics like toughness, clarity and oil/grease resistance. It also showed almost double stiffness, higher HDT (heat distortion temperature) and improved clarity, thus making it an ideal barrier layer in multilayer PET bottles. By combining nanocomposite and O_2 scavenger technologies, a new family of barrier PAs was developed for use in multilayer packaging structures, particularly in multilayer, co-injection stretch blow molded PET bottles for extended shelf life packaging of O_2-sensitive foods and beverages. In another commercial application, the addition of nanoclay to amorphous PA-MDX6 as the core of a three-layer PET bottle could reduce the OTR by a 100-fold compared with that of neat PET. An EVOH copolymer nanocomposite has achieved the O_2 barrier requirement for meals ready to eat (MRE).

Less spectacular improvements have been reported for other polymers. For example, LDPE containing 4 wt% nanoclay exhibited a decrease in O_2 permeability of 24% compared with the pure material. PP nanocomposites containing 5 wt% nanoclay reportedly showed a reduction in O_2 permeability of 57% and CO_2 permeability of 48%. A PS nanocomposite with 7 wt% clay exhibited a decrease in O_2 permeability of over 60%.

The improvements in properties seem to plateau at levels of about 4 wt%, although in PA-6, levels of 7 wt% have been reached because of hydrogen bonding between the amide groups and the nanoclay particles (Nguyen and Baird, 2006). It is clear that the expected improvements are not always attained. Reasons for this include incomplete exfoliation of the nanoclay and incompatibility between the clay and the polymer. In general, there is still a need for a deeper understanding of the composition-structure-processing properties relationships in PCNs at both a laboratory and an industrial scale. Moreover, because most studies related to nanoclays have been carried out using few nanoclay grades (most are based on MMT), there is still a lot of room for variation and maturation in the PCN area. The main kinds of nanoparticles that have been studied for use in food packaging, as well as their effects and applications, were reviewed by De Azeredo (2009).

5.6.6 BIONANOCOMPOSITES

Bionanocomposites has become a common term to designate those nanocomposites involving a naturally occurring polymer (biopolymer) in combination with an inorganic moiety, and showing at least one dimension on the nanometer scale. These were discussed in Section 3.3.12 and reviewed by Lagarón and Sanchez-Garcia (2008) and Lagarón (2011). The biopolymers typically considered are PLA, PCL, PHA and starch. Reductions in O_2 and water vapor permeability range from 12% to 65% and 11% to 80%, respectively.

Ray and Bousmina (2005) reviewed the use of biodegradable polymers in PCN. An interesting aspect of nanocomposite technology is the enhancement in biodegradability after nanocomposite formation. A recent article described the mathematical modeling of mechanical and barrier properties of bionanocomposites using analytical micromechanics (Kumar et al., 2011).

5.6.7 FUTURE DEVELOPMENTS

Most applications of nanocomposites in plastics have made use of laminar clays and, in some cases, of carbon nanotubes. However, other types of reinforcing elements such as biodegradable cellulose nanowhiskers (CNW) and nanostructures obtained by electrospinning are promising in several application fields. The electrospinning method is a simple and versatile technology that can generate ultrafine fibers that have large surface-to-mass ratios (up to 10^3 higher than a microfiber), excellent mechanical strength, flexibility and lightness. The procedure is not mechanical but electrostatic and is applied to the polymer in solution or to polymer melts. As a result of the latter, it is a suitable technique for the generation of ultrafine fibers of biodegradable materials that are, in general, easy to dissolve. It has been reported that around 100 different polymers (including biopolymers) and polymer blends have been nanofabricated by electrospinning (Sanchez-Garcia and Lagarón, 2009).

Recently, Compton et al. (2010) reported the exceptional ability of a graphene-based nanofiller to limit both O_2 permeation and light transmission in polymer films. At only 0.02 vol%, crumpled graphene nanosheets significantly densified PS films, thus lowering the free volume within the polymer matrix. This resulted in an unprecedented reduction in O_2 solubility, which manifested as a considerable decrease in O_2 permeability. At such a low concentration, crumpled graphene sheets were as effective as clay-based nanofillers at ~25 to 130 times higher loadings. In addition, this low loading of graphene significantly reduced the light transmittance of ~0.028 cm-thick PS films at 350 nm from 94% to 31%. Thus, the addition of low concentrations of graphene nanosheets offers a simple, inexpensive means to significantly enhance the barrier properties of polymer-based packaging materials for air- and light-sensitive products.

An alternative approach to improving the barrier properties of polymers using nanoclays is layer-by-layer (LbL) assembly, an aqueous coating technology that is capable of building multifunctional thin films. These films are produced through alternate exposure of a charged (or polar) substrate to water-based solutions (or mixtures) containing charged (or polar) ingredients. Each pair of complementary layers is referred to as a bilayer, which is typically 1–100 nm thick (Jang et al., 2008). Thin films of sodium MMT clay and cationic polyacrylamide were grown on a PET film using LbL assembly. After 30 clay–polymer layers were deposited with a thickness of 571 nm, the resulting transparent film had an OTR below the detection limit of commercial instrumentation (<0.001 mL m^{-2} day^{-1}). This low OTR, which is unprecedented for PCN, is believed to be due to a brick wall nanostructure comprised of completely exfoliated clay in a polymeric mortar. With an optical transparency greater than 90% and potential for microwavability, this thin composite is a good candidate for foil replacement in food packaging (Jang et al., 2008).

More recently, Priolo et al. (2010) reported LbL assembly of a three-component system to further increase the space between clay layers as the film is deposited. The resulting PCN thin films also had unprecedented barrier performance, with O_2 permeability below that of SiO_x at a thickness of just 51 nm, produced with only eight bilayers (or four quadlayers). Coupling high flexibility, transparency and barrier protection, these films are good candidates for a variety of food packaging applications.

Another recent development was the report by Park et al. (2011) of gravure-ink-containing nanoclays as an alternative O_2 barrier material for OPP film. Barrier properties of OPP films coated with three different types of gravure-ink-containing nanoclays (1 wt%) reduced OTR by 12%–37%. However, no remarkable differences were evident in the water vapor barrier performance of control and coated OPP films. As nanoclay content and dispersion time increased, OTR values of the coated OPP films decreased.

As the secrets of nature's methodology to optimize material properties by nanolevel construction are unlocked (biomimetics), translation of these findings to PCNs should allow for further advances (Paul and Robeson, 2008).

5.7 ORIENTATION

Orientation of polymer films is a means of improving their strength and durability in order to broaden their scope of application and make them serviceable in thinner gauges. Films may be oriented in either one direction (uniaxial orientation) or, more commonly, in two directions, usually at right angles to each other (biaxial orientation [BO]). Virtually all thermoplastics can be oriented to some extent, but amorphous films can be more readily oriented than crystalline films.

Orientation of thermoplastic film involves stretching the material in such a manner so as to line up the molecular chains in a predetermined direction. Once lined up, the ordered arrangement is frozen in the strained condition. BO films possess superior tensile and impact strengths, improved flexibility, clarity, stiffness and toughness and increased shrinkability.

It is difficult to generalize the effect of orientation on the gas and water vapor permeability of polymers; permeability in some polymers is unaffected by orientation, while, in others, increases or decreases are observed depending on the type of polymer, and the degree and temperature of orientation. Gas and water vapor permeabilities for amorphous polymers (e.g., PS and PET) tend to decrease by about 10%–15% when oriented. Crystalline polymers (e.g., PP and PVdC copolymer) show significant reductions in permeability of over 50% when oriented. This difference is greatest at low degrees of crystallinity (10%–15%) and gradually becomes less as the degree of crystallinity increases, until, at 40%–50% crystallinity, no differences are discernible (see Table 4.7). The gas permeabilities are largely dependent on the amorphous content, which outweighs any effect introduced by orientation. The permeability of an amorphous polymer below or not far above its T_g depends on the degree of orientation of the molecular segments; it is normally reduced compared to that at high temperatures, although sometimes some small strains increase the permeability.

Orientation generally has a detrimental effect on elongation, ease of tear propagation and the sealability of the film. The heat sealability range is narrowed and the film may vary in properties with age. Oriented film cannot be easily heat sealed because it shrinks and puckers at temperatures below the sealing temperature. A suitable solution is to apply a surface coating of some thermoplastic having a lower melting point. For example, OPP may be coated with a dispersion of PVdC copolymer, or a copolymer of PP with a small quantity of LDPE.

Among the more common commercially oriented films are PET, PA, PVdC copolymers, PP and LDPE, the latter commonly being irradiated before blowing into film. Because radiation cross-links the molecules (see Section 5.8), the film can be stretched without becoming fluid at the melting point of a nonirradiated film, resulting in greatly improved tensile strength and shrink tension compared to nonirradiated LDPE. HDPE is not oriented because its very rapid rate of crystallization limits the extent to which it can be stretched. When the resin is blended 70:30 with LDPE, the rate of crystallization is slowed. The crystallinity imparts properties similar to those achieved through radiation cross-linking. The largest application of orientation techniques is in the manufacture of OPP, which results in a considerable improvement in its barrier properties.

In the case of crystalline polymers, the action of orientation induces additional crystallization, with the crystalline structure aligned in the direction of stretching. The induced crystallinity is general and does not occur in spherulite form; therefore, oriented films usually have a high degree of clarity, because of the relative absence of spherulites that cause light scattering. Orientation decreases the permeability of PET to almost one-third that of the unoriented, amorphous polymer because of decreases in both the diffusion coefficient and the solubility coefficient. Crystallization by heat setting above the T_g does not dramatically affect the permeability.

For many applications, shrinkage is not desirable and a greater degree of heat stability is required. Films can be annealed by the application of heat to partially relax the forces while maintaining the film in a highly stretched condition. It is then cooled to room temperature and the restraint on the film released. Such a film is referred to as *heat set* and will not shrink if heated to below the annealing temperature. The procedure of annealing does result in some reduction in dimension in the stretched direction or directions.

5.7.1 ORIENTATION PROCESSES

The most common method used to orientate a thermoplastic film is to stretch it after it has been heated to a temperature at which it is soft. This temperature is below the flow temperature at which the molecules would readily glide past one another when the material is stressed, but above the T_g. As a result of this stretching, the direction of the molecules changes toward that in which the material is stressed, and the molecules are extended like springs. The temperature is then dropped below the softening point of the material, while the molecules are held in this configuration so that the molecules are frozen in the strained position.

Films can be oriented using two processes: *tenter frame* and *double-bubble*. In the tenter frame process, thick (500–600 µm) cast film is fed to a system of differential draw rolls that are heated to bring the film to a suitable temperature below its melting point. The film is stretched in the machine direction (MD) and the extent of orientation is determined by the ratio of the width of the film entering to the width of the film leaving the system. The film is then fed to a tenter frame (Figure 5.9), where a series of clips (mounted side by side on endless chains that diverge at constant angle) grasp both edges of the film and draw it in the transverse direction (TD) as it travels forward at an increasing speed. Stretch rate is determined by the chain speed, divergence angle and extent of orientation. Draw ratios in both directions normally vary between 4:1 and 10:1. After tentering, the film is annealed, passed over a cooling roller and reeled up.

A new simultaneous BO system called LISIM® (linear motor simultaneous stretching system) has been developed. It features individually driven clips with linear motors to drive the clips and imparts MD stretch as the film travels down the diverging tenter rails (Breil, 2010). This has replaced

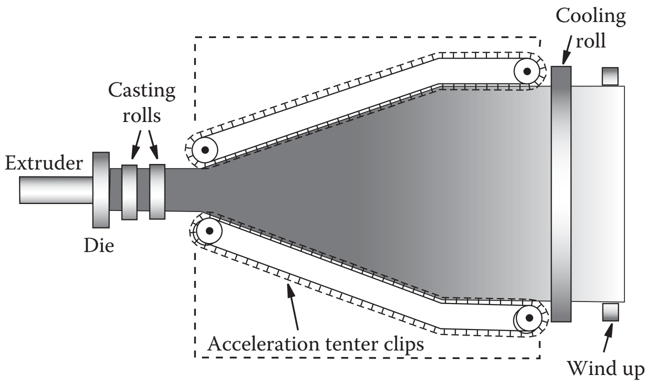

FIGURE 5.9 Flat sheet orientation process using a tenter.

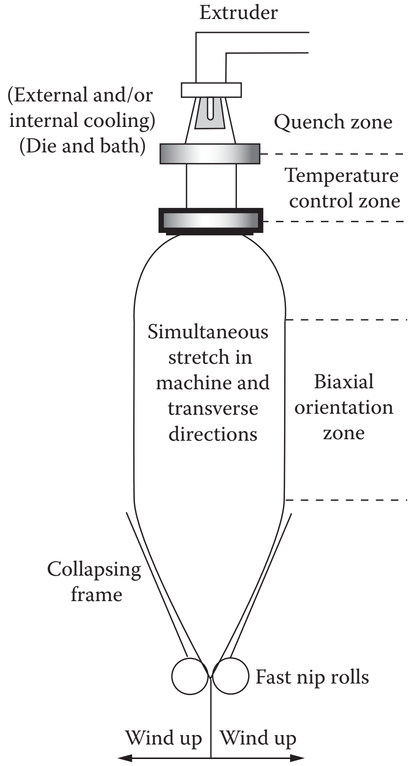

FIGURE 5.10 Orientation by the double bubble process.

the mechanical complexity of the earlier simultaneous systems with electronic control complexity that is readily handled by computer. This new tenter design has been implemented commercially and results in improved mechanical properties due to higher stretching ratios.

In the double-bubble process (Figure 5.10), molten polymer is extruded as a tube from an annular die and then quenched and gauged in cold water. The tube is flattened by passing through nip rolls and reheated to a uniform temperature. The air pressure in the tube is increased to expand the film transversely, the draw ratio being varied by adjusting the volume of entrapped air. Pinch or collapsing rolls at the end of the bubble are run at a faster speed than rolls at the beginning of the bubble, thus causing drawing of the film in the MD. After trimming the edges, the film is separated into two webs and wound up.

The amount of orientation imparted to a film depends on the stretching temperature, the amount of stretching, the rate of stretching and the quench. Quenching is carried out either by extruding the web onto a chill roll or by passing it through a quench tank prior to orientation. Generally, orientation is increased by decreasing the stretching temperature, increasing the amount of stretch, increasing the rate of stretch and increasing the amount of quench. Films such as PVdC copolymer and PP that have T_gs below room temperature show an appreciable crystallization rate even at room temperature and, therefore, have to be quenched and oriented immediately after extruding.

The potential energy stored in the extended molecules is the *elastic memory*, characteristic of oriented, nonheat-set thermoplastics. When such a film is reheated to its orientation temperature, it shrinks as the molecules tend to return to their original size and spatial arrangement. At elevated temperatures, but below the orientation temperature, some shrinkage will occur but to a lesser extent. BOPP is typically oriented 700%–800%, while other films are oriented 200%–1000% in either direction.

5.7.2 SHRINK FILMS

Shrink films are composed of three basic categories: polyolefins, PVC and PVdC copolymer. With the exception of PVdC copolymer film, which can be shrunk in hot water, most of the other shrink films require temperatures above 100°C to obtain a suitable degree of shrinkage, necessitating the development of hot air tunnels or heat guns.

Three properties of shrink films are important when selecting a film for a particular application. First is the range of temperature over which a film will shrink. The lower the shrink temperature, the simpler and less expensive is the shrink process. Films with a wide softening range are usually preferred as this makes temperature control of the heating equipment less critical.

The degree of shrinkage is also important, with some applications requiring a higher degree of shrinkage than others. The amount of shrink can vary from 15% to 80% depending on the polymer composition and manufacturing techniques. Of particular interest is the relationship between the degree of shrinkage and temperature. Films with a steep shrink/temperature curve (e.g., PP, where a ±5°C variation in tunnel temperature could vary the degree of shrinkage by up to 20%) are more difficult to handle because of the closer temperature control necessary.

Shrink tension, the stress exerted by the film when it is restrained from shrinking at elevated temperatures, is the third important factor. Generally, the lower the temperature at which orientation was carried out, the greater is the shrink tension. Tension of 300–1000 kPa is desirable in order to provide a tight package after shrinking. With shrink tension above 2000 kPa, care must be taken to prevent crushing and distortion of the package; this can be achieved by limiting shrink temperature and time.

Balanced orientation is especially important for printed films because uniform shrinkage is essential to avoid distortion of the print after shrinkage. Even a balanced BO film may not shrink evenly in both directions if the product is of a very irregular shape. In these situations it may be necessary to choose a print design that is not affected by such distortion.

Since the early 1990s, multilayer coextruded shrink films have become available, enabling films to be designed with greater control over the desired characteristics.

5.7.3 STRETCH FILMS

Although unrelated in a strict sense, stretch or stretch/cling films will be discussed here as they compete in many end uses with oriented films. Stretch films were first introduced in the early 1970s and have replaced shrink wrapping for large pallet loads and several other applications. In stretch wrapping, the film is stretched around the article and the loose end "wiped" against the underlying film, where the film-to-film adhesion or cling is sufficient to hold it in place. Other less common ways of attaching the end are heat sealing, adhesives, mechanical fasteners and tying. Orientation of the polymer chains occurs on stretching to give a stiffer film, improving the tightness of the wrap and the stability of the load. The residual tension in the film gives a tight contour wrap.

The main polymers used in stretch/cling films are LDPE, LLDPE, VLDPE, PVC, EVA copolymer and PP, the choice depending on such factors as appearance (i.e., requirements for clarity, sparkle and so on) and the protection required (gas and moisture barrier, and/or physical protection in preventing pallet loads from disintegrating). Recently, metallocene-catalyzed LLDPEs have been adopted as they exhibit higher tensile strength, elongation and tear resistance than EVA or PVC films, and can be processed at a substantially lower thickness. Most stretch/cling films are coextruded structures containing three to five layers. Common structures are EVA-VLDPE-LLDPE 10:80:10 and VLDPE-LLDPE-MLLDPE-LLDPE-VLDPE 10:25:30:25:10 with thicknesses ranging from 15 to 30 μm.

LDPE is classed as a low stretch film with a stretchability of about 30%. Under ideal conditions, LLDPE can stretch up to 400%, although the practical limit is nearer 200%. About 60% of the initial stretch is retained by this film, and the figure for LDPE is about 70%. The trend is toward lighter gauge films (20 μm is common) with some as thin as 13 μm.

An important property of stretch films is their cling, with blown LLDPE having much less cling than PVC or EVA copolymer. While polyethylenes require adhesive additives to develop significant tack strength for use in cling film applications, EVA films are inherently tacky and the tack strength is dependent on the ratio of ethylene to VA comonomer, the higher the VA content the stronger the tack performance (McNally et al., 2005). Additives such as glyceryl mono-oleate and polyisobutylene are added by film manufacturers to improve cling. Elevated humidity can sometimes enhance film cling because some cling additives function by attracting moisture from the atmosphere. Moreover, antioxidants, antistatic agents and antiblock agents (the latter preventing the layers of film on a roll from becoming permanently bonded together) are also frequently added.

One problem is that different films retain different stress, since all films start to relax immediately after they have been stretched. Most of the relaxation (about 99%) occurs within 24 h. The opposite of relaxation is stress retention, which is defined as the capacity of a film to maintain the applied tension during stretch wrapping.

5.8 CROSS-LINKING

Cross-linking of crystalline thermoplastic polymers interferes with molecular packing, reduces the level of crystallization and, consequently, results in a polymer with a lower hardness and yield strength. Three main approaches are used for cross-linking polyethylene as follows:

1. Radiation cross-linking
2. Peroxide cross-linking
3. Vinyl silane cross-linking

Only the first will be considered further here. The effect of irradiation on polymeric materials has been widely investigated and the properties that can be improved by cross-linking include the following:

1. Mechanical properties such as tensile strength
2. Scratch resistance
3. Performance at higher temperatures, often with an increase in the melting temperature
4. Resistance to chemicals because of lowered solubility in organic solvents
5. Gas permeation reduction
6. Shape memory retention

TABLE 5.3
Properties of Standard and Irradiated Oriented Polyethylene Film

	Irradiated Polyethylene	Standard Polyethylene
Yield ($m^2\ kg^{-1}$)	42.7	42.7
Density	0.916	0.916
Tensile strength (kPa) at 22°C	8,000–16,000	1500–3000
Tensile strength (kPa) at 93°C	1500–3000	100–200
Elongation (%) at 22°C	100–200	50–600
Heat sealing range (°C)	150–300	110–150
Percent shrink at 98°C	20–80	0–60
Orientation release stress (kPa) at 96°C	100–500	0–10

Radiation cross-linking is normally carried out using an electron beam accelerator that produces high energy β rays. The irradiation cross-links the C–C bonds such that the film can still be stretched but no longer becomes fluid at its original melting point. It therefore retains a relatively high orientation release stress that promotes tight shrink wraps. One of the advantages of radiation cross-linking is that the amount of cross-linking can be controlled by the amount of dose used.

One of the most successful applications has been the cross-linking of LDPE film. Irradiated LDPE film is made as follows: after extrusion and quenching, the thick-walled tube is irradiated and then oriented using the double bubble process. The cross-linking increases tensile strength, orientation release stress and heat sealing range to make a practical shrink film from LDPE. The film toughness is similar to that of PVdC copolymer film, while its flexibility at low temperatures is superior. A comparison of irradiated and standard oriented polyethylene film is given in Table 5.3.

The use of ionizing radiation as a nonthermal process to preserve or extend the shelf life of certain foods can cause changes to plastic packaging materials resulting in the formation of radiolysis products that could migrate into the food. Packaging materials for irradiation of prepackaged foods are closely regulated and a detailed review has been presented by Komolprasert (2007).

5.9 MICROPERFORATION

With the increasing commercialization of MAP (see Chapter 16), a demand has arisen for so-called breathable films for high respiring, fresh horticultural products. The permeabilities of normal polymeric films (even at very thin gauges) are too low to meet the requirements. Downgauging of films to increase gas transmission rates is rarely the solution, since it makes machinability problematic. Therefore, many attempts have been made to develop more porous structures so as to increase their permeability properties.

The following three generic approaches have been taken to create additional porosity:

1. *Inorganic fillers*: Since the 1980s, commercial ceramic-filled polymer films have been available. The films typically contain about 5% of very fine ceramic powder, and the manufacturers claim that these films emit far-infrared radiation and/or absorb C_2H_4, but such claims have not been confirmed by independent laboratories. Gas permeabilities can be manipulated by adjusting the filler content, the particle size of the filler and the degree of stretching. The permeability of ceramic-filled LDPE to O_2, CO_2 and C_2H_4 is higher than plain LDPE, making these films more suitable for packaging produce with a high respiration rate. Unfortunately, clarity decreases, thus limiting the commercial success of such films.
2. *Porous patch*: A porous patch containing a permeable membrane is placed over a die-cut hole in the film. The porosity of the patch can be changed to suit different respiration needs of various fresh produce. This method is discussed further in Section 15.3.4.

3. *Perforations*: Punching large holes with hot needles or on-machine syringes in plastic films used to package fresh produce has been practiced for many years. However, this relatively unsophisticated approach results in holes that are too large to be useful in creating a modified atmosphere inside the package. Microperforation laser technology creates numerous, precise holes with diameters in the range of 40–200 μm but typically 50–60 μm. The focused laser beam heats, melts and instantaneously vaporizes plastic film, leaving a very small, well-defined, reinforced hole. By altering the diameter and number per unit area of the microperforations, gas permeability through a package can be altered to meet well-defined product requirements. Microperforation laser technology with controlled score depth can also be used for easy-open packaging that allows for easy tear propagation of film without affecting the barrier properties of the package. It has also enabled applications for microwave steam release venting.

Microperforation—a post-extrusion converting process—was patented in England in 1989 and is now commercialized worldwide. It originally used spark technology but today laser technology is used to make consistent, tiny holes in films at commercial speed.

The latest development is laser beam compression in which the laser pulse is manipulated and guided to direct all its energy to a single point on the film, independent of the web speed. It allows web speeds to be increased by three or four times, up to 360 m min^{-1} over systems without beam compression. This new patented technology allows for the efficient use of lower powered lasers to produce the same or better results than higher powered lasers. Although OPP is the most common polymer film used for microperforation, the technique can be applied to most polymer films using both monolayer and coextruded structures. With microperforation, the inherent permeability of the film is largely irrelevant and films are selected for other properties such as toughness.

Allan-Wojtas et al. (2008) reported that microperforations in the range of 30–100 μm in diameter exhibited a linear increase of both OTR and CDTR with hole area, for diffusion under calm conditions. Microperforations larger than 55 μm in diameter lost their diffusion constant if convection was present and, therefore, holes with a diameter less than 55 μm should be used to provide consistent OTR results under convective conditions. The best results are achieved using numerous small holes rather than fewer large ones. They also reported that the permselectivity β of microperforated films varied from about 0.85 under calm conditions to 0.95 under fans. OTR and CDTR values at 5°C for microperforated PP film of 30 μm thickness are presented in Table 4.1.

5.10 INJECTION MOLDING

The injection molding process consists essentially of softening thermoplastic material in a heated cylinder and injecting it under high pressure into a relatively cool mold where solidification takes place. After the plastic has solidified, the mold is opened and a part in the shape of the mold cavity is removed. It is a major technique for converting thermoplastics and is widely used for producing tubs and jars (such as those used for packaging yogurt and margarine), as well as various caps, spouts and dispensers. It is also used to manufacture PET preforms.

The injection molding process or cycle occurs in three consecutive steps as follows:

1. Feeding and thermally plasticizing a stock of granules by means of an extrusion-type screw that rotates until the required amount of melt has been conveyed to the front of the barrel
2. Injecting a metered amount of hot plastic into a cold cavity at high pressure
3. Cooling and ejecting the molded component

High production rates are possible, but because injection molds are expensive, short production runs are uneconomic. Most molds are made of hardened high-quality tool steel. Reverse tapers and sharp undercuts cannot be molded by this method because the finished articles would not be able to be removed from the mold. For a threaded part, for example, a bottle cap, part of the mold must be rotated to remove the article from the mold. Amorphous plastics shrink less than crystalline plastics, and mold designs must take into account that cooled moldings are always smaller than the cavity, owing to shrinkage. Injection molded products can be recognized by a small surface protrusion (known as the *gate*), which indicates the point of entry of molten plastic into the mold. It is clearly evident on the base of PET bottles because the preform is injection molded.

Resins that are commonly injection molded include LDPE, HDPE, PP and PET, the latter as a preform for stretch blown beverage bottles.

5.11 BLOW MOLDING

Blow molding is a process to produce hollow objects. It was practiced with glass from ancient times, and the basic techniques used by the plastics industry have been derived from those developed by the glass industry. Currently, a wide range of blow molded bottles and containers are produced for use in food packaging.

In blow molding, a molten tube of thermoplastic (known as a *parison*) is surrounded by a cooled mold having the desired shape. A gas (usually air but occasionally N_2) is introduced into the tube causing the molten mass to expand against the walls of the mold where it solidifies on cooling. The mold is then opened and the bottle or jar ejected.

Generally, the process for manufacturing plastic bottles and jars consists of three stages: melting the resin, forming the parison and blowing the parison to produce the final shape. The blowing step may take from a few seconds to more than a minute for large shapes; the rate limiting step is the cooling of the molded shapes.

There are two techniques of plasticizing resin (i.e., making the material flow) and forming the parison:

1. Extrusion, which produces a continuous parison that has to be cut; this is the most common method used
2. Injection molding, where the parison is formed in one mold and then transferred into another mold for blowing

5.11.1 EXTRUSION BLOW MOLDING

Extrusion blow molding (EBM) uses many arrangements for making and forming the parison (Irwin, 2009). In the simplest method, a mold is mounted under an annular die and the parison extruded between the open halves of the mold. When the parison reaches the proper length, the extruder is stopped, the mold is closed around the parison, and the bottom of the parison is pinched together by the mold. A blow pin mounted inside the die head allows air to enter and blow the parison, which expands to fill the mold. The shape of the bottle or jar is defined, but the distribution of material (and, thus, wall thickness) is less well controlled. The cycle restarts after the part has cooled and the mold opened, as shown in Figure 5.11.

Since the extrusion of the parison is a continuous process, numerous systems have been developed to use the full capacity of the extruder. One uses more than one mold, moving the filled mold away to cool while another is moved into position to receive the next section of extruded tube. The molds can be reciprocating ones, or can be mounted on a rotary table. In several food packaging applications (e.g., pasteurized milk), the bottles are blow molded and filled online in a continuous operation.

EBM is widely used with the following resins: HDPE, PP, PVC and AN copolymers. The most common blow molding resin is HDPE used to produce containers ranging in size from 30 mL to 200L. The common grades of PET cannot be extrusion blown.

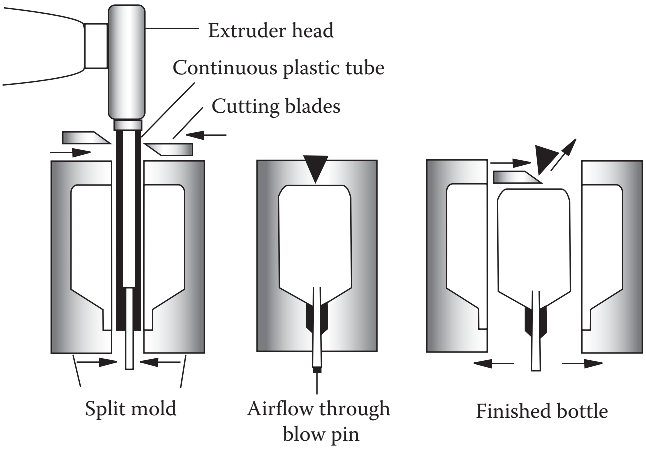

FIGURE 5.11 Extrusion blow molding of plastic bottles.

A related process is the production of coextruded bottles, where two or more extruders, each handling different plastic materials, produce a multilayer parison having the desired properties. For example, a high barrier, high cost material might be sandwiched between layers of a relatively low cost material to give a bottle with the desired barrier properties at an economical price. Coextruded structures with up to seven layers, of which one or more can be a barrier layer, are common today.

5.11.2 INJECTION BLOW MOLDING

Injection blow molding (IBM) is a noncontinuous cyclic process shown in Figure 5.12, and most closely resembles the blowing of glass bottles. The parison is formed in one mold and then, while still molten, is transferred to a second mold where blowing with compressed air forms the final shape. After cooling, the mold is opened and the bottle ejected. Several molds must be available if the injection molding machine is to operate near full capacity.

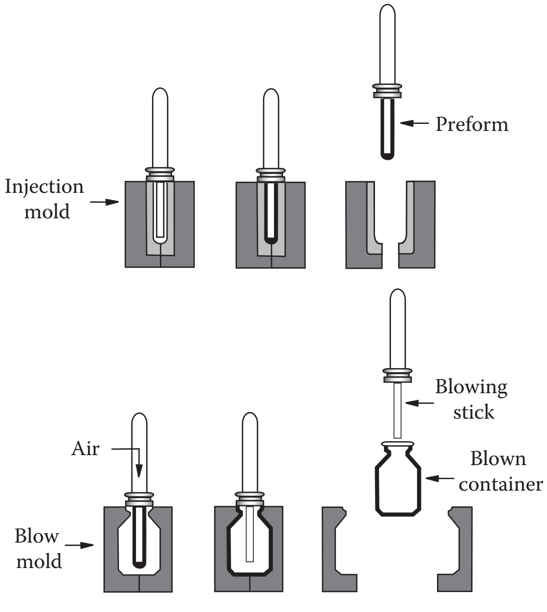

FIGURE 5.12 Injection blow molding of plastic bottles.

The major advantage of IBM over EBM is that the process is virtually scrap-free, the finished parts usually requiring no further trimming, reaming or other finishing steps. In addition, the dimensions of the bottle (including the neck finish) show very little variation from bottle to bottle, and with some materials, improved strength and clarity are obtained due to the effect of a limited degree of biaxial orientation (see Section 5.7).

The resins most commonly used for IBM are HDPE, PP, PS, PVC and PET. PET has replaced PVC in many countries, especially in Europe where PVC has a poor image among many consumers.

Coinjection blow molding has been developed using two or three injection units working with one mold to produce a preform that is later blow-formed using compressed air inside a mold to make a bottle or jar. The various component materials are metered into cavities in such an order that the barrier material flows through the main structural material to create a multilayer structure. This process is used to produce five layer retortable containers from three materials, typically PP as a structural layer and EVOH copolymer as a barrier layer with tie layers in between.

5.11.3 STRETCH BLOW MOLDING

Stretch blow molding (SBM) is a process where bottles with appreciable orientation in both longitudinal and TDs are produced; it is sometimes known as biaxial orientation blow molding (Irwin, 2009). Orientation in the TD only is produced in normal EBM, while appreciable transverse and some longitudinal orientation are produced in IBM. True biaxial orientation produces bottles with improved properties including increased tensile and impact strength, improved surface gloss, reduced creep, improved gas and water vapor barrier properties and a reduction in haze in transparent bottles. As a result, lighter weight, lower cost bottles can be produced.

To produce a biaxially molded bottle, a preform or parison (produced either by injection molding or extrusion of a continuous tube or parison, which is then cut to the required length and closed at one end) is stretched longitudinally under heat and blown into a bottle with consequent transverse orientation. A metal stretch rod enters the bottle to assist in the stretching process (Figure 5.13).

The process of SBM is particularly important in the field of carbonated beverage packaging using PET. For best results, the resin molecules must be conditioned, stretched and oriented at just above the T_g where the resin can be moved without the risk of crystallization. Although PET is the major stretch blown resin, PVC, PP and AN copolymer resins are also stretch blow molded.

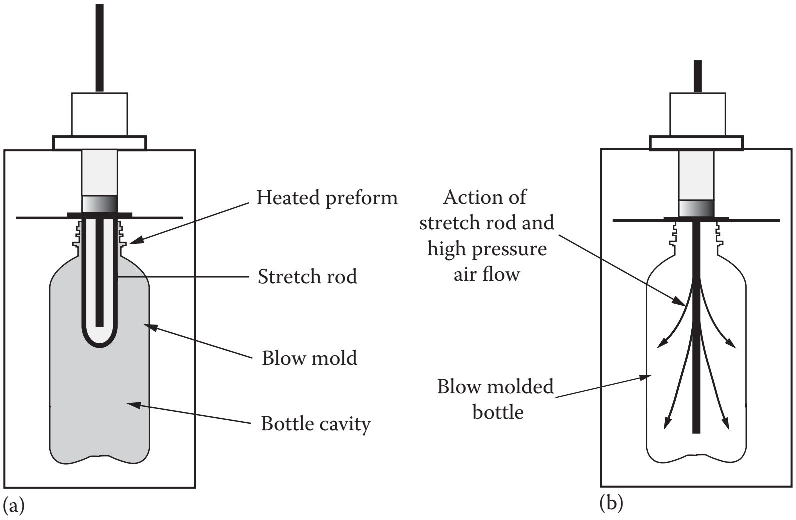

FIGURE 5.13 Stretch blow molding process. (a) Mold closed on preform. (b) Stretching and blowing. (From Irwin, C., Blow molding, in: *The Wiley Encyclopedia of Packaging Technology*, 3rd edn., Yam K.L. (Ed.), John Wiley & Sons, New York, pp. 137–154, 2009.)

Two different stretch blow techniques are available for SBM. In the one-stage method, parison injection molding, temperature conditioning and blow molding take place in the same machine. This method is commonly used for widemouthed jars and bottles with unusual cross-sectional shapes. In the two-stage method (also known as the "reheat and blow" method), the parisons are first injection molded in a completely separate stage and stored at ambient temperature until required. They are then reheated to between 90°C and 110°C and blown to their final shape. For many PET bottles, the preform length is typically less than half the final bottle height. No stretch occurs at the top and bottom of the bottle. Typical stretch ratios for a 2-L PET bottle are 2.3:1 in the axial (longitudinal) direction and 3.9:1 in the hoop (transverse) direction. Often production of performs and bottles are physically separated in different facilities, with the SBM often being done on-site by the filler or the packaging supplier in a hole-through-the-wall (HTW) operation.

For hot fill applications, heat resistant PET bottles are required, since a normal PET SBM bottle cannot be filled much above 65°C without causing bottle shrinkage. Manufacture of a heat resistant bottle is called the "heat set process" and involves further heating after being stretched so that it undergoes "after crystallization" (known as thermally induced crystallization). This increases the crystallinity, mainly in the sidewalls, to about 30% or more as opposed to 20% in a container produced by the conventional blow molding process (Tekkanat, 2002). Increased crystallinity gives the material significantly enhanced thermal stability; the T_g and rigidity also increase.

Two methods are used. In the first, a single mold method, the preform is stretch blow molded into a hot mold where the mold halves are up to 160°C and the mold base 90°C–95°C, resulting in the preform being heated to between 100°C and 110°C, about 10°C hotter than in the conventional blow molding process. Heat setting takes place as the blown container encounters the surface of the hot mold while being constrained by high pressure against the mold. The container is then cooled down to below its T_g before it can be removed from the mold using compressed air on the inside.

In the second (dual mold) method, the preform is first stretch blow molded into a first mold, followed by a reheating in an oven to relieve stresses and shrivel the shape, followed by reblowing in a second mold to produce the final bottle shape (Irwin, 2009). To avoid unsightly bottle appearance as a result of vacuum formation inside the bottle after hot filling, hot fill bottles are molded with sidewall panels and base designs that move inward as the product cools and ensure that the vacuum-induced forces do not distort the bottle. As a rule of thumb, shrinkage of heat set containers after hot filling should be limited to <10% (Tekkanat, 2002).

Production of multilayer co-injection preforms is the most economical way to achieve enhanced properties in a rigid PET container. Multilayer co-injection is the process by which one or more interior layers of material are totally encapsulated by outer virgin PET layers. It is the only technology able to provide any combination of clarity, gas barrier, gas scavenger and recycled PET (rPET) in a single process (Swenson, 2002). Multilayer parisons can be produced by either extrusion or injection-molding techniques.

Co-injection SBM was a major breakthrough, enabling longer shelf lives for beverages to be achieved. It has been used to produce three-layer (PET-MXD6-PET) and five-layer (PET-rPET-PET-MXD6-PET) bottles, mainly in smaller sizes where the lack of a barrier layer would severely limit shelf life. Although EVOH copolymer could be used as a barrier layer, MXD6 is preferred as it has similar melt flow characteristics to PET. Although multilayer PET bottles have been commercialized, the focus has now turned to coating bottles with oxides of silicon or aluminum or with HCs (see Section 5.5).

Aseptic blow molding is becoming increasingly popular for the packaging of beverages. It is usually based on the extrusion process where the bottle is blow molded in a commercially sterile environment, often with the product filler combined with the blow molder. In one system, the bottle is molded and sealed in the blow molding machine and then stored for minutes or days. At the filler, the outside of the bottle is resterilized and the top seal area cut off; after filling aseptically with sterilized product, the bottle is resealed. In an alternative approach, bottle blow molding, filling and sealing are all carried out in a commercially sterile environment (Irwin, 2009).

5.12 THERMOFORMING

In this relatively old and simple process, a sheet (generally 75–250 µm thick) of thermoplastic material is heated to its softening temperature, usually by means of an infrared radiant panel heater. Pigmentation of the sheet aids the heating process. By either pneumatic or mechanical means, the sheet is forced against the mold contours and, after cooling, is removed and trimmed. Typical thermoplastics used for thermoforming include HIPS, PVC, PP and PA.

There are two dominant means of thermoforming sheet for food packaging containers: the *melt phase* process and the *solid phase pressure forming* (SPPF) process (Chougule and Piercy, 2009). The melt phase process is most applicable to monolayer structures that have relatively high melt strength at thermoforming temperatures, for example, HIPS, PVC and PC. The SPPF process is primarily used to thermoform PP, a crystalline polymer that is difficult to thermoform uniformly in melt phase machines due to the sharp decrease in melt strength (viscosity) at its melting point (Brown, 1992).

Thermally stable PET containers are in common use for dual ovenable (i.e., conventional and microwave) applications for chilled and frozen foods, as well as retortable, shelf stable applications where the food can be reheated in the package using either a microwave or a conventional oven. These containers are known as crystallized PET (CPET) and are stable at temperatures up to 230°C, compared to amorphous PET (APET), which begins to soften at temperatures over 63°C. The CPET process is based on conventional reheat thermoforming where an extruded PET sheet containing nucleating agents to speed up and maximize crystallization is reheated to around 170°C where it softens. It is then thermoformed into a hot mold and held long enough for the optimum amount of crystallinity to develop, after which it is transferred into a second mold where it is cooled. CPET containers must be crystalline enough to be heat resistant but not so crystalline as to be too brittle for the application, for example, impact resistance at freezer temperatures. The optimum amount of crystallinity is 28%–32%. Foamed CPET is also available.

The SPPF process involves forming at lower temperatures below the crystalline melting point, that is, 5%–8% lower than melt phase forming, depending on the material. For example, PP is melt phase thermoformed at 154°C–157°C and SPPF at 141°C–146°C where it is still virtually a solid with high viscosity, requiring the application of strong forces. In SPPF, the sheet is heated by infrared heaters and stretched into the mold cavity with a heated plug. Cold air at pressures of up to 700 kPa then force the hot sheet against the cooled inner wall of the mold, finishing the forming operation at a high speed. This process (developed mainly for PP) improves the strength of the containers as well as their clarity, and because lower temperatures are used, the containers are free from odor and taint, thus making them very suitable for food packaging.

The ability to produce extruded PS foam sheet has provided additional packaging markets for thermoforming. The first of these was meat and produce trays, followed later by egg cartons. Other applications include fast-food carry-out cartons, institutional dinnerware and inserts for rigid boxes.

5.13 FOAMED (CELLULAR) PLASTICS

Foamed or cellular plastics are defined as plastics whose apparent density is decreased substantially by the presence of numerous cells dispersed throughout their mass. The terms foamed plastic, cellular plastic, expanded plastic and plastic foam are used interchangeably. These materials have been used widely since the 1940s, due largely to their desirable properties that include a high strength-to-weight ratio and good insulating and cushioning properties. A wide range of plastic polymers can be foamed, including LDPE, HDPE, PP, EVA, PS and polyurethane. The market is dominated by the latter two polymers, with PS being used in preference to polyurethane for food contact applications.

Plastic foams are classified as either flexible or rigid, and may have an open or closed cell structure; in the former, the cells are interconnected, whereas in the latter most cells are closed and separate. Cell formation is initiated by foaming agents. Physical foaming agents are compounds that change their physical state during cell growth and the most important are volatile liquids (typically aliphatic HCs and CO_2) with boiling points below 110°C at atmospheric pressure. Chemical foaming agents decompose under heat to at least one gaseous decomposition product, commonly N_2.

PS foams can be produced by two processes: injection molding and extrusion. With injection molded foam, machines similar to normal injection molding machines are used, except that steam is injected to heat the beads that contain a foaming agent. Extruded PS foam is produced by free expansion of hot PS, blowing agents and additives through the slit orifice of a high *L*/*D* ratio extruder to about 40 times the pre-extrusion volume. The amount and type of blowing agent control the density of the foam produced. The major food packaging uses for extruded PS foam sheet are egg cartons and meat and poultry trays.

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6 Paper and Paper-Based Packaging Materials

6.1 PULP

Pulp is the fibrous raw material for the production of paper, paperboard, corrugated board and similar manufactured products. It is obtained from plant fiber and is therefore a renewable resource. Paper derives its name from the reedy plant papyrus, which the ancient Egyptians used to produce the world's first writing material by beating and pressing together thin layers of the plant stem. However, complete defibering which is characteristic of true papermaking was absent (Smook, 2002). The first authentic papermaking, which is the formation of a cohesive sheet from the rebonding of separated fibers, has been attributed to Ts'ai-Lun of China in 105 AD, who used bamboo, mulberry bark and rags.

Since then, many fibers have been used for the manufacture of paper including those from flax, bamboo and other grasses, various leaves, cottonseed hair and the woody fibers of trees. The influence of the raw material can be largely assigned to the length and wall thickness of the fibers rather than to their chemical composition. About 97% of the world's paper and board is made from wood pulp and about 85% of the wood pulp used is from spruces, firs and pines—coniferous trees that predominate in the forests of the north temperate zone. Today, an increasing quantity of wood pulp is being sourced from sustainably managed forests, defined as "the stewardship and use of forests and forest lands in a way, and at a rate, that maintains their biodiversity, productivity, regeneration capacity, vitality and their potential to fulfill, now and in the future, relevant ecological, economic and social functions, at local, national and global levels, and that does not cause damage to other ecosystems." Although there are more than 50 certification standards worldwide for sustainably managed forests, the two largest umbrella certification programs are those of the Programme for the Endorsement of Forest Certification (PEFC) schemes and the Forest Stewardship Council (FSC).

There are three main constituents of the wood cell wall:

1. *Cellulose*. This is a long-chain, linear polymer built up from a large number of glucose molecules (weight-average DP 3500 for native wood cellulose in situ) and is the most abundant, naturally occurring organic compound. The fiber-forming properties of cellulose depend on the fact that it consists of long, relatively straight chains that tend to lie parallel to one another. Cellulose is moderately resistant to the action of chlorine and dilute sodium hydroxide under mild conditions, but is modified or dissolved under more severe conditions. It is relatively resistant to oxidation (e.g., with bleaching agents), and, therefore, bleaching operations can be used to remove small amounts of impurities such as lignin without appreciable damage to the strength of the pulp.
2. *Hemicelluloses*. These are lower MW (weight-average DP 15) mixed-sugar polysaccharides consisting of one or more of the following molecules: xylose, mannose, arabinose, galactose and uronic acids, with the composition differing from species to species. The principal hemicelluloses are xylan in hardwoods and glucomannon in softwoods. Hemicelluloses are usually soluble in dilute alkalis. The quantity rather than the chemical nature of the hemicelluloses appears to determine the paper properties. Hemicelluloses are largely responsible for hydration and development of bonding during beating of chemical pulps.

3. *Lignin*. This is the natural binding constituent of the cells of wood and plant stalks. It is a highly branched, three-dimensional (3D), alkylaromatic, thermoplastic polymer of uncertain size, built up largely from substituted phenylpropane or propylbenzene units. Hydroxyl or methoxyl groups are attached to the benzene carbon atoms. It has no fiber-forming properties and is attacked by chlorine and sodium hydroxide with formation of soluble, dark brown derivatives. It softens at about 160°C.

6.1.1 INTRODUCTION TO PULPING

The cell walls of softwoods, which are preferred for most pulp products, typically contain 40%–44% cellulose, 25%–29% hemicelluloses and 25%–31% lignin by weight (Smook, 2002). The average composition of softwoods and hardwoods is shown in Figure 6.1. Compared to hardwoods, softwoods have fibers that are generally up to 2.5 times longer. As a result, hardwoods produce a finer, smoother but less strong sheet.

Pulping refers to the process wherein wood or other fibrous raw materials are reduced to a fibrous mass. The purpose of pulping is to separate the fibers without damaging them so that they can then be reformed into a paper sheet in the papermaking process. The intercellular substances (primarily lignin) must be softened or dissolved to free individual fibers. Commercial pulping methods take advantage of the differences between the properties of cellulose and lignin in order to separate fibers. However, breaking and weakening of the fibers does occur to a greater or lesser degree at various stages during the pulping process.

Pulping is accomplished by either mechanical, thermal, chemical or a combination of these treatments. Pulps that retain most of the wood lignin consist of stiff fibers that do not produce strong papers; they deteriorate in color and strength quite rapidly. These properties can be improved by removing most or all of the lignin by cooking wood with solutions of various chemicals; the pulps thus produced are known as *chemical pulps*. In contrast, *mechanical pulps* are produced by pressing logs onto a grindstone when the heat generated by friction softens the lignin so that the fibers separate with very little damage. Mechanical pulps can also be formed by grinding wood chips

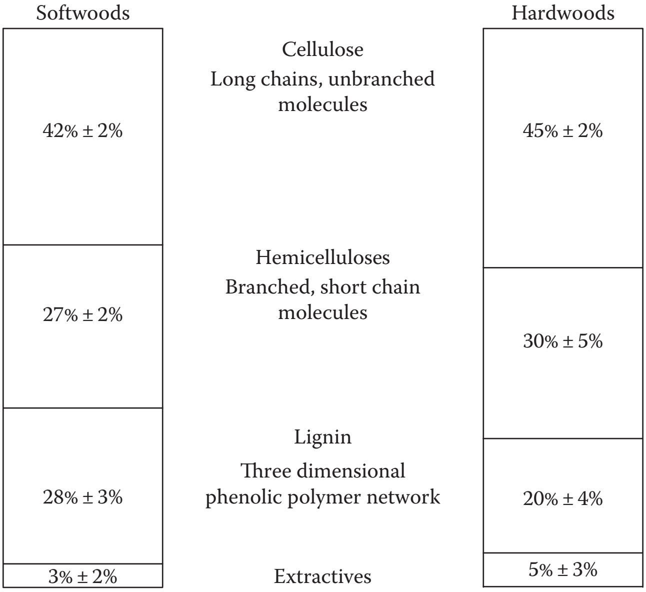

FIGURE 6.1 Average composition of softwoods and hardwoods. (Adapted from Smook, G.A., *Handbook for Pulp and Paper Technologists*, 3rd edn., Angus Wilde Publications, Canada, Vancouver, 2002.)

between two rotating refiner plates. In addition, there are some processes which are categorized as *semichemical* and *chemimechanical*. The most prevalent process is chemical pulping, which accounts for >70% of the worldwide production of pulp, of which kraft pulping is the most prevalent at 80% (Kadla and Dai, 2006).

6.1.2 MECHANICAL PULPS

Groundwood pulp is produced by forcing wood against a rapidly revolving grindstone. Practically all the wood fiber (both cellulose and lignin) is utilized. This contrasts with several chemical processes where the lignin is dissolved to varying degrees. As a result, the yield of chemical pulp is about one-half that of the mechanical process. The fibers vary in length and composition since they are effectively torn from the pulpwood.

Groundwood pulp contains a considerable proportion (70%–80%) of fiber bundles, broken fibers and fines in addition to the individual fibers. The fibers are essentially wood with the original cell-wall lignin intact. Therefore, they are very stiff and bulky, and do not collapse like the chemical pulp fibers. Although mechanical pulps have a high energy demand, they are relatively low in cost because of the high yield (Kadla and Dai, 2006).

Most groundwood pulp is used in the manufacture of newsprint and magazine papers because of its low cost and quick ink-absorbing properties (a consequence of the frayed and broken fibers). It is also used as board for folding and molded cartons, tissues and similar products. The paper has high bulk and excellent opacity, but relatively low mechanical strength.

Mechanical pulps can be bleached using oxidative (e.g., hydrogen peroxide and sodium hypochlorite) or reductive (e.g., sodium hydrosulfite) bleaching agents. Bleaching is done in a lignin-conserving manner called *brightening* in which the chromophores are modified and little solubilization of the lignin occurs. Paper and paperboard containing mechanical pulps have poor brightness stability, even after bleaching, particularly in the presence of UV radiation.

In the 1950s, the *refiner mechanical pulping* (RMP) process was developed, which produced a stronger pulp and utilized various supplies of wood chips, sawmill residues and sawdust. RMP results in more long fibers than stone groundwood and subsequently stronger paper. However, the energy requirements of RMP are higher and the pulp does not have the opacity of groundwood fibers (Kadla and Dai, 2006).

Thermomechanical pulping (TMP) presteams chips between 110°C and 150°C so that they become malleable and do not fracture readily under the impact of the refiner bars. This material is highly flexible and gives good bonding and surface smoothing to the paper. The production of TMP pulps increased dramatically after its introduction in the early 1970s because they could be substituted for conventional groundwood pulps in newsprint blends to give a stronger paper.

Chemithermomechanical pulping (CTMP) increases the strength properties of TMP pulps even further by a mild pretreatment with sodium sulfite. CTMP pulps are obtained by a comparatively mild chemical treatment followed by pressurized refining. In general, CTMP pulps have a greater long fiber fraction and lower fines fraction than comparable TMP pulps. CTMP is suitable for the middle layer of multi-ply boards where it adds bulk and rigidity (stiffness) at lower cost than kraft pulp.

6.1.3 CHEMICAL PULPS

There are several chemical pulping methods, each of which are based, either directly or indirectly, on the use of sodium hydroxide. The primary goal of chemical pulping is to selectively remove as much lignin as possible, especially from the middle lamella, without degrading the carbohydrate components and negatively effecting pulp properties. Therefore, the nature of the pulping chemicals influences the properties of the residual lignin and the residual carbohydrates, and the selectivity of delignification is determined by the weight ratio of lignin removal to carbohydrate removal. The pulp and paper industry uses the "kappa number" to express the lignin content of a pulp, a high kappa number indicating a high lignin content. The kappa number of bleachable softwood and hardwood pulps is 30–40 and 18–20, respectively (Kadla and Dai, 2006). For the production of chemical pulps, the bark is removed and the logs are passed through a chipper. The chipped wood is charged into a digester with the cooking chemicals, and the digestion carried out under pressure at the required temperature.

6.1.3.1 Alkaline Processes

6.1.3.1.1 Soda Process

The first process for the manufacture of chemical wood pulp was invented by Englishmen Hugh Burgess and Charles Watt in 1851 and was patented in 1854. The first successful soda mill commenced operation in 1866. The soda process consisted of boiling wood in 4%–6% sodium hydroxide liquor at a high temperature (170°C). A later patent in 1865 covered the incineration of the spent soda liquor to recover most of the alkali used in the process (Smook, 2002). Less than 2% of the pulp produced today uses this process which is very similar to the sulfate process, except that only sodium hydroxide is used. Essentially all former soda mills have converted to the sulfate process.

6.1.3.1.2 Sulfate (Kraft) Process

In 1879, German chemist Carl F. Dahl developed the sulfate method of pulping wood. The process was essentially a modification of the soda process, but instead of sodium hydroxide, sodium sulfate was the major chemical used as the cooking liquor. The new sulfate process produced a much stronger pulp which is more commonly known as *kraft* pulp after the German and Swedish word for strength. Although Dahl commenced construction of a kraft mill in his native Germany, it was never completed due to lack of finance (Ainsworth, 1959). He moved to Sweden and the first kraft mill was built in Munksjö, Sweden in 1885. The location of the first kraft mill in the United States is disputed; one author (Smook, 2002) claims it was built in 1911 in Pensacola, Florida, while another (Ainsworth, 1959) states that the Halifax Paper Company in Roanoke Rapids, North Carolina made the first kraft pulp.

Today, the sulfate process is the dominant chemical wood pulping process and uses an aqueous solution of sodium sulfide (Na_2S) and sodium hydroxide known as "white liquor" for cooking the chips. It takes its name from the fact that sodium sulfate (or bisulfate) was used as the make-up chemical in the recovery process, with sodium sulfate being reduced to sodium sulfide in the recovery furnace by reaction with carbon. The sulfate process has the ability to pulp any wood species, particularly pines, which are more resinous than firs and spruces and not easily pulped by the acid sulfite process.

Pulp produced by this process is stronger than that produced from the same wood by the acid sulfite process, and the use of sulfate pulps in liner board has enabled the replacement of wooden cases by corrugated cartons. The sulfate and acid sulfite processes together account for over 90% of the chemical wood pulp currently produced in the world.

6.1.3.2 Sulfite Processes

The invention of this process is generally credited to the American chemist Benjamin Chew Tilghman who, in 1857, found that wood could be softened and defibered with a solution of calcium bisulfite ($Ca(HSO_3)_2$) and sulfurous acid. Swedish chemist Carl Daniel Ekman treated wood with magnesium bisulfite in 1870 and constructed the first sulfite paper mill in 1872 in Bergvik, Sweden. A German modification of the American sulfite process was developed by the German chemist Dr Alexander Mitscherlich and involved cooking (using indirect steam heating) at lower temperatures and pressures and for longer times than previously. This was the dominant pulping process until 1937 when kraft pulping became the foremost chemical pulping process.

Several pulping processes are based on the use of sulfur dioxide as the essential component of the pulping liquor. Sulfur dioxide dissolves in water to form sulfurous acid, and a part of the acid is neutralized by a base during preparation of the pulping liquor. The various sulfite processes differ in the kind of base used and in the amount of base added. These differences govern the resulting acidity or pH of the liquor. These processes depend on the ability of sulfite solutions to render lignin partially soluble.

For certain applications, sulfite pulps are still preferred and remain an important commodity, especially for specialty papers (e.g., glassine) and as a source of cellulose for non-paper applications. Sulfite pulps have higher brightness, higher yields at a given kappa, lower odor and lower investment costs as compared to kraft pulps (Kadla and Dai, 2006). A special grade of bleached sulfite pulp is known as “dissolving pulp” and is used for a variety of cellulose derivatives including RCF and cellulose acetate.

6.1.4 SEMICHEMICAL PULPS

Semichemical pulping combines chemical and mechanical methods in which wood chips are partially softened or digested with conventional chemicals, such as sodium hydroxide, sodium carbonate or sodium sulfate, after which the remainder of the pulping action is supplied mechanically, most often in disk refiners.

The object of this process is to produce as high a yield as possible commensurate with the best possible strength and cleanliness. The hemicelluloses, mostly lost in conventional chemical digestion processes, are retained to a greater degree and result in an improvement in potential strength development. Although less flexible, semichemical pulps resemble chemical pulps more than mechanical pulps.

The *neutral-sulfite semichemical* (NSSC) process (applied mainly to hardwood chips) uses sodium sulfite and a small amount of sodium hydroxide or sodium carbonate to give a slightly alkaline liquor. The NSSC pulp is obtained in higher yield but with higher lignin content than in the other sulfite processes. It is used mainly for the manufacture of corrugating medium.

6.1.5 DIGESTION

The digestion process essentially consists of treating wood in chip form in a pressurized vessel under controlled conditions of time, liquor concentration and pressure/temperature. The main objectives of digestion are as follows:

1. To produce a well-cooked pulp, free from the noncellulosic portions of the wood (i.e., ligninand to a certain extent hemicelluloses)
2. To achieve a maximum yield of raw material (i.e., pulp from wood) commensurate with pulp quality
3. To ensure a constant supply of pulp of the correct quality

Currently, most pulping processes are continuous, and to give an indication of the processing conditions encountered, the widely used Kamyr continuous digester is now briefly described. After steaming at low pressure, during which time turpentine and gases are vented to the condenser, the chips are brought to the digester pressure of 1000 kPa. They are picked up in a stream of pulping solution and their temperature is raised to 170°C over 1.5 h. After holding at this temperature for a further 1.5 h, the digestion process is essentially complete.

After digestion, the liquor containing the soluble residue from the cook is washed out of the pulp, which is then screened to remove knots and fiber bundles that have not fully disintegrated. The pulp is then sent to the bleach plant or paper mill.

6.1.6 BLEACHING

Bleaching is a chemical process applied to chemical and mechanical pulps, primarily to increase their brightness but it also improves the cleanliness of pulp through removing extractives and other contaminants. Pulps vary considerably in their color after pulping, depending on the wood species, method of processing and extraneous components. The whiteness of pulp is measured by its ability to reflect monochromatic light in comparison to a known standard (usually magnesium oxide). Brightness is an index of whiteness, measured as the reflectivity of a paper sample using light at 457 nm. Unbleached pulps exhibit a range of brightness values from 15 to 60. Cellulose and hemicellulose are inherently white and do not contribute to color; it is the chromophoric groups on the lignin that are largely responsible for the color of the pulp.

Basically, there are two types of bleaching operations: Those that chemically modify the chromophoric groups by oxidation or reduction but remove very little lignin or other substances from the fibers, and those that complete the delignification process and remove some carbohydrate material. To fully remove lignin from pulp, multiple bleaching stages are required. In a typical bleaching process, individual bleaching stages are generally separated by washing stages to remove residual chemicals and degraded lignin.

Chemical methods must be used to improve the color and appearance of the pulp; these are bleaching treatments and involve both the oxidation of colored bodies and the removal of residual encrusting materials (the principal one being lignin) remaining from the digestion and washing stages. Since bleaching reduces the strength of the pulp, it is necessary to reach a compromise between the brightness of the finished sheet and its tensile properties.

In 1986, the production process for bleached chemical pulp was identified as a major contributor of polychlorinated dioxins and dibenzofurans to the environment. Because these compounds are powerful toxins and carcinogens (see Section 22.5.1 for further discussion), considerable investigative activity was carried out in Europe and North America to identify point sources and corrective measures (Smook, 2002). Chlorine bleaching was identified as the major source of these compounds. In addition to dioxins and furans, a host of other chlorinated organic compounds (known collectively as *adsorbable organic halides* or AOX) are formed during chlorine bleaching. Strict regulations now limit the production of these chlorinated compounds, resulting in a move away from molecular chlorine bleaching to chlorine dioxide (so-called ECF or elemental chlorine free bleaching) and to oxygen and peroxide (so-called TCF or total chlorine free bleaching). These changes have been introduced to enable pulp and paper mills to meet tough new antipollution laws and regulations, and to conserve wood, chemicals and energy (Bajpai, 2010).

6.1.6.1 Mechanical Pulps

Lignin is the main contributor to the color of mechanical pulps. An increase in the brightness of mechanical pulps is achieved by modifying the lignin structures (chromophores) in the pulp furnish. The process is sometimes referred to as brightening to distinguish it from lignin-removing bleaching methods for chemical pulps (Ni and Liu, 2002).The most effective bleaching agent for most groundwoods is hydrogen peroxide, and since the bleaching is performed in alkaline solutions, sodium peroxide is also used. The reaction typically requires 3 h at 40°C and is followed by neutralization and destruction of excess peroxide with SO_2.These pulps may be improved in color to only a limited extent since they contain virtually all the lignin from the original wood. Peroxide bleaching allows brightness to be increased by nearly 20%.

6.1.6.2 Chemical Pulps

The residual lignin content in chemical pulp accounts for 2%–5% of the mass and is responsible for the dark color of the unbleached pulp. The reagents for full bleaching of chemical pulp are mostly oxidative and since the carbohydrates are also susceptible to oxidation, bleaching must be accomplished under the mildest conditions. Bleaching of chemical pulps is basically stepwise purification of colloidal cellulose, and bleaching can therefore be regarded as a continuation of the cooking process. The bleaching of pulp is done through chemical reactions of bleaching agents with lignin and coloring matter in the pulp. The bleaching is performed in a number of stages utilizing one or more of the following: chlorine dioxide, oxygen, ozone and peroxide. Between these stages, the pulp is treated with alkali to dissolve degradation products. Full details of these processes are given elsewhere (Dence and Reeve, 1996; Ni and Liu, 2002).

6.1.6.3 Recycled Pulps

Recycled or secondary fibers are an important raw material in terms of volume and utilization for the paper industry in many countries, due to market pressures resulting from government legislation, increasing public awareness of issues like sustainability and a dwindling supply of virgin fibers in some regions. The recycling of paper is an example of the sustainable use of resources, and although recycling is generally both economically and ecologically sound, recovered paper cannot be used in all paper grades. The quality and brightness of the recycled fiber furnish will dictate its end use. The removal of colored complexes such as dyes and other unwanted materials (i.e., ink and stickies) is an important operation to produce a recycled pulp with good properties. Generally, the conditions used for bleaching/brightening of recycled fibers are similar to those used for mechanical and chemical pulps.

6.2 PAPER

Stock preparation is the interface between the pulp mill and the papermaking process in which pulp is treated mechanically and, in some instances, chemically by the use of additives and is thus made ready for forming into a sheet or board on the paper machine. During the stock preparation steps, the pulps are most conveniently handled as aqueous slurries. However, in the papermaking process utilizing purchased pulps and waste paper which are received as dry sheets, the first step is the separation of all the fibers from one another, and their dispersion in water with a minimum of mechanical work to avoid altering the fiber properties. This process is known as slushing or repulping and is carried out in a machine such as the hydrapulper (see Figure 6.2), so-called because of the hydraulic forces that are developed. When the pulping and papermaking operations are adjacent to one another, pulps are usually delivered to the paper mill in slush form directly from the pulping operation.

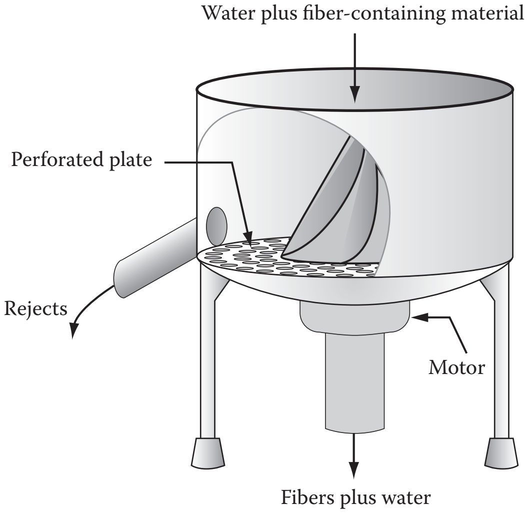

FIGURE 6.2 Batch hydrapulper.

6.2.1 BEATING AND REFINING

Stock—as fibrous material is commonly called—is prepared by two chief processes commonly referred to as *beating* and *refining*. Both operations are fundamentally the same; in many situations, the two terms are used synonymously. Beating and refining are used to improve the strength and other physical properties of the finished sheet, and to influence the behavior of the system during the sheet-forming and drying steps (Hubbe, 2005).

The object of beating is to increase the surface area of the fibers by assisting them to imbibe water. As a result, additional bonding opportunities are provided for between cellulose molecules of neighboring fibers. The beating also makes the fibers more flexible, causing them to become relatively mobile and to deform plastically on the paper machine. The mixture of pulp (known as the *furnish*) is passed into the beater and brought to a consistency of 5%–7%. The fibers are then beaten while suspended in the water in order to impart to them many of the properties that will determine the character of the final product.

The quality and characteristics of the finished paper depend to a great extent on the treatment in the beater. Because papermaking fibers are stiff and springy, the resulting paper would be flabby and weak if made into a sheet of paper without beating. There would be little adhesion between the fibers and they could not be consolidated under the presses of the paper machine. A sheet formed from an unbeaten pulp has a low density, and is rather soft and weak, whereas if the same pulp is beaten, then the resultant paper is much more dense, hard and strong. If taken to the extreme, beating produces very dense, translucent, glassine-type sheets (Hubbe, 2005). Thus, beating can be controlled to produce paper types as widely different as blotting and greaseproof paper.

Since its invention in Holland around 1690, the principle of the batch-operated hollander beater has remained substantially the same. It consists of a cylindrical roll containing rectangular, blunt-tipped blades (bars) that revolves over a stationary bedplate which also contains a set of bars. Circulating stock passes between the roll and the bedplate; the severity of beating is controlled by adjusting the load of one against the other. Circulation is continued until the pulp is considered ready to be made into the desired paper. In many paper mills, beaters have been replaced by continuous refiners, such as disk refiners (where rotary disks rotate against a working surface) and conical refiners. However, the batch beater is a convenient vessel for adding chemicals and mixing them intimately with the pulp in order to give special properties to the final paper.

In papermaking, chemicals such as strength additives, adhesives, mineral fillers and sizing agents may be added at the beater stage prior to sheet formation (i.e., internal addition), or to the resulting sheet after complete or partial drying, depending primarily on the desired effects. Strength additives are usually added internally if uniform strength throughout the sheet is desired, but they are applied to the surface if increased surface strength is needed. Fillers can improve brightness, opacity, softness, smoothness and ink receptivity, and are essentially insoluble in water under the conditions of use. Because filler particles are much smaller than the fibers used in papermaking, often ~0.5 to 3 mm in diameter, they usually contribute to a smoother product. Fillers also tend to increase the efficiency with which light is scattered by paper, yielding increases in the paper's opacity and brightness (Hubbe, 2005). Calcium carbonate is the most important papermaking filler followed by kaolin clay, with limited use of titanium dioxide. The main drawback is that the materials added may be lost through the wire of the paper machine in the large amount of water used. Therefore, if an additive cannot be retained efficiently from dilute pulp slurry, then it is better to apply it to the surface of the sheet (Dulany et al., 2011).

Sizing is the process of adding materials to the paper in order to render the sheet more resistant to penetration by liquids, particularly water. Rosin is the most widely used sizing agent, but starches, glues, caseins, synthetic resins and cellulose derivatives are also used (Dulany et al., 2011). The sizing agents may be added directly to the stock as beater additives to produce internal or engine sizing. Alternatively, the dry sheet may be passed through a size solution to produce a surface size (see Section 6.1.3.2).

The required wet strength (up to 50% of the dry paper strength can be retained) is obtained with the aid of wet-strength additives that are capable of covalently bonding in order to preserve paper strength in the presence of water. Linerboard, carrierboard, bleached carton and liquid paperboard are some of the principal grades that require an amount of wet strength to be functional. There are two theories regarding the mechanism of wet strength (Auhorn, 2006). The first states that the wet strength effect is due, at least in part, to a reaction between the resin and the cellulose, which leads to the formation of ether bonds. The second theory assumes that the wet strength additives cross-link on exposure to heat in the dryer section to form a 3D network, wrap themselves around the points where the fibers intersect and thus protect the points of intersection from water penetration and swelling.

The most widely used class of such additives is the polyamidoamine-epichlorohydrin (PAAE) resins which were first introduced in the late 1950s. During the formation of a PAAE resin, the epichlorohydrin can be hydrolyzed to produce 3-monochloropropane-1, 2-diol (3-MCPD) which is not an approved food additive or GRAS. Although 3-MCPD has not been proven carcinogenic to humans, there is sufficient human health concern that threshold levels have been established. Pace and Hartman (2010) detected 3-MCPD at up to 9.87 mg kg^{-1} (ppm) in polyethylene-coated bleached paperboard and showed that it does not migrate through the polyethylene food contact surface into an aqueous/acidic food simulant. They also demonstrated that no significant amount of 3-MCPD migrated from the unskived seam edges on the food contact side of the paperboard structure.

Braga et al. (2009) gave the history and current status of regulations in Germany with respect to chlorinated monomers like DCP (dichloropropanol) and MCPD from wet-strength additives. They are associated with AOX emissions in the effluent from paper mills. Today's products (3rd generation) offer DCP contents in the ppm range compared to values of up to 1% in 1st generation products. As a result, papermakers now have a choice of products meeting all environmental regulations.

6.2.2 PAPERMAKING

6.2.2.1 Fourdrinier Machine

The principle of operation of the modern paper machine differs little from that of the first Fourdrinier machine of 1804, named after its financiers Henry and Sealy Fourdrinier, two prosperous London stationers who purchased the patent interests of the Frenchman Didot Frères. He had obtained the patent rights from a clerk (one Louis Robert) at his mill who had built a paper machine in 1799. On behalf of the Fourdrinier brothers, Englishman John Gamble commissioned the engineering firm of Hall to build a prototype. The task was assigned to one of Hall's apprentices, Bryan Donkin (who was also involved in the development of the tinplate can [see Chapter 7]). The Fourdrinier brothers spent the whole of their private fortune in developing a practical paper machine, eventually becoming bankrupt and dying in poverty. Despite their misfortune, their name has been familiar to generations of papermakers for the development of a machine, the essential principles of which are still in use today.

Paper is made by depositing a very dilute suspension of fibers from a very low consistency aqueous suspension (greater than 99% water) on to a relatively fine woven screen, over 95% of the water being removed by drainage through the wire. The fibers interlace in a generally random manner as they are deposited on the wire and become part of the filter medium.

Although paper is the general term for a wide range of matted or felted webs of vegetable fiber that have been formed on a screen from a water suspension, it is usually subdivided into paper and paperboard. However, there is no rigid line of demarcation between the two, with structures <300 μm thick being considered paper regardless of the grammage or weight per unit area. Paper is generally termed paperboard when its basis weight (grammage) exceeds 250 g m^{-2} (i.e., grams per square meter or gsm), but there are exceptions (see Section 6.3).

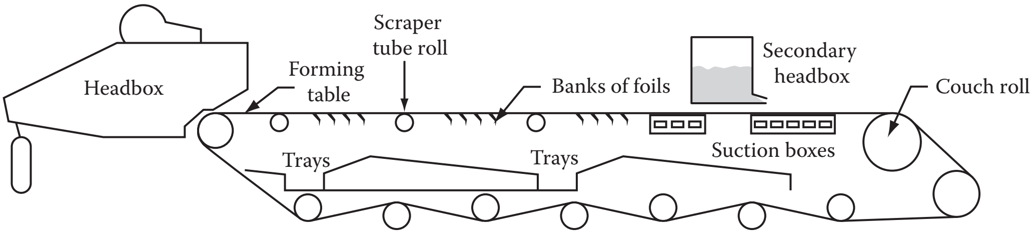

FIGURE 6.3 Fourdrinier machine. (Redrawn from Paper, in: *The Wiley Encyclopedia of Packaging Technology*, 3rd edn., Yam, K.L. (Ed.), John Wiley & Sons, New York, pp. 908–912, 2009. Reproduced with permission.)

The modern Fourdrinier paper machine consists essentially of an endless woven wire gauze or forming fabric stretched over rollers. The forming section of a Fourdrinier machine (illustrated in Figure 6.3) is made up of two essential parts: the flow box and the drainage table. The operation of both parts can influence the structure of the resulting paperboard web (Attwood, 2009). The concentration of the fiber suspension delivered to the moving screen is generally 0.4%–1.2% and increases as a result of free drainage through the screen. The relative speeds of the stock and wire affect the degree to which the fibers are aligned along the direction of travel. The concentration increases between 3% and 4% further down the Fourdrinier table where a vacuum is applied in the suction boxes. For the production of multi-ply paperboard, a secondary flow box is often used. Fourdrinier machines are standard in the industry and are used to produce all grades of paper and paperboard.

6.2.2.2 Cylinder Machine

A second system was developed in 1809 by John Dickinson of England and is known as the cylinder or vat machine process. A cylinder covered with a wire cloth is rotated partially submerged in a stock suspension. Because of a vacuum applied inside the cylinder, water drains inward through the wire cloth, and the paper web is formed on the outside. The web is picked up by a felt, which is pressed onto the top of the cylinder by a rubber roll. A series of vats provide individual plies of fiber which are subsequently matted together. Cylinder machines are used to produce heavy multi-ply boards. They produce a sheet that is much stronger in the direction of flow than that produced on Fourdrinier machines.

Cylinder-vat formation differs basically from Fourdrinier formation because the cylinder picks up individual fibers from the stock suspension, in contrast to the Fourdrinier wire on which fibers are deposited from an inflowing stock suspension where water is immediately removed by draining.

The advantage of the cylinder machine for the manufacture of boards is that a number of cylinder units can be arranged so that the fiber mat from each is deposited as a layer and all the layers can be combined to make a multi-ply paperboard.

6.2.2.3 Twin-Wire Formers

The twin-wire method for forming paper and paperboard was developed in the United Kingdom in the 1950s. The paper web is formed between two converging forming screens by means of a flow box and the water is drained from the slurry by pressure and later by vacuum. A typical twin-wire forming unit is the Inverform (shown in Figure 6.4), which was designed to provide a new method for the manufacture of single and multi-ply sheets at high speeds. Successive layers of fiber are laid down sequentially on the felt, with water being removed upwardly, overcoming the difficulty experienced in the conventional downward removal of water through several layers of board at high speed.

Twin-wire formers have replaced the Fourdrinier wet ends on many machines, particularly for lightweight sheets, corrugated media and linerboard grades.

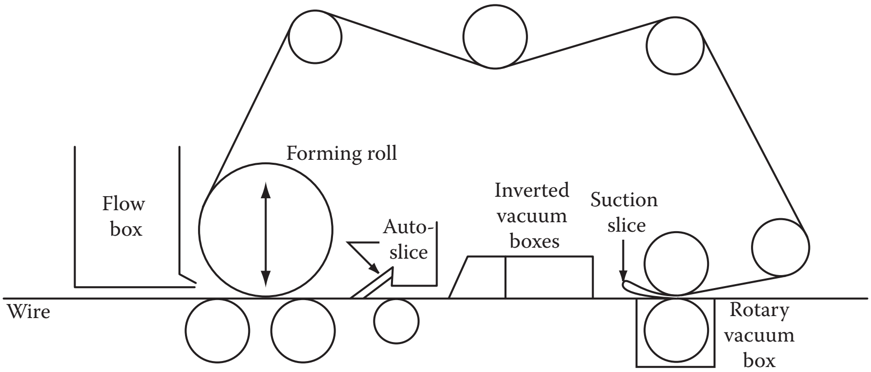

FIGURE 6.4 Inverform twin-wire forming unit. (Redrawn from Paper, in: *The Wiley Encyclopedia of Packaging Technology*, 3rd edn., Yam, K.L. (Ed.), John Wiley & Sons, New York, pp. 908–912, 2009. Reproduced with permission.)

6.2.2.4 Presses and Dryers

After leaving the forming fabric of the papermaking machine, the sheet (which has a moisture content of 75%–90% depending on type) passes to the press and dryer sections for further water removal. Rotary presses (which may have solid or perforated rollers, often with internal suction) receive the sheets on continuous felts, which act as conveyers and porous receptors of water. On leaving the press, the moisture content is typically 60%–70%, again depending on type.

The paper is then passed through a series of steam-heated rollers and dried to a final moisture content between 4% and 10%. Other types of dryers are used for special products or situations. For example, the Yankee dryer is a large, steam-heated cylinder, which dries the sheet from one side only, and is used extensively for tissues and to produce *machine glazed* (MG) papers, the latter having a glazed or shiny surface from intimate contact with the polished dryer surface.

6.2.3 CONVERTING

Almost all paper is converted by undergoing further treatment after manufacture, such as embossing, impregnating, saturating, laminating and the forming of special shapes and sizes such as bags and boxes. Further surface treatment involving the application of adhesives, functional products and pigments are common, depending on the end use of the paper. The incorporation of strength additives, adhesives, fillers and sizing agents throughout the whole paper was briefly described in Section 6.2.1. Surface treatment applies similar materials on the web.

Because of the widespread use of paper and paperboard in direct contact with foods, most mills use paper chemicals that have been cleared for use with food by regulatory authorities such as the U.S. Food and Drug Administration (FDA).

6.2.3.1 Calendering

In many applications, the surface of the sheet needs improvement so that any characters imposed on the sheet are legible. This is achieved by calendering, a process that reorients the surface fibers in the base sheet of paper (or the coating applied to the surface) through the use of pressure. This serves to smooth the surface, control surface texture and develop a glossy finish. Such papers are known as *machine finished* (MF).

Supercalendering, as well as smoothing the surface of the sheet by pressure, also alters the optical reflectance of the sheet by friction, giving a higher finish than that obtained on calenders. As the paper passes between steel or fiber rollers under great pressure, moisture is added. Only the bottom roller is powered; the others provide a certain amount of slippage which irons the sheet.

The slipping action of the sheet against the polished steel rollers results in a gloss while smoothing and leveling the surface contours.

6.2.3.2 Sizing

Surface treatments such as sizing and coating are extensively applied to improve the appearance of products. Paper may be coated either on equipment that is an integral part of the paper machine (i.e., on-machine coating) or on separate converting equipment. The most common method for the application of chemicals to the surface of a paper web is with a size press, where dry paper is passed through a flooded nip and a solution or dispersion of the functional chemical contacts both sides of the paper. Excess liquid is then squeezed out in the press and the paper is redried (Dulany et al., 2011).

Surface-sizing agents prevent excess water penetration and improve the strength of the paper. The sizing agent penetrates far enough into the paper to increase the fiber bonding and the dependent properties such as bursting, tensile and folding strengths (Rhim, 2010). An additional effect is an improvement in the scuffing resistance of the paper surface.

The most commonly used materials for surface sizing are starches, usually chemically modified (e.g., oxidized starches, cationic starches and hydroxyethylated derivatives). They are used not only for sizing, but also to improve strength, especially surface strength, and to impart smoothness. Other film-forming materials which can be used for surface sizing include carboxymethyl cellulose (CMC) and poly(vinyl alcohol) (PVOH) which provide oil and grease repellent coatings, improve paper strength and decrease paper porosity. Other polymeric sizing agents such as polyurethanes and styrene-maleic anhydride copolymers (SMAs) are used as surface-sizing and strength-enhancing agents, but their cost is relatively high compared with other sizing agents (Dulany et al., 2011).

6.2.3.3 Barrier Coatings

Paper and paperboard are poor barriers to gases and water vapor. For example, a sized commercial kraft (54% pine and 46% eucalyptus) linerboard of 200 gsm has a water vapor transmission rate (WVTR) at low humidity (50% RH/23°C) of 426 g m^{-2} day^{-1} (Kugge and Johnson, 2008). Therefore, in many packaging applications, a barrier may be needed against water vapor or gases such as O_2. A water barrier can be formed by changing the wettability of the paper surface with sizing agents. Coating the paper with a continuous film of a suitable material will confer gas or vapor barrier properties.

Paraffin wax is low in cost, resists water vapor and is free of color, odor, taste or toxicity. It is applied by passing the paper through a molten bath or nip, removing the excess paraffin and cooling rapidly on a chill roll so that the wax forms a glossy surface. Modifiers, for example, microcrystalline wax, LDPE or EVA copolymer can improve the durability and film strength, raise the softening point and increase the gloss and heat seal strength of the coating (Hubbe, 2005). The main disadvantage with wax coatings is the difficulties associated with recycling of the paperboard, because the wax must be separated from the fibers so that they can be repulped. Wax has been largely replaced by LDPE applied by extrusion coating which results in a more durable and flexible coating that can be heat sealed to itself and is easily removed in a hydrapulper (see Section 5.3.2).

In theory, there is no reason why any thermoplastic which is normally processed by extrusion techniques cannot be coated onto paperboard. In practice, most extrusion coating technology that has been developed utilizes LDPE, although PP, PAs and PET are also used. For example, PET-coated paperboard is used in dual ovenable trays, where a 38 µm PET coating is put on 500–625 µm boardstock.

An increase in the water resistance of paperboard by coating it with PLA was reported by Rhim et al. (2007). When the coating thickness was varied from 4.7 to 42.7 µm, the water vapor permeability measured at 25°C/50% RH decreased from 4.8 to 25.5 times, while the water absorptiveness measured at 20°C decreased from 11.9 to 17.9 times. An optimum concentration of coating solution for improving water resistance of paperboard was 3 w/v% which gave a coating thickness of 28 µm equivalent to 49.5 gsm. The moisture barrier and heat sealability properties of PLA extrusion coated paperboard (20 gsm) were reported by Lahtinen et al. (2009) who also presented a simple equation enabling calculation of the WVTR as a function of PLA coating weight at 23°C, 30°C and 38°C and 50%–90% RH.

Andersson (2008) and Aulin and Lindstrom (2011) reviewed recent developments of functional materials to improve the barrier properties of paperboard with particular emphasis on biobased polymers including starch and cellulose derivatives, chitosan, alginate, wheat gluten, whey proteins, polycaprolactone, PLA and polyhydroxyalkanoates. Their processability, convertibility, recyclability and biodegradability were discussed with a focus on novel application techniques. Khwaldia et al. (2010) reviewed the barrier, mechanical and other properties of biopolymer-coated paper and discussed existing and potential applications for bioactive coatings on paper packaging materials. These biopolymer coatings may retard unwanted moisture transfer in food products, are good O_2 and oil barriers, are biodegradable and, in their view, have potential to replace current petrochemical-based coatings. Han et al. (2010) reported on the use of two types of bilayer coating systems on paperboard (bees wax and either whey protein isolate (WPI)/cellulose film or poly(vinyl butyral) (PVB)/zein). The BW-PVB/zein bilayer system was more efficient than the BW-WPI/cellulose film bilayer system, with a strong reduction in WVTR of 95% as compared to uncoated paperboard. The WVTR of the BW-PVB/zein bilayer approached the desired industrial requirement for paperboard-based food containers of 10 g m^{-2} day^{-1}.

Perfluorochemicals and fluorochemicals are used in paper coatings for oil and moisture resistance in microwave popcorn bags, and fast-food paper packaging for muffin and french-fry bags, sandwich/burger wrappers and small pizza and burger boxes (Begley et al., 2008). The perfluorocarbon moiety in these classes of products has the effect of lowering the surface energy of the individual paper fibers which greatly contributes to the holdout of low surface energy liquids such as greases and oils. Begley et al. (2008) reported that fluorochemical paper additives migrate to food during actual package use. For example, microwave popcorn contained 3.2 mg fluorochemical kg^{-1} popcorn after popping. Residual perfluorooctanoic acid (PFOA) concentrations in the paper coatings result from reactions of starting materials, while fluorotelomer alcohols are actual starting ingredients in some formulations such as DuPont's Zonyl® RP used to produce the fluorochemical paper additive. The human body breaks down fluorotelomers into PFOA that accumulates in the human body.

A major shift in industrial fluorochemical production occurred in 2000, when 3M, the major manufacturer of perfluorochemicals, began phasing out its PFOA materials.

In 2007, DuPont announced that it had successfully commercialized a new, patented manufacturing process (termed LX platform) to remove greater than 97% of trace levels of PFOA, its homologues and direct precursors from its fluorotelomer products. DuPont also announced its commitment to eliminate the need to make, buy or use PFOA by 2015. Trier et al. (2011) have given a very informative update on polyfluorinated surfactants used to coat paper and board for food packaging, including analytical names, trade names, uses, suppliers and structures.

Recently, Jinkarn et al. (2012) showed that sulfur hexafluoride (SF_6) plasma treatment of paperboard surfaces can improve water resistance properties significantly, beginning with only a 2 s treatment time; oil resistance properties can be improved with a longer treatment time. Plasma treatment had no effect on tensile strength of treated paperboard; however, machine direction (MD) compression strength, as well as MD and cross direction (CD) folding endurance of treated paperboard was significantly lower than that for an untreated sample. The WVTR and OTR of treated paperboard were higher with increasing treatment time, because of etching of cellulose fibers caused by fluorine atoms and electron bombardment.

Barrier properties can be enhanced by incorporation of nano-sized materials in the coating. Nanocomposites are particle-filled polymers for which at least one dimension of the dispersed particles is in the nanometer range. Extrusion coating was used to obtain MMT/LDPE-coated paperboard (Krook et al., 2005). The WVTR measured at 23°C/100% RH was essentially independent of clay content and close to that of LDPE. The powerful melt mixing in the extrusion coating process triggered the separation of the clay stacks into small, evenly distributed entities. It also seemed that the same process yielded voids and pinholes that negatively affected the barrier properties.

A nano-structured copolymerized coating using high shape factor engineered (HSFE) clays that reduced permeation via a tortuous path was developed by Pal et al. (2008) for solid bleached sulfate (SBS) paperboard. The WVTR of the copolymerized acrylic coatings (2-ethylhexyl acrylate and methyl methacrylate) were reduced up to five times compared to the untreated baseboard with coating weights up to 20 gsm. The effects of pigment shape, baseboard, coat weight, calendering, RH and temperature on barrier properties were studied. The board samples showed almost zero gas permeability and a significant reduction of up to 90% in WVTR.

The use of micro-fibrillated cellulose (MFC) as a surface layer on base paper to significantly increase the strength of paper sheets and reduce their gas permeability dramatically was discussed in Section 3.3.5.2.3 Hult et al. (2010) deposited MFC and shellac on fiber-based substrates using a bar coater or a spray coating technique. The OTR decreased by several logarithmic units and the WVTR reached values considered as high barrier in food packaging (6.5 g m^{-2} day^{-1}). It was suggested that the utilization of a combined MFC and shellac coating on paper could be a viable alternative in the search for sustainable packaging. A pilot plant to produce MFC-coated liquid paperboard commenced production in Finland in 2012.

An alternative to extrusion coating is dispersion coating which has several advantages, including higher machine speeds and fewer processing stops than in the case of extrusion coating. Barrier dispersion coatings are typically compostable, less expensive and easier to apply.

An exciting new technique is atomic layer deposition (ALD) which was discussed in Chapter 5 Section 5.5.3. Hirvikorpi et al. (2010) studied the influence of corona pretreatment on the O_2 and water vapor barrier performance of polymer-coated paperboards additionally coated at 100°C with Al_2O_3 and SiO_2 by ALD. The effect of corona pre-treatment was negligible or even negative on the water vapor barrier, especially with the PLA-coated board.

6.2.3.4 Pigments

Though functionally and chemically similar, fillers and pigments are distinguished from one another in that fillers are added at the wet end of the paper machine and serve to fill the sheet; pigments are added at the size press and serve to alter the surface of the sheet.

Pigments comprise 70%–90% of the dry solids in paper coatings and are generally designed to mask or change the appearance of the base stock, improve opacity, impart a smooth and receptive surface for printing or provide special properties for particular purposes. The primary function of the adhesive in pigment coating is to bind the pigment particles together and to the raw stock. The type and proportion of the adhesive controls many of the characteristics of the finished paper such as surface strength, gloss, brightness, opacity, smoothness, ink receptivity and firmness of the surface. The strength must be sufficient to prevent the coating from being picked up by tacky printing inks (Hubbe, 2005).

The pigments which are used in paper coatings are similar to the materials that are used for paper, with kaolin clay being the largest-volume pigment for this application, followed by calcium carbonate. Plastic pigments based on PS are used in combination with mineral pigments to improve the gloss of coated papers (Dulany et al., 2011).

6.2.4 PHYSICAL PROPERTIES

Most properties of paper depend on direction. Paper has a definite grain caused by the greater orientation of fibers in the direction of travel of the paper machine, and the greater strength orientation that results partly from the greater fiber alignment and partly from the greater tension exerted on the paper in this direction during drying. The grain direction is known as the *machine direction* (MD), while the *cross direction* (CD) is the direction of the paper at right angles to the

MD. The grain of paper must be taken into account in measuring all physical properties. Most of the physical properties of paper depend on direction, that is, the MD, CD and thickness direction (*z*-direction) and these must be clearly indicated when reporting test results (Hubbe, 2005). An excellent review on the physics of paper was made by Alava and Niskanen (2006).

Papers vary in MD:CD strength ratios, with cylinder machine papers having a higher ratio than Fourdrinier papers, the latter values varying from about 1.5 to 2.5 (Hubbe, 2005). Usually, there is less variation in paper properties in the MD than in the CD because variations occur slowly in the MD, whereas in the CD they may occur quite suddenly for a variety of process-related reasons. In addition, the CD strength normally varies depending on how far the sample was taken from the edge of the sheet. In general, papers should be used to take greatest advantage of the grain of the paper.

6.2.5 Types of Paper

Paper is divided into two broad categories: (1) fine papers, generally made of bleached pulp, and typically used for writing paper, bond, ledger, book and cover papers, and (2) coarse papers, generally made of unbleached kraft softwood pulps and used for packaging.

6.2.5.1 Kraft Paper

Kraft paper is typically coarse with exceptional strength, often made on a Fourdrinier machine and then either machine-glazed on a Yankee dryer or machine-finished on a calender. It is sometimes made with no calendering so that when it is converted into bags, the rough surface will prevent them from sliding over one another when stacked on pallets.

6.2.5.2 Bleached Paper

Bleached paper is manufactured from pulps which are relatively white, bright and soft and receptive to the special chemicals necessary to develop many functional properties. It is generally more expensive and weaker than unbleached paper. Its aesthetic appeal is frequently augmented by clay coating on one or both sides.

6.2.5.3 Greaseproof Paper

Greaseproof paper is a translucent, machine-finished paper which has been hydrated to give oil and grease resistance. Prolonged beating or mechanical refining is used to fibrillate and break the cellulose fibers which absorb so much water that they become superficially gelatinized and sticky. This physical phenomenon is called hydration and results in consolidation of the web in the paper machine with many of the interstitial spaces filled in.

The satisfactory performance of greaseproof papers depends on the extent to which the pores have been closed. Provided that there are few interconnecting pores between the fibers, the passage of liquids is difficult. However, they are not strictly “greaseproof” because oils and fats will penetrate them after a certain interval of time. Despite this, they are often used for packaging butter and similar fatty foods since they resist the penetration of fat for a reasonable period.

6.2.5.4 Glassine Paper

Glassine paper derives its name from its glassy, smooth surface, high density and transparency. It is produced by further treating greaseproof paper in a supercalender where is it carefully dampened with water and run through a battery of steam-heated rollers. This results in such intimate interfiber hydrogen bonding that the refractive index of the glassine paper approaches the 1.02 value of amorphous cellulose, indicating that very few pores or other fiber/air interfaces exist for scattering light or allowing liquid penetration (Paper, 2009). The transparency can vary widely depending on the degree of hydration of the pulp and the basis weight of the paper. The addition of titanium dioxide makes the paper opaque, and it is frequently plasticized to increase its toughness.

6.2.5.5 Vegetable Parchment

Vegetable parchment takes its name from its physical similarity to animal parchment (vellum) which is made from animal skins. The process for producing parchment paper was developed in the 1850s, and involves passing a web of high quality, unsized chemical pulp through a bath of concentrated sulfuric acid. The cellulosic fibers swell and partially dissolve, filling the interstices between the fibers and resulting in extensive hydrogen bonding. Thorough washing in water, followed by drying on conventional papermaking dryers, causes reprecipitation and consolidation of the network, resulting in a paper that is stronger wet than dry (it has excellent wet strength, even in boiling water), free of lint, odor and taste, and resistant to grease and oils (Paper, 2009). Unless specially coated or of a heavy weight, it is not a good barrier to gases.

Because of its grease resistance and wet strength, it strips away easily from food material without defibering, thus finding use as an interleaver between slices of food such as meat or pastry. Labels and inserts in products with high oil or grease content are frequently made from parchment. It can be treated with mold inhibitors and used to wrap foods such as cheese.

Parchment paper with great shock-absorbing capability can be produced by wet creping, resulting in extensibility combined with natural tensile toughness. Special finishing processes provide qualities ranging from rough to smooth, brittle to soft and sticky to releasable. It was first used for wrapping fatty foods such as butter, an application still used today.

Glazed imitation parchment (GIP) is made from strong sulfite pulp, which is heavily engine-sized and glazed to give the necessary degree of protection.

6.2.5.6 Waxed Paper

Waxed papers provide a barrier against penetration of liquids and vapors. Many base papers are suitable for waxing, including greaseproof and glassine papers. The major types are wet-waxed, dry-waxed and wax-laminated. Wax-sized papers, in which the wax is added at the beater during the papermaking process, have the least amount of wax and therefore give the least amount of protection.

Wet-waxed papers have a continuous surface film on one or both sides, which is achieved by shock-chilling the waxed web immediately after application of the wax. This also imparts a high degree of gloss on the coated surface. Dry-waxed papers are produced using heated rollers and do not have a continuous film on the surfaces. Consequently, exposed fibers act as wicks and transport moisture into the paper. Wax-laminated papers are bonded with a continuous film of wax that acts as an adhesive. The primary purpose of the wax is to provide a moisture barrier and a heat sealable laminant. Frequently, special resins or plastic polymers are added to the wax to improve adhesion and low temperature performance and to prevent cracking as a result of folding and bending of the paper. However, replacement of wax coatings by thermoplastics is a continuing trend.

6.3 PAPERBOARD PRODUCTS

Paper is generally termed board when its grammage exceeds 250 gsm. Various types of paperboards are manufactured, and a partial listing of paperboard grades is given in Table 6.1. Boards can be manufactured in a single Fourdrinier wire, a single cylinder former or on a series of formers of the same type or combination of types (Smook, 2002).

Multi-ply boards are produced by the consolidation of one or more web plies into a single sheet of paperboard which is then subsequently used to manufacture rigid boxes, folding cartons, beverage cartons and similar products. One advantage of multi-ply forming is the ability to utilize inexpensive and bulky low grade waste materials (mostly old newspapers and other postconsumer waste papers) in the inner plies of the board where low fiber strength and the presence of extraneous materials (e.g., inks, coatings, etc.) have little effect on board properties (Smook, 2002). However, multi-ply boards containing postconsumer waste papers should not be used for food contact purposes.

TABLE 6.1
Paperboard Grades

Linerboard—board having at least two plies, the top layer being of relatively better quality; usually made on a Fourdrinier machine with 100% virgin pulp furnish
Foodboard—board used for food packaging having a single-ply or multi-ply construction, usually made from 100% bleached virgin pulp furnish
Folding boxboard—multi-ply board used to make folding boxes; middle plies are made from mechanical pulp sandwiched between two layers of virgin chemical pulp
Chipboard—multi-ply board made from 100% recovered (secondary) fiber
Baseboard—board that will ultimately be coated or covered

6.3.1 Folding Cartons

Folding cartons are containers made from sheets of paperboard (typically with thicknesses between 300 and 1100 μm) which have been cut and scored for bending into desired shapes; they are delivered in a collapsed state for erection at the packaging point (Obolewicz, 2009).

The boards used for cartons have a ply structure and many different structures are possible, ranging from recycled fibers from a variety of sources (as in chipboards), through fibers where the outer ply is replaced with better quality pulps to give white-lined chipboards, to duplex boards without any waste pulp and solid white boards made entirely from bleached chemical pulp. The most widely used types of paperboard are as follows:

1. *Coated Solid Bleached Board (SBB) or Solid Bleached Sulfate (SBS)*: this grade is typically made from pure bleached chemical pulp with two or three layers of coating on the top surface and one layer on the reverse. It is used for chocolate confectionary, cheese, coffee, tea, reheatable products and frozen foods (Robertson, 2012). It can also be combined with SUB and other materials to make liquid packaging board (LPB).
2. *Coated Solid Unbleached Board (SUB) or Solid Unbleached Sulfate (SUS)*: this is 100% virgin, unbleached, chemical furnish and typically has two to three layers of mineral or synthetic pigment coating on the top and one layer on the reverse side. It is also known as Coated Unbleached Kraft (CUK). Recycled fibers are sometimes used to replace the unbleached chemical pulp. The primary reason for coating unbleached or natural kraft paperboard with a thin layer of kaolin clay is to improve its printing surface.
3. *Folding Box Board (FBB)*: This grade is typically made from middle layers of mechanical pulp sandwiched between two layers of chemical pulp with up to three layers of coating on the top or printing surface and one layer of coating on the reverse. The mechanical pulp gives high stiffness with high bulk and the chemical pulp gives high strength. It is used for products such as drinks, confectionery, frozen and chilled foods, tea, coffee, bakery products and cookies/biscuits.
4. *White Lined Chipboard (WLC)*: This grade is typically made using predominantly recovered fibers. It is manufactured in a number of layers each of which use selected grades of raw materials. It typically has two or three layers of coating on the top or printing surface which consists of bleached chemical pulp. The second layer is made of bleached chemical or mechanical pulp while the middle layers (commonly three in total) are unbleached recycled pulp from mixed paper or carton waste. The bottom or inside layer is specially selected recycled pulp (underliner). Some uncoated paperboard is produced with a top ply of white recovered fiber. WLC is used in a range of applications such as frozen and chilled foods, dried food and breakfast cereals.

In the absence of a functional barrier, mineral oil hydrocarbons (MOHs) from printing inks and recycled fibers tend to migrate from paper-based food packaging materials through the gas phase into dry food. Concentrations exceed the limit derived from the ADI by a factor of up to 100. The main sources of mineral oil in paperboard are offset printing inks, either directly applied for decorating the food packaging material or entering via recycling of fibers contaminated by mineral oil-containing inks, primarily from newspaper. The contamination of powdered baby milk and other dry foods packed in cardboard boxes over several weeks with MOHs at concentrations of 10–150 mg kg^{-1} was first reported in 1997; internal paper bags with a plastic layer did not stop the migration. The migration of MOHs threatens the use of paperboard made of recycled fibers for food packaging. As a short-term measure, the mineral oil content could be reduced through the selection of the paper and board fed into the recycling process. The most favorable starting materials available in sufficient amount, such as corrugated board, might reduce the concentration of the migrating mineral oil by a factor of 5, but the ADI would still be exceeded by up to 20 times. To meet the legal limit, a total elimination of mineral oil from offset printing inks (not only in newspapers but also in other printed matter) has been suggested (Biedermann et al., 2011). This topic is discussed further in Section 22.5.4.

A number of steps are involved in converting paperboard into cartons. Where special barrier properties are required, coating and laminating are carried out. Wax lamination provides a moisture barrier, lining with glassine provides grease resistance and laminating or extrusion coating with plastic materials confers special properties including heat sealing. The use of barrier materials in cartonboard is restricted by the inability of the normal types of carton closure to prevent the ingress of moisture directly.

Coating of the outer board greatly enhances the external appearance and printing quality, and clay and other minerals are used for such purposes. The coating can be applied either during the board-making operation or subsequently. Foil-lined boards are also used for various types of cartons, to (in certain applications) improve reheatability of the contents.

The conventional methods of carton manufacture involve printing of the board, followed by creasing and cutting to permit the subsequent folding to shape, the stripping of any waste material which is not required in the final construction, and the finishing operation of joining appropriate parts of the board, either by gluing, heat sealing or (occasionally) stitching. During creasing and folding, cartonboard is subjected to complex stresses, and the ability of a board to make a good carton depends on its rigidity, ease of ply delamination and the stretch properties of the printed liner. It is important that the surface layer on the top of the board is of an elastic nature and relatively high strength compared with the properties of the underlying layers since they will be in compression.

An exciting new development is 3D forming of paperboard (Hauptmann and Majschak, 2011). Although still only at the first stage of R&D, it promises to revolutionize paperboard packaging if successfully commercialized.

6.3.2 BEVERAGE CARTONS

The first records of paper being used to carry liquids on a commercial scale are found in reports, dated 1908, of a Dr Winslow of Seattle. He remarked on paper milk containers which were invented and sold in San Francisco and Los Angeles by a G.W. Maxwell as early as 1906. Paraffin wax was used to moisture proof the paper but achieving a liquid-tight bond at the joins was more difficult. In 1915, John Van Wormer, owner of a toy factory in Toledo, Ohio was granted a U.S. patent for a "paper bottle" (actually a folded blank box) for milk that he called Pure-Pak. The crucial and unique feature was that this box would be delivered flat to be folded, glued, filled and sealed at the dairy. This offered significant savings in delivery and storage in comparison with preformed glass bottles, then the predominant package for milk, having being introduced in 1889. The challenge came with the design of the machinery to be sold or leased to the dairy to form, fill and seal the cartons. The detailed development history of the paper beverage carton has been described by Robertson (2002).

The carton normally consists of layers of SBB and (outside North America and Japan) SUB coated internally and externally with LDPE, resulting in a carton which is impermeable to liquids and in which the internal and external surfaces may be heat sealed. There may also be a thin layer of aluminum foil, which acts as a gas and light barrier. The structure and functions of the various layers in an aseptic paperboard carton are described in Section 13.3.1.

The modern gable top carton retains the simple basic geometry of earlier years although flat-topped and plastic-topped versions are available (Lisiecki, 2009). Added refinements such as plastic screw caps and reclosable spouts are also available. Incorporation of an aluminum foil layer permits longer shelf life of chilled premium juice products; in some cases, the foil is replaced by a barrier polymer such as EVOH or SiO_x-coated PET. If the foil is replaced, then the carton must be sealed using ultrasonic sealing or heated jaws rather than induction sealing.

Liquid-tight, hermetically-sealed brick-shaped cartons are widely used for the aseptic packaging of a wide range of liquid foods including milk, juices, soups and wines to give packs which will retain the product in a commercially sterile state for years. The end of shelf life (typically 6–9 months) is determined by organoleptic changes as a result of undesirable chemical and physical reactions. In 2011, the Tetra Evero 1L aseptic carton bottle (billed as the world's first) for white milk was launched. It consists of the standard aseptic paperboard-foil-plastic body with an injection molded plastic cap and top.

A blank-fed, retortable, square-shaped paperboard carton for soups, ready meals, vegetables and pet food has been commercialized as a replacement for the metal can and a competitor for the retort pouch; it is known as Tetra Recart. Of basically similar structure to the aseptic carton (see Chapter 13) but with PP replacing LDPE, products packaged in it have a shelf life under ambient conditions of 18 months.

In recent years, there has been considerable publicity about the development of paper bottles. The GreenBottle® in the United Kingdom consists of a molded pulp outer with an inner plastic pouch complete with screw cap. The Ecologic Brands paper bottle in California consists of a molded pulp outer shell and an inner plastic pouch made from LDPE with a patented resealable spout made from PP. Both packages are basically bag-in-box technology: a paperboard shell for rigidity with an LDPE internal pouch to hold the product. The 360 Paper Water Bottle is a single serve water bottle made from sustainable sheet stock such as bamboo, palm leaves, etc. An internal PLA film provides the liquid barrier and enables the two pressed halves to be sealed. Rather than being unscrewed, the bottle features a lid which peels off into two pieces: one piece keeps the top clean from dust or other contaminants and the other can be reattached to seal the bottle. The design enables the self-bundling of multiple containers to eliminate the need for separate six pack packaging.

6.3.3 MOLDED PULP CONTAINERS

The term "molded pulp" is used to describe 3D packaging and food service articles that are manufactured from an aqueous slurry of cellulosic fibers and formed into discrete products on screened molds (Waldman, 2009). Typically, the raw materials consist of virgin mechanical and chemical wood pulp, and waste paper pulps with or without the addition of the former materials.

The forming process is similar in many ways to the paper-making process, except that a mold fitted with a screen is used in place of the moving wire screen. Two molding processes are used. In the pressure injection process, air under pressure and at a temperature of approximately 480°C is used to form a pulp and water mixture in a mold. This process is semiautomatic and moldings have a thicker and variable wall thickness; it is less suitable for producing more complicated designs and has been largely superseded by the suction molding process in which the pulp mixture is pumped into a perforated mold where water is removed by a partial vacuum. The molded item is then dried.

Typical uses of pressure-molded containers include the packaging of bottled wines and spirits where a pulp sleeve molded to the profile of the glass bottles enables them to be packed head to tail in a carton, thus saving a considerable amount of space. Well-known forms of molded pulp articles made by the suction-molding process include egg cartons, food trays and many other forms of tray-shaped articles for packing fruit and other commodities. Thin thermoplastic films such as PET can be laminated to one surface of a molded pulp tray, enabling it to function as a dual ovenability container (i.e., suitable to be used in microwave and convection ovens) for such products as frozen dinners.

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7 Metal Packaging Materials

7.1 INTRODUCTION

Four metals are commonly used for the packaging of foods: steel, aluminum, tin and chromium. Tin and steel, and chromium and steel, are used as composite materials in the form of tinplate and electrolytically chromium-coated steel (ECCS), the latter being somewhat unhelpfully referred to as tin-free steel (TFS). Aluminum is used in the form of purified alloys containing small and carefully controlled amounts of magnesium and manganese. Copper is used as a wire electrode during the welding of three-piece tinplate containers but does not become part of the finished container. The safety aspects of these different metals, together with can coatings, are discussed in Chapter 22.

The first commercial manufacture of tinplate commenced in England in 1699 and in France in 1720, where it was used for a variety of purposes including household utensils such as plates. Some time in about the middle of the eighteenth century, the Dutch navy began to use foods preserved by packing them in fat in tinned iron canisters (Thorne, 1986). After cooking and while still hot, the material to be preserved was placed into the canister, covered with hot fat and the lid immediately soldered on. Records show that from 1772 to 1777, the Dutch Government supplied its navy (which had been sent out to Suriname [formerly Dutch Guiana in South America] to quell a revolt) with roast beef packed in this way (Farrer, 1980).

Before the end of the eighteenth century, the Dutch had also established a small industry to preserve salmon in a similar manner. Freshly caught salmon were cleaned, cooked in boiling brine, smoked over a wood fire for 2 days and then placed in a tinplated iron box. The spaces were filled up with hot salted butter or olive oil and a lid was soldered onto the box (Thorne, 1986). A famous London firm of snuff merchants supplied 13 tins of Dutch salmon to one of its clients in 1797 (Farrer, 1980). Thus, a canning industry of sorts had been established in Holland independently of, and prior to, Appert's work.

The French confectioner Nicolas Appert discovered a method of "conserving all kinds of food substances in containers," and, in 1804, produced preserved meat for the French navy by packing it in glass champagne bottles, sealing them with a cork held in place with wire and heating in boiling water for several hours (Garcia and Adrian, 2009). Appert received an ex gratia payment of 12,000 francs in 1810 from the Ministry of the Interior's Bureau of Arts and Manufactures on condition that he publish details of his process; Appert obliged and 200 copies of his book were printed the same year. Appert deliberately avoided tinplate in his early work because of the poor quality of the French product, according to the fourth (1831) and fifth (1858) editions of his book. However, the quality of tinplate in England was good and it was freely available.

After almost two centuries of history, there is still controversy as to who introduced the tin can as a package. The latest account, based on extensive research of early-nineteenth-century archives (Cowell, 2007), has thrown additional light on those involved in the genesis of the canning industry and has revealed a new name: the French inventor Phillipe de Girard. It appears that he got Durand (a broker in London) to patent the process in 1810, the patent referring to the substitution of glass jars and bottles with tin cases. A successful trial with the Royal Navy was undertaken at Durand's request in 1811, and the patent was acquired by Bryan Donkin in 1812 for which Girard received £1000. Donkin had become interested in the tinning of iron as early as 1808 and, as mentioned in Chapter 6, was involved with John Gamble in developing the Fourdrinier papermaking machine.

Donkin applied to the British Admiralty for a test of his product and the first substantial orders were placed in 1814 with the London firm of Donkin, Hall and Gamble for meat preserved in tinplate canisters (John Hall was the founder of the famous Dartford Iron Works). By the 1820s, canned foods were a recognized article of commerce in Britain and France.

To complete the historical record, William Underwood left London and arrived in New Orleans in 1817. He traveled up to Boston where he started a business preserving food in glass jars by Appert's method. In 1819, Thomas Kennsett, also from England, started a similar business in preserved foods in New York in partnership with his father-in-law Ezra Daggett. The first offering of preserved provisions in tin cans in America is assumed to be the announcement by Daggett and Kensett in the New York *Evening Post* of July 18, 1822 (Bishop, 1978), although it was not until 1825 that they took out a patent in which "vessels of tin" were mentioned.

The American Civil War provided the opportunity for canning to become a great industry, and by the end of the war in 1865, canners had increased their output sixfold. For many years, the cans were made slowly and laboriously by hand. Both ends were soldered to the can with a hole of about 25 mm in diameter left in the top. After the can was filled through this hole, a metal disc was soldered into place. The mechanical roll crimping (commonly known as double seaming) of the can ends onto a body with a soldered side seam was patented in 1896 by Max Ams of New York (Thorne, 1986), making it possible to develop high-speed equipment for the making, filling and closing of these cans. In 1892, the first pineapple cannery was established in Hawaii. The first canned soup was produced in the United States in 1897.

Today, materials like tinplate and aluminum have become universally adopted for the manufacture of containers and closures for foods and beverages, largely due to several important qualities of these metals. These include their mechanical strength and resistance to working, low toxicity, superior barrier properties to gases, moisture and light, ability to withstand wide extremes of temperature and ideal surfaces for decoration and lacquering.

7.2 MANUFACTURE OF TINPLATE

The term tinplate refers to low-carbon, mild steel sheet varying in thickness from around 0.15–0.5 mm with a coating of tin between 2.8 and 17 gsm (g m^{-2}) (0.4–2.5 μm thick) on each surface of the material. The combination of tin and steel produces a material that has good strength, combined with excellent fabrication qualities such as ductility (the capability to undergo extensive deformation without fracture) and drawability (these attributes arise from the grade of steel selected and the processing conditions employed in its manufacture) as well as good weldability, nontoxicity, lubricity, lacquerability and a corrosion-resistant surface of bright appearance (these latter properties are due to the unique properties of tin). Furthermore, the tin coating adheres sufficiently to the steel base so that it will withstand any degree of deformation that the steel is able to withstand without flaking.

Continuous demand for improved quality and more economic production has led to the development of highly sophisticated manufacturing techniques. These are outlined in this section, together with their effects on the metallurgical and mechanical characteristics. The chemical composition of the base steel has a very significant effect on the subsequent corrosion resistance and mechanical properties of the tinplate.

7.2.1 MANUFACTURE OF PIG IRON

The iron ores used are generally hematite (Fe_2O_3) with some magnetite (Fe_3O_4). Commercial extraction of iron from its ores is carried out in blast furnaces, where a mixture of iron ores, solid fuel (coke) and fluxes (limestone and dolomite) are heated to around 1800°C. This results in the reduction of most of the iron oxides to metallic iron (m.p. $\approx$ 1200°C). Today, modern blast furnaces are capable of producing molten iron of near constant composition at high rates.

7.2.2 STEELMAKING

The pig iron from a blast furnace contains 3.5%–5.0% carbon, 0.3%–1.0% silicon and up to 2.5% manganese, 1% phosphorous and 0.08% sulfur depending on the ore. Carbon is the most important alloying element for steel and effects the strength of cans. A higher carbon content is usually combined with a higher manganese content, resulting in higher strength steel. Lower carbon content improves material formability and weldability. These metalloids must be substantially reduced in the steelmaking stage, and this is commonly accomplished using a basic oxygen furnace. From the furnace, the steel is cast into ingots, which are subsequently rolled into slabs about 250 mm thick or, more commonly today, continuously cast into slab form.

The thick slabs are hot rolled down to about 2 mm and, during this process, substantial layers (0.01 mm thick) of oxides or scale are formed as a consequence of the steel being heated to elevated temperatures for rolling. Next, the scale is removed by a process called "pickling," which uses a dilute aqueous solution of acid (traditionally sulfuric acid but now mainly hydrochloric acid) near its boiling point. After pickling, the oxide-free strip is recoiled and coated with an oil to prevent rust formation and act as a lubricant in subsequent operations.

The final stage of thickness reduction (typically 90% from about 2 mm to <0.2 mm) is carried out by cold rolling. The effects of cold rolling are to increase the strength and hardness of the steel, but this is done at the expense of ductility.

Cold rolling is followed by annealing where the steel is heated to temperatures of 600°C–700°C to relieve the stresses from the rolling process; annealing results in recrystallization of the elongated ferrite grains into new fine grains. Two different annealing processes are used after cold rolling: continuous annealing (which results in a strong material with a fine grain structure) and batch annealing (which has a coarse grain structure but excellent formability).

After annealing, the material is either temper rolled or cold rolled for the second time. Steel that is temper rolled is known as "single reduced" (one cold rolling operation); steel that is cold rolled after annealing is known as "double reduced." Double reduced (DR) material is very strong and stiff and has a higher hardness for a given thickness, allowing the use of comparatively thin gauges for many applications. However, it has only limited forming possibilities. Minimum thicknesses currently in use are 0.18 mm for single reduced (SR) and 0.12 mm for DR plate.

Some types of tinplate display excellent deep-drawing behavior thanks to a high Lankford coefficient (or coefficient of anisotropy), which is a measure of the plastic anisotropy of rolled sheet metal; it is used as an indicator of the formability of recrystallized low-carbon steel sheets. It ensures near-identical behavior, irrespective of the orientation of the deformation in relation to the rolling direction, an important consideration in drawn and redrawn (DRD) can manufacture.

To reduce the possibility of severe fluting, paneling or creasing, and to impart the desired surface finish, the steel is given a final, very light cold rolling (generally a reduction of less than or equal to 5.0% in thickness) in a "Temper" mill. This imparts "springiness" to the steel but changes the temper or surface hardness only slightly. Temper refers to an arbitrary number designation that indicates the forming properties of tin mill products and is the summation of interrelated mechanical properties such as elasticity, stiffness, springiness and fluting tendency (Kraus and Tarulis, 2009).

At this stage, the uncoated steel sheet is referred to as *blackplate*, thus called because some of the early production was covered with black iron oxide. It is the raw material for electrolytic tinplate (ETP) and ECCS. The Rockwell hardness test has been adopted as the industry standard to express temper because of its simplicity and overall good correlation with fabrication requirements. A 1.6 mm diameter ball penetrator with a 30 kg load is impressed into the plate surface and the measurement is expressed as a Rockwell 30 T reading, which is then converted into plate temper values using an arbitrary scale. Typical temper values for blackplate and ETP are presented in Table 7.1, where both the former and current designations are listed as the former designations are still used in some countries. The four main grades of steel product for subsequent use in tinplate production are shown in Table 7.2.

TABLE 7.1
Tinplate Temper Designations

Temper			Rockwell Hardness 30T Scale	Formability	Applications
TS230	T50	T1	46–52	Soft for extra-deep drawing	Nozzles, spouts and closures;
TS245	T52	T2	50–56	Moderate deep drawing	Rings and plugs, dome tops, closures and shallow-drawn cans
TS275	T57	T3	54–63	Shallow drawing and general purpose	Can ends and bodies, large-diameter closures and crown caps
TH415	T61	T4	58–64	General purpose where increased stiffness required	Crown caps, can ends and bodies for noncorrosive products
TH435	T65	T5	62–68	Increased stiffness to resist buckling	Can ends and bodies
—	T70	T6	67–73	Very stiff	
TH550	DR550	DR8	70–76	High strength and stiffness	Small diameter round can bodies and ends
TH620	DR620	DR9	73–79	High strength and stiffness	Large diameter round can bodies and ends
—	DR660	DR9M	74–80	High strength and stiffness	Beer and carbonated beverage ends and DRD cans
—	DR690	DR10	77–83	Maximum strength and stiffness	Ends

Note: Some products may be either batch annealed or continuously annealed. Although the temper of the plate will be the same, the mechanical properties may differ as continuously annealed plate has a finer grain structure.

TABLE 7.2
Types of Steel Produced for Subsequent Use in Tinplate

	Composition (%) (Maximum)								
Type	C	Mn	P	S	Si	Cu	Al	Properties	Application
D	0.12	0.60	0.02	0.05	0.02	0.20	0.06	Stabilized steel and, therefore, nonaging Less C than other tinplate steels	Used for severe drawing operations (e.g., D&I cans)
L	0.13	0.60	0.015	0.05	0.01	0.06	0.08	High purity; low in residual elements	Used where high internal corrosion resistance is required
MR	0.13	0.60	0.02	0.05	0.01	0.20	0.08	Similar to L but Cu and P maxima are raised. Is most widely used tinplate steel	Vegetable and meat packs where internal corrosion resistance is not too critical
N	0.13	0.60	0.015	0.05	0.01	0.06	0.06	Nitrogenized steel with up to 0.02% N to increase strength	Used where high strength and rigidity required (e.g. can ends)

Packaging steels generally fall into two groups: those that are created specifically for strength and those that are created for formability. Higher strength steels are suitable for welded food cans, while softer, more formable grades are better for drawn cans and components such as aerosol tops and bottoms, fish or beverage cans.

7.2.3 TINPLATING

The traditional method for tinplating involved dipping or passing the steel through a bath of molten pure tin, but, since the 1930s, the process of depositing tin by electroplating has been used. The introduction of the electroplating process enabled a different thickness of tin to be applied to the two surfaces of the steel. This "differential tinplate" is of economic benefit to the user because it enables the most cost-effective coating to be selected to withstand the different conditions of the interior and exterior of the container.

There are a number of methods of electroplating, but the two principal methods are the acid stannous sulfate process (generally known as the Ferrostan process) and the halogen process (Morgan, 1985). Plating by either method is preceded by cleaning in a pickling and degreasing unit, followed by thorough washing to prepare the surface. After the plating stage, the coating is flow melted, passivated and then lightly oiled.

Flow melting consists of heating the strip to a temperature above the melting point of tin (typically, 260°C–270°C), followed by rapid quenching in water. During this treatment, a small quantity of the tin–iron compound $FeSn_2$ is formed; the weight and structure depend on the time and temperature, as well as other factors such as the surface condition of the steel. The structure and weight of this alloy layer plays an important role in several forms of corrosion behavior.

Because the naturally formed oxide layer on the surface of the tin will readily grow in the atmosphere to form a yellow stain (especially when heated, e.g., during stoving after the application of organic enamels, which are also known as lacquers or varnishes), the steel strip is given a passivation treatment to render its surface more stable and resistant to the atmosphere. Many types of treatments have been developed, but an electrolytic treatment in a sodium dichromate electrolyte is the most widespread. It results in the formation of a film (usually $<1\,\mu m$ thick), consisting of chromium, chromium oxides and tin oxides, the quantity and form of these basic constituents determining the varying properties of the film. The process ensures that the only species present are Cr^{O} and Cr^{III} and not Cr^{IV}, which is the toxicologically important species. Although the level of migration from uncoated tinplate cans is negligible, work on alternative passivation treatments is continuing (Whitaker, 2007). These include titanium sulfate, titanium and potassium oxalates, and zirconium sulfate and fluoride treatments (Catalá et al., 2005).

After passivation, the plate is given a light oiling (oil film weights are generally in the range of 5–10 mg m^{-2}) to help preserve it from attack, and to assist the passage of sheets through container-forming machines without damaging the soft tin layer. It is obviously essential that the oil used is approved for use in food packaging; cotton seed oil was used for many years but this has now been largely superseded by dioctyl sebacate (DOS). The oil is applied by electrostatic precipitation or direct plate immersion. The quantity of oil (applied uniformly to both sides) is carefully controlled because an excessive oil film can cause dewetting of enamels and printing inks, which are applied during subsequent container manufacture. Finally, the strips are sheared into sheets or coiled, and then packed for shipment to the can manufacturers.

The final structure of the completed coating is shown in Figure 7.1, and consists of a tin/iron alloy layer (principally $FeSn_2$) adjacent to the steel base, free tin, a film of mixed oxides formed by the passivation process and an oil film.

Tinplate sheets are described in terms of a base box, a hangover from earlier times when tinplate was sold in units of 112 sheets, each 356 × 508 mm (14 × 20 in.). Such a package was known as a base box, and the area it contained (20.2325 m^2 or 31,360 in.^{2}) survives today as the unit area for the

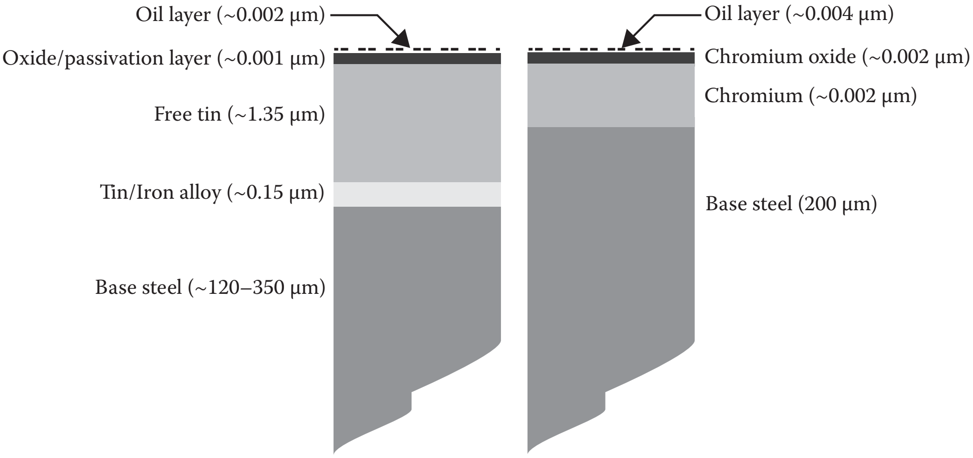

FIGURE 7.1 Schematic structure (not to scale) of tinplate and ECCS showing the main functional layers.

selling of tinplate. In the original system, a 1 lb base box meant that 1 lb of tin was applied evenly to both sides of the plate, that is, each side received 0.5 lb (equivalent to 11.2 gsm) of tinplate. This was given the designation in the United States of No. 100 (Turner, 2001).

The standard grades of ETP available in most countries, together with their nominal tin coating masses, are given in Table 7.3. The designation of ETP with 11.2 gsm of tin on each surface of the sheet is shown as E.11.2/11.2, and this represents a thickness of tin of ~1.54 μm on each surface. Tinplate is now commonly graded using the metric unit SITA (Système International Tinplate Area), which is based on 100 m^2. One SITA equals 4.9426 base boxes. The standard method for determining the mass of tin coating is the iodine titration procedure.

TABLE 7.3
Standard Grades and Nominal Masses of ETP

Code		Nominal Coating Mass per Surface	
Euronorms (145–146)	**ASTM (624–626)**	**(gsm)**	**(lb/Base Box)**
	No. 10	1.1/1.1	0.05/0.05
E.2.8/2.8	No. 25	2.8/2.8	0.125/0.125
E.5.6/5.6	No. 50	5.6/5.6	0.25/0.25
E.8.4/8.4	No. 75	8.4/8.4	0.375/0.375
E.11.2/11.2	No. 100	11.2/11.2	0.50/0.50
D.2.8/0	—	2.8/0	0.125/0
D.5.6/2.8	No. 50/25	5.6/2.8	0.25/0.125
D.8.4/2.8	No. 75/25	8.4/2.8	0.375/0.125
D.11.2/2.8	No. 100/25	11.2/2.8	0.50/0.125
—	No. 135/25	15.1/2.8	0.675/0.125
D.8.4/5.6	No. 75/50	8.4/5.6	0.375/0.25
D.11.2/5.6	No. 100/50	11.2/5.6	0.50/0.25
D.15.1/5.6	—	15.1/5.6	0.675/0.25

E, equal coatings on each surface; D, differential coatings on each surface.

7.3 MANUFACTURE OF ECCS

The production of electrolytic chromium/chromium-oxide-coated low-carbon steel sheet (to give ECCS its full name) is very similar to electrotinning, the only essential differences being that, in the former case, flow melting and chemical passivation are not involved. The initial development work was carried out in Japan in the 1960s when tin was on occasions in short supply, and the price extremely variable.

The process involves cathodic deposition in a dilute chromium plating electrolyte (e.g., 50 g L^{-1} CrO_3 and 0.5 g L^{-1} H_2SO_4) at a temperature in the range of 50°C–70°C. As shown in Figure 7.1, ECCS consists of a duplex coating of metallic chromium and chromium sesquioxide. The ideal range of coating weights for ECCS is between 0.07 and 0.15 gsm chromium metal and between 0.03 and 0.06 gsm trivalent chromium present as oxide, giving a total coating weight of approximately 0.15 gsm. This is much thinner than the lowest grade of electrolytic tinplate which has a tin thickness of 5.6 gsm. ECCS is coated equally on both sides of the steel. Unlike tinplate, ECCS is not subject to a passivation treatment. Finally, an oil coating of either DOS or butyl stearate oil (BSO) is applied.

Recently Li et al. (2011) showed that the different modes of annealing and rolling have remarkable effects on the surface morphology and grain size of ECCS products. In compact surface chromium-coating of batch-annealed (BA) plate with low porosity, the grains were larger and coarser in comparison with that of continuously annealed (CA) plate. Evidence of microcracks was found on the surface of chromium-coated DR plate. The chemical composition of ECCS oxide film on steel consisted of CrOOH or $Cr(OH)_3$ as the main components, plus Cr_2O_3 and a small amount of H_2O. $Cr(OH)_3$ is mainly formed from cathodic films generated in the electroplating process. CrOOH was an intermediate product formed in process of $Cr(OH)_3$ losing water to generate Cr_2O_3.

The surface of ECCS is more acceptable for protective enamel coatings or printing inks and varnishes than tinplate, and the lack of a low melting point (232°C) tin layer means that higher stoving temperatures and consequently shorter stoving times can be used for the enameling of ECCS. Unlike flow-brightened tinplate, ECCS is a dull bluish color, which necessitates modification of decoration processes to allow for its poor reflection.

ECCS is less resistant to corrosion than tinplate as it has no sacrificial tin layer and, therefore, must be coated on both sides with an enamel or polymer coating. Polymer coatings are applied either by laminating film or extruding polymer directly onto the substrate; this is normally done on both sides.

ECCS containers cannot be soldered and, therefore, bonding of ECCS components must be by welding or the use of organic adhesives. If welded, then ECCS must be edge cleaned prior to welding to remove the chromium layer. This is a slow, costly and mechanically inefficient process. Typically, ECCS is used for components that do not have to be welded, such as ends for tinplate bodies, lids, crown corks, twist-off caps and aerosol bottoms and tops.

7.4 MANUFACTURE OF ALUMINUM

Aluminum is the earth's most abundant metallic constituent, comprising 8.8% of the earth's crust, with only the nonmetals O_2 and silicon being more abundant. Alumina or aluminum oxide (Al_2O_3) is the only oxide formed by aluminum and is found in nature as the minerals corundum (Al_2O_3), diaspore ($Al_2O_3 \cdot H_2O$), gibbsite ($Al_2O_3 \cdot 3H_2O$) and, most commonly, bauxite, an impure form of gibbsite. Because bauxite contains only 30%–54% alumina (the remainder is a mixture of silica, various iron oxides and titanium dioxide), it must be purified before it can be refined to aluminum. The Bayer process (invented in 1887 by Karl Bayer in St. Petersburg, Russia) is the principal industrial means of refining bauxite. A solution of NaOH at 175°C converts alumina to $Al(OH)_3$, which dissolves in the hydroxide solution; the other components that remain insoluble are filtered off. On cooling, the dissolved $Al(OH)_3$ precipitates as a white, fluffy solid and, when heated to 980°C (calcined), decomposes to alumina.

Hans Christian Oersted, a Danish physicist and chemist, first isolated aluminum in 1825 using a chemical process involving potassium amalgam. Between 1827 and 1845, Friedrich Wöhler, a German chemist, improved Oersted's process by using metallic potassium. In 1854, a French chemist Henri-Étienne Sainte-Claire Deville obtained the metal by reducing aluminum chloride with sodium. Aided by the financial backing of Napoleon III, Deville established a large-scale experimental plant and displayed pure aluminum at the Exposition Universelle of 1885 in Paris, where it was considered a precious metal (more valuable than gold or platinum) and used mainly for jewelry. In 1886, Charles Martin Hall in the United States and Paul Héroult in France independently and almost simultaneously discovered that alumina would dissolve in fused cryolite (Na_3AlF_6), and could then be decomposed electrolytically to a crude molten metal. A low-cost technique (the Hall-Héroult process) is currently the only method used for the commercial production of aluminum, although new methods are under study. In 1888, Hall opened the first large-scale aluminum production plant in Pittsburgh, which would eventually evolve into the Alcoa Corporation, the world's leading producer of aluminum.

Owing to the chemical stability of its oxides, the energy requirements for smelting are extremely high. This has led to the production of aluminum in areas where cheap electrical power is available. Currently, a typical aluminum process can be described as follows. First, alumina is dissolved in cryolite in carbon-lined steel boxes called cells. Then a carbon electrode or anode is lowered into the solution and an electric current of 50–150 MA is passed through the mixture to the carbon cathode lining of the cell. The current reduces the alumina into aluminum and O_2, the latter combining with the anode's carbon to form CO_2, while the aluminum (denser than cryolite) settles to the bottom of the cell.

Most commercial uses of aluminum require special properties that the pure metal cannot provide. Therefore, alloying agents are added to impart strength, improve formability characteristics and influence corrosion characteristics. A wide range of aluminum alloys is commercially available for packaging applications, depending on the container design and fabrication method used. The chemical composition and typical usage of some of the more commonly used aluminum alloys (the aluminum is at least 99% pure) are shown in Table 7.4. The alloys are identified by four-digit numbers where the first digit 1–8 gives the series family and indicates the alloy type and principal alloying element. Commercially pure (unalloyed) aluminum (e.g., 1050) contains different levels of impurities, with Fe and Si being the most common. It is used for the manufacture of foil and extruded containers since it is the least susceptible to work hardening. Type 3xxx alloy contains Mn, and type 5xxx alloy contains 4%–5% Mg and 0.5% Mn, producing a very rigid material suitable for manufacturing beverage can ends. Type 8xxx series includes miscellaneous alloys that cannot be placed within the other series designations (Reboul and Baroux, 2011).

The general effect of several alloying elements on the corrosion behavior of aluminum is as follows:

- Copper reduces the corrosion resistance of aluminum more than any other alloying element and leads to a higher rate of general corrosion.
- Manganese slightly increases corrosion resistance.
- Magnesium has a beneficial influence and Al–Mg alloys have good corrosion resistance.

TABLE 7.4

Some Aluminum Alloy Composition Limits (% Weight) and Applications

Alloy	Typical Application	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti
1050	Foils and flexible tubes	0.25	0.4	0.05	0.05	0.05	0.05	0.03	0.03
3104	Beverage can ends and D&I can bodies	0.60	0.7	0.25	1.4	1.3	—	0.25	0.10
5042	Full panel EOE and DRD can bodies	0.20	0.35	0.15	0.5	4.0	0.10	0.25	0.10
5182	Easy-open beverage can ends and tabs	0.20	0.35	0.15	0.5	5.0	0.10	0.25	0.10
8011	Pilfer-proof caps	0.90	1.00	0.10	0.20	0.05	0.05	0.10	0.08
8079	Foil for lamination	0.30	1.3	0.05	—	—	—	0.10	—

- Zinc has only a small influence on corrosion resistance in most environments, tending to reduce the resistance of alloys to acid media and increase their resistance to alkalis.
- Silicon slightly decreases corrosion resistance, depending on its form and location in the alloy microstructure.
- Chromium increases corrosion resistance in the usual amounts added to alloys.
- Iron reduces corrosion resistance and is probably the most common cause of pitting in aluminum alloys; a high iron content increases the bursting strength but reduces the corrosion resistance.
- Titanium has little influence on corrosion resistance of aluminum alloys.

Compared with tinplate and ECCS, aluminum is a lighter, weaker but more ductile material that cannot be soldered. The reduction in metal thickness of the can body has continued incrementally over the past 30 years, at times facilitated by alloy development but mostly through optimization of can design, and continues today in many parts of the world.

7.5 CONTAINER-MAKING PROCESSES

7.5.1 End Manufacture

The can end or lid is of complex design developed for optimum deformation behavior, the latter being dependent on plate thickness, the precise contour of the expansion rings and the countersink depth. It is important that the ends are able to deform under internal and external pressure without becoming permanently distorted. In effect, they must act like diaphragms, expanding during thermal processing and returning to a concave profile when vacuum develops inside the can on cooling. The cross-section of a typical end design is shown in Figure 7.2.

The ends are stamped on power presses from tinplate sheet (generally of high temper grade), which has been previously enameled. After stamping, the ends fall through the press into the curler to form the outside curl and diameter.

A lining or sealing compound is then applied into the seaming panel; the sealant used is based on natural or synthetic rubber and is dispersed in water or solvent. Its constituents are subject to stringent food regulations. The purpose of the sealant is to assist the formation of a hermetic seal by providing a gasket between adjacent layers of metal.

Several types of easy-opening devices, such as the key-opening scored strip found in solid meat or shallow fish cans, have been available for many years. However, an increased demand for convenience features has seen the development of easy-open ends (EOEs) of two broad types: those that provide a pouring aperture for dispensing liquid products, and those that give a near-full aperture opening for removing more solid products. The first EOE for canned beverages was patented in 1962 by Ermal Cleon Fraze of Dayton, Ohio who, in the late 1950s, was forced to open a beverage can on a car bumper at a family picnic because no one had brought along a can opener.

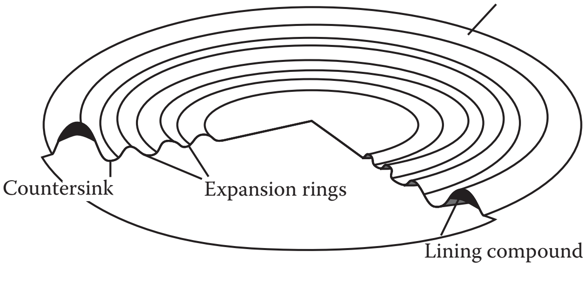

FIGURE 7.2 Profile of a typical can end.

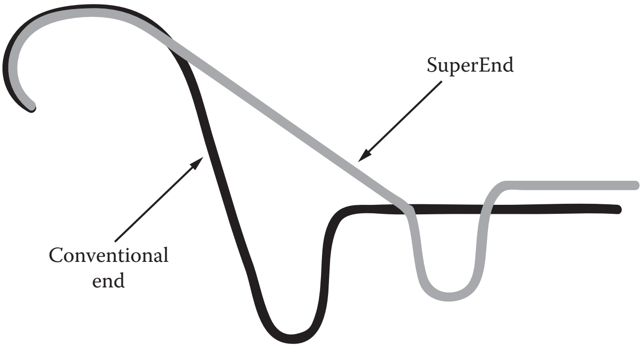

FIGURE 7.3 Cross-section of the end profile of a conventional end and a SuperEnd®.

Being intimately familiar with working metal, he knew there had to be a better way. By the early 1960s, he had refined a technology for attaching a tab to the top of the can end, using nothing but the parent material of the end itself. It was test marketed and emerged in 1965 as the familiar ring-pull tab. However, because it was detachable it resulted in litter and, in 1975, a patent was granted to Daniel F. Cudzik from Reynolds Metals in Richmond, Virginia for a can end with an inseparable tear strip; this soon became the industry standard, and, in various formats, is known as the stay-on tab.

Most designs incorporate an EOE consisting of a scored portion in the end panel and a levering tab (formed separately) that is riveted onto a bubble-like structure fabricated during pressing. Most (but not all) of the entire aperture circumference is scored, leaving sufficient unscored portion to function as a hinge when the tab is pressed in. Close control of scoring conditions is vital to ensure adequate resistance to bursting without requiring an unduly high tearing load to open. Particular attention must be paid to metal exposure resulting from enamel fracture at the score.

Because of the greater ease of fabrication, integrated rivet ends have usually been made from aluminum, but this presents problems when such ends are used with steel cans. For example, the corrosion of carbonated soft drinks in such cans is accelerated because of the bimetallic container. These problems have led to the development of steel EOEs.

A significant reduction in the amount of material required to make an aluminum end became commercial in 2001 when Crown Cork and Seal introduced the SuperEnd®, achieving about a 10% decrease in weight while increasing the buckle failure strength of the end. Figure 7.3 shows a comparison of profiles of the new SuperEnd and the older designs. The innovative ends utilize a unique angled chuck-wall design, which significantly reduces metal use and improves end performance. This unique design provides 20% more finger access to lift the opening tab, thus making it easier to open; it has become an industry standard for beverage ends.

7.5.2 THREE-PIECE CAN MANUFACTURE

7.5.2.1 Welded Side Seams

In developed countries, the majority of three-piece tinplate cans used for food have welded side seams. Compared to soldered side seams (see below Section 7.5.2.2), welding offers savings in material, since the overlap needed to produce a weld uses less metal than an interlocked soldered seam. In addition, the side seam is stronger, it is easier to seam on the ends and a greater surface area is available for external decorating.

Prior to welding, sheets of steel are enameled and, if necessary, printed, with the area where the weld will be made left bare. The sheets are then slit into individual blanks. Each blank is rolled into a cylinder with the two longitudinal edges overlapping. The two edges are then welded together.

The wire-welded operation used today for the high-speed welding of tinplate and ECCS containers utilizes a sine wave alternating current (and in the case of tinplate, a continuous copper wire

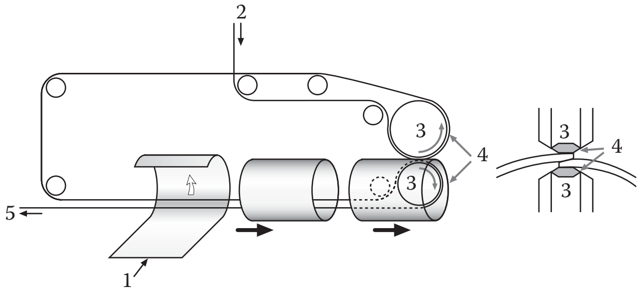

FIGURE 7.4 Stages in the formation of a three-piece welded can: (1) blank rolled to cylindrical shape, (2) copper wire, (3) welding electrodes, (4) copper wire contacts and (5) used wire to recycling. (Redrawn from Turner, T.A., *Canmaking: The Technology of Metal Protection and Decoration*, Blackie Academic & Professional, London, U.K., 1998.)

electrode) to produce a weld with an extremely low (0.4–0.8 mm) metal overlap (Turner, 2001). The use of copper wire as an intermediate electrode is necessary to remove the small amount of tin picked up from the tinplate during the welding process, which would otherwise reduce welding efficiency (Kraus and Tarulis, 2009). High electrical resistance causes the interface temperature to rise rapidly to at least 900°C, resulting in solid phase bonding at all locations along the seam (see Figure 7.4). The tensile strength of a good weld is equal to that of the base plate.

To prevent traces of iron being picked up by some types of beverages and acidic foods, repair side striping (enameling) of the internal surface of the weld is required. The side stripe generally comprises polymer resin powders that are applied by fusing or the like to the inside and/or the outside seam areas. Powder coating is usually applied electrostatically to the interior of the side seam.

A system of chemical bonding of side seams has been developed, mainly for dry or otherwise neutral products such as powders and oils. It utilizes a thermoplastic polyamide adhesive, which is applied to one edge of the preheated body blank before it is rolled into a cylinder, providing complete protection of the raw edges of the blank. A strong bonded lap seam is produced that is able to withstand the high in-can pressures generated by beers and carbonated soft drinks during can warming or pasteurization. This method can only be used with ECCS cans because the melting point of tin is close to the fusion temperature of the plastic. However, since the advent of high-speed welding operations, the use of chemically bonded side seams has declined.

7.5.2.2 Soldered Side Seams

With the exception of some developing countries, very few food cans are produced with soldered side seams, the concern of public health authorities being that lead from the tin/lead (2:98) solder would migrate into the food. Since the 1970s, most countries insisted that only pure tin solder be used on cans intended for baby foods, which added significantly to the cost of such cans. The use of tin/lead solder ceased when the U.S. FDA issued a final rule in July 1995 prohibiting its use in food containers.

7.5.2.3 Double Seaming

After the side seam has been welded, the bodies are transferred to a flanger for the final metal forming operation: necking and flanging for beverage cans, and beading and flanging for food cans. The can rim is flanged outward to enable ends to be seamed on. The top of beverage cans is necked to reduce the overall diameter across the seamed end to below that of the can body wall, yielding savings in the cost of metal through the use of smaller diameter ends. This allows more effective packing and stacking methods to be adopted, and prevents damage to the seams from rubbing against each other. Simultaneous creation of the neck and flange using a spin process is used. Double-, triple- and quadruple-neckings are now quite common, the latter reducing the end diameter from 68 to 54 mm for the common beverage can.

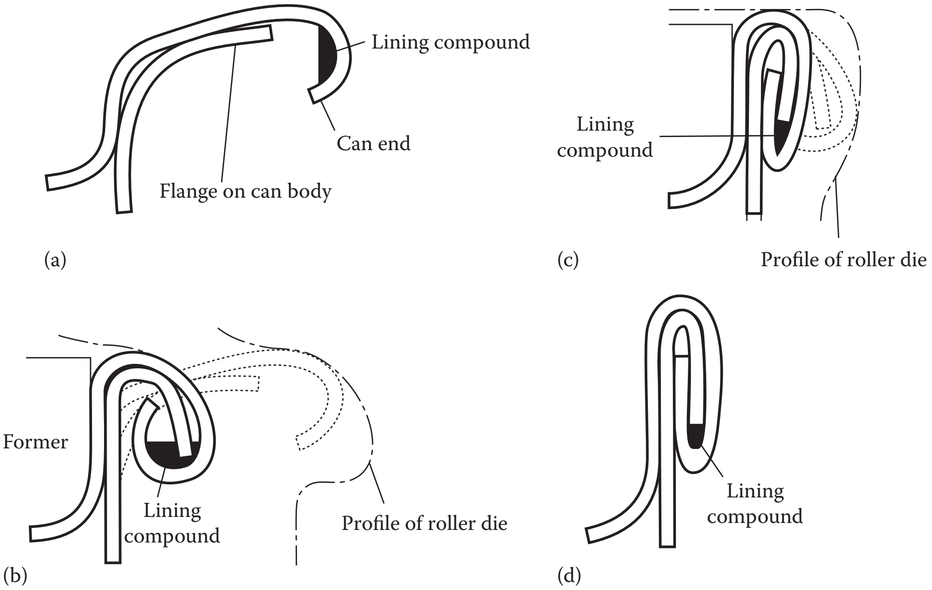

FIGURE 7.5 Double seaming of metal ends on to metal containers: (a) end and body are brought together, (b) first seaming operation, (c) second seaming operation and (d) section through final seam.

For food products where the cans may be subjected to external pressure during retorting or where they remain under high internal vacuum during storage, the cylinder wall may be beaded or ribbed for radial strength. There are many bead designs and arrangements, all of which are attempts to meet certain performance criteria. In essence, circumferential beading produces shorter can segments that are more resistant to paneling (implosion), but such beads reduce the axial load resistance by acting as failure rings.

The end is then mechanically joined to the cylinder by a double seaming operation. This is illustrated in Figure 7.5 and involves mechanically interlocking the two flanges or hooks of the body cylinder and end. It is carried out in two stages. In the first operation, the end curl is gradually rolled inward radially so that its flange is well tucked up underneath the body hook, the final contour being governed by the shape of the seaming roll. In the second operation, the seam is tightened (closed up) by a shallower seaming roll. The final quality of the double seam is defined by its length, thickness and the extent of the overlap of the end hook with the body hook. Rigid standards are laid down for an acceptable degree of overlap and seam tightness. The main components of a double seam are shown in Figure 7.6. Finally, the cans are tested for leakage using air pressure in large wheel-type testers; leaking cans are automatically rejected.

7.5.3 Two-Piece Can Manufacture

A major innovation in canmaking was the introduction of the seamless or two-piece aluminum can in the 1950s and tinplate can in the 1970s. For many years, canmakers have manufactured in a single pressing, shallow-drawn two-piece containers such as the familiar oval fish can. However, the technology to produce deep-drawn cans is a more recent innovation, although the basic concept dates back to the Kellver system for producing cartridge cases developed in Switzerland during World War II.

There are two main methods used commercially to make two-piece cans: the drawn and ironed (D&I) process, which can be adapted to produce a can for pressure packs (including carbonated beverages) and for food containers, and the DRD process, which is a multistage operation and produces a can mainly suitable for food products. Both processes depend on the property of the metal to

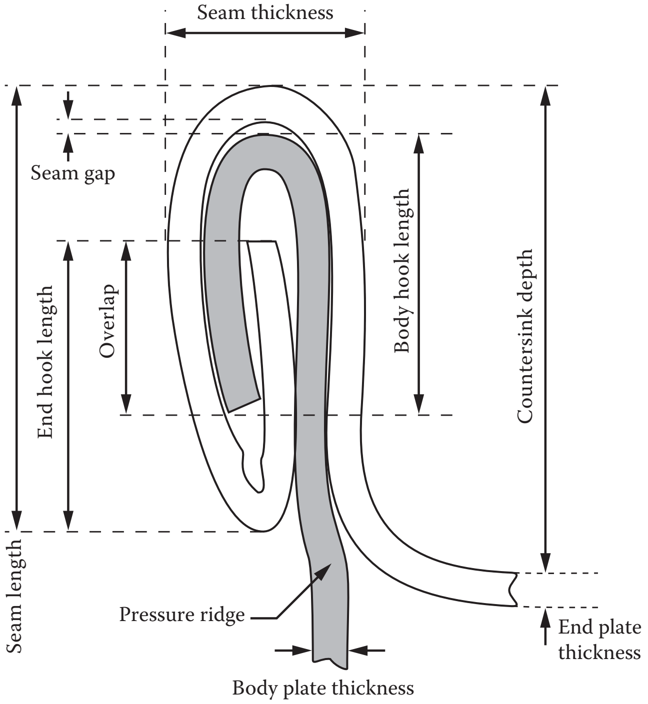

FIGURE 7.6 Main components of a double seam.

"flow" by rearrangement of the crystal structure under the influence of compound stresses, without rupturing the material.

The first aluminum D&I cans were introduced in the United States by a brewery in 1958, but it was not until 1971 that the first tinplate D&I can was launched. By comparison, the first three-piece soldered tinplate can for beer was introduced by the Krueger Brewing Company in the United States in 1935.

Two-piece cans have technical, economic and aesthetic advantages in comparison with soldered or welded three-piece cans. In terms of integrity, the two-piece can has no side seam and only one double seam, which is more easily formed and controlled because of the absence of a side seam lap juncture. The internal enamel does not have to protect a soldered side seam or weld cut edge, and there are material savings in solder and (in the case of D&I cans) plate, the latter being up to 35% lighter than a standard three-piece can. Since 1970, through the conversion of three- to two-piece cans and subsequent lightweighting, the weight of a 350 mL tinplate soft drink can has been reduced by 50% to 30 g, and that of the inherently lighter two-piece aluminum can by 39% to 13 g. Technology exists to continue this trend, especially with tinplate cans. Finally, the absence of a side seam permits all-round decoration of the outside of the can, increasing the effective printing area and leading to a more aesthetically pleasing appearance.

7.5.3.1 Drawn and Ironed

The D&I (also known as *drawn and wall ironed* [DWI]) tinplate or aluminum container is made from a circular disc stamped from a sheet or coil of uncoated plate, formed into a shallow cup with effectively the same side wall and base thicknesses as the starting material, as shown in Figure 7.7. The forming process involves a flat sheet being formed into a cup or cylinder by the action of a punch drawing it through a circular die (Silbereis, 2009), the wall thickness of the cup being uniform throughout. The plate is covered with a thin film of water-soluble synthetic lubricant prior to forming.

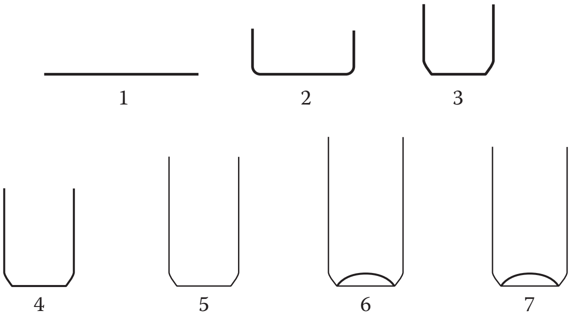

FIGURE 7.7 Sequential stages in the production of two-piece D&I cans: (1) disc cut from coil, (2) drawn into shallow cup, (3) redrawn into smaller diameter cup, (4, 5 and 6) wall thinning by ironing (diameter remains constant) and (7) finished can trimmed to required height.

The cup is transferred to an ironing press where it is held on a punch and passed successively through a series of ironing dies. As a consequence of the ironing process, the wall thickness is reduced (typically from 0.30 to 0.10 mm) and the body height is correspondingly increased. Concurrently, the integral bottom end is domed and profiled to provide added strength, with the end retaining essentially the original sheet thickness. Because the can wall may not iron to the same height all around the circumference due to slight variation in material properties, cans are "overdrawn" and then trimmed to the correct height.

The trimmed cans are chemically cleaned to remove drawing lubricants and prepare the surface for receiving exterior and interior coatings. If the cans are to be used for beverages, they are then necked; D&I food cans are commonly beaded for added strength against body collapse under partial vacuum conditions. The cans are then flanged.

Tinplate is the best material for D&I cans as the tin coating is soft and ductile and imparts lubricity to the steel while remaining bonded to it throughout. ECCS plate is not suitable for ironing as the chromium-based coating is too hard. Some aluminum is made into D&I cans for food packaging, but these are mainly shallow-drawn containers. Most D&I aluminum cans are used for beverage packaging (i.e., beer and soft drinks). Aluminum beverage bottles having screw tops with diameters of 28 and 38 mm were launched in the Japanese market in 2000 in keeping with the modern-day drinking habits of consumers and to compete with the reclosable PET bottles. However, a majority of consumers feel that the 28 mm opening is too small and the 38 mm opening is too large (Chihara and Yamazaki, 2012). Results of an optimization study showed that when the opening diameters are 35.4 and 34.4 mm in the case of green tea and carbonated beverage, respectively, the actual volume of fluid in the mouth is closest to the ideal volume and the participants feel most comfortable. These results were in agreement with the results of an earlier study by the same authors that found that an opening diameter of 33 mm was optimum for young Japanese adults.

TULC (Toyo Ultimate Can) is a two-piece can developed by Toyo Seikan Kaisha in Japan in 1991. ECCS, laminated with PET film on the interior and exterior surfaces, is processed into cups, similar to how D&I cans are processed. It is then drawn, stretched and ironed to reduce the thickness of the side walls but, unlike D&I cans, no coolant (lubricant) is used during the forming process, thus eliminating the need for coolant rinsing and wastewater treatment. Due to the internal layer of PET, no internal enamel/lacquer coating is required, resulting in a significant reduction in CO_2 emissions, a by-product of the internal lacquer curing process. More recently, a PET-laminated aluminum two-piece can known as aTULC has been developed.

7.5.3.2 Drawn and Redrawn

For many years, canmakers have manufactured shallow-drawn containers. However, the novelty of the DRD process is the use of multistage drawing to produce a can with a higher height-to-diameter ratio. This process is essentially identical to the initial stages of the D&I technique, except that the

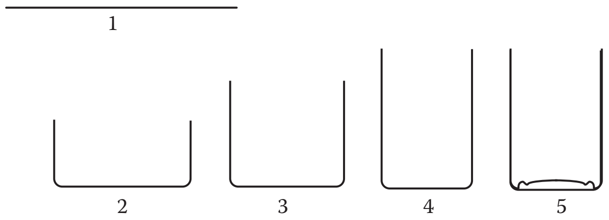

FIGURE 7.8 Sequential stages in the production of DRD cans: (1) body blank, (2) drawn cup, (3 and 4) diameter decreases as cup is redrawn and (5) finished trimmed can with profiled base.

final height and diameter of the container is produced by sequentially drawing cups to a smaller diameter—that is, causing metal to flow from the base to the wall of the container rather than ironing the container wall. As a consequence, the wall and base thickness, as well as the surface area, are identical to the original blank. This contrasts to the D&I can where the wall thickness is much less than the base thickness. A typical DRD process is illustrated in Figure 7.8.

In the D&I process, the internal diameter of the body remains constant throughout the ironing stages, whereas the internal diameter of the DRD can is progressively reduced as the height is increased during the various redrawing stages. Therefore, the DRD cans do not offer the same economies as D&I cans because, in the former, the metal cannot be selectively distributed as it can during wall ironing. Because the end is integral and is normally the thickest region, this governs the material gauge and the result is often excessive side wall thickness. Typically, 0.2 mm thick prelacquered tinplate and ECCS is used for the DRD process. DRD cans are currently used in the packaging of food rather than beverages since a greater wall thickness is required to withstand pressure reversals. The body is beaded, and ECCS is used more than tinplate since better enamel adhesion is achieved with the former.

7.5.4 PROTECTIVE AND DECORATIVE COATINGS

Container coatings provide a number of important basic functions (Turner, 1998):

- They protect the metal from the contents.
- They avoid contamination of the product by metal ions from the container.
- They facilitate manufacture.
- They provide a basis for decoration and product identification.
- They form a barrier to external corrosion or abrasion.

7.5.4.1 Protective Coatings

Internally enameled metal containers are used when the product and the plain container would interact to reduce the shelf life or the quality of the product to an unacceptable level. Thus, most vegetables, colored berry fruits, flesh foods and beer and soft drinks are packed in enameled containers; that is, containers in which organic coatings have been applied to the inside (and sometimes the outside) surfaces. The primary function of interior can coatings is to prevent interaction between the can and its contents, although some enamels have special properties that allow products such as meat loaf to be easily removed from the cans, while others are used merely to improve the appearance of the pack. Exterior can coatings may be used to provide protection against the environment (e.g., when the cans will be marketed in particularly humid or salt-laden climates), or as decoration to give product identity as well as protection. Generally, some external coating of tinplate and ECCS containers is necessary for products stored in hot humid atmospheres to prevent external corrosion, particularly at the side seam region for three-piece cans.

There are several essential requirements needed in an interior coating: it has to act as an inert barrier, separating the container from its contents and not imparting any flavor to the contents; it must resist physical deformation during fabrication of the container and still provide the required chemical resistance; and the enamel must be flexible, spread evenly, completely cover the substrate and adhere to the metal surface. Adhesion failure may occur during, or as a result of, mechanical deformation during heat processing or undermining by corrosion.

For most containers, the enamel is applied to the metal in the flat before fabrication, typical film masses being in the range between 3 and 9 gsm (4–12 μm thick). However, because of the considerable amount of metal deformation with substantial disruption of the surface that takes place in the D&I operation, such containers must be coated internally after fabrication. Control of the dry film weight is essential if the enamel is to function correctly. A dry film that is too thin may not cover the surface completely, while an overly thick film leads to brittleness and impaired protection, as well as being uneconomical. As the enamel film has imperfections and is damaged during container manufacture, it does not give complete protection to the can. Where it is essential to minimize product–container interactions, for example, for canned beer and soft drinks where metal pickup can affect flavor and clarity, the cans are given a post-fabrication repair lacquering.

Many types of internal enamel coatings are available for food containers including epoxy–phenolic, epoxy–amino, epoxy–acrylate, epoxy–anhydrite, vinyl organosol, thermoset polyester, thermoset polymer coated, phenolic and oleoresinous (see Table 7.5). The original can coatings were based on oleoresinous products that include all those materials made by fusing natural gums and rosins and blending them with drying oils such as linseed or tung (Chinese wood oil). Oleoresinous coatings were popular largely because of their low applied cost, but their open micellar structure made them prone to corrosion/staining problems with sulfur-bearing products unless they were pigmented with zinc oxide. In addition, they lacked resistance to retorting processes and had poor color retention and taste characteristics. For these reasons, a move has been made to synthetic epoxy-based resins and, apart from some specific applications, oleoresinous-based coatings find little general usage today.

The terminology used for epoxies can be confusing. Epoxy groups (also called epoxides) are three-membered cyclic ethers that, strictly speaking, should be called oxiranes. Most commercially important epoxy resins are derived from (chloromethyl)oxirane, more commonly known as epichlorohydrin (ECH). The resins generally contain oxiranylmethyl ethers or esters, usually called glycidyl ethers or esters (Wicks et al., 2007).

The first epoxy resins used in coatings were bisphenol A (BPA) epoxies made by reacting BPA with ECH. Under basic conditions, the initial reaction is formation of a BPA anion (BPA^-), which attacks ECH and results in the elimination of a chloride anion (Cl^-) and the formation of the monoglycidyl ether of BPA (MGEBPA). Analogous reaction of the phenolic group of MGEBPA with NaOH and ECH gives the diglycidyl ether of BPA (DGEBPA) commonly known as bisphenol A diglycidyl ether (BADGE). The epoxy groups of MGEBPA and DGEBPA react with BPA^- to extend the chain. These reactions introduce alcohol groups on the backbone and continuation of these reactions results in linear polymers, since both the BPA and ECH are difunctional. Bisphenol A epoxy resins are made with excess ECH, so the end groups are glycidyl ethers (Wicks et al., 2007). MW is controlled by the ratio of ECH to BPA, and as the ratio of ECH to BPA is reduced, the MW increases. The lowest MW epoxy resin used is BADGE.

Epoxy resins based on BPA and ECH have been used in coatings for metal packaging since the 1950s and are the single most widely used class of resin in use today for metal packaging, with epoxy–phenolic coatings finding the largest application (Oldring and Nehring, 2007). Epoxy resins are cross-linked through both their hydroxyl and oxirane functionalities, using phenolic or amino resins and occasionally an anhydride oligomer. The success of epoxies as coatings for food cans is due to their desirable flavor-retaining characteristics, their excellent chemical resistance and their outstanding mechanical properties. Some epoxy components and the by-products of epoxy resins are known to migrate from the cured epoxy-based can coating into foods. Particular interest and concern has been given to BPA, BADGE, BADGE derivatives and epoxidized soya bean oil (ESBO). The safety aspects of these chemicals are discussed in Chapter 22.

TABLE 7.5
Metal Can Coatings

Coating Type	Properties	Main Applications
Epoxy–phenolic	High-MW epoxy resins cross-linked with phenolic resole resins	Most widely used coating
	Provides good flexibility and very good pack resistance for aggressive acid products	Universal golden coating for three-piece and shallow-drawn cans
Epoxy–amine and epoxy–acrylate	High-MW epoxy resins cross-linked with amino or acrylate resins	Universal lacquer for beer and beverage cans
	Employed now in waterborne coatings	Sideseam stripe in high solids form for welded cans
Epoxy–anhydride	High-MW epoxy resins cross-linked with anhydride hardeners	Internal white coating for three-piece cans and ends
	Good fabricability; withstands beading	
	Very good chemical resistance	
Vinyl organosol	PVC dispersed in an appropriate solvent and stabilized with low-MW epoxy resin or ESBO	Drawn cans Easy-open ends Often used over epoxy-phenolic base coat
	Good fabricability; superior corrosion resistance	
Thermoset polyester	Polyester resins cross-linked with phenolic or amino resins	Internal and external coating for two-piece and three-piece cans and ends for meat, fish and vegetables
	May contain low-MW epoxy resins	
	Very good chemical resistance	
	Good fabricability and withstands beading	
Thermoplastic polymer coated	Extrusion coated or laminated film of polypropylene, polyester, polyamide or combinations thereof	Shallow drawn cans Easy-open and standard ends
Phenolic	Low cost	Drums and pails where flexibility is not a critical factor
	Poor flexibility but excellent resistance, particularly for aggressive foods	
Oleoresinous	Naturally occurring oils and fatty acids with synthetic modification	A general-purpose, golden-colored, inexpensive coating Once very common but now very limited use

Source: Adapted from Whitaker, R., Metal packaging and chemical migration into food, in: *Chemical Migration and Food Contact Materials*, Barnes, K.A., Sinclair, C., Watson, D.H. (Eds), CRC Press, Boca Raton, FL, pp. 251–270, 2007; Hernandez, R.J. and Giacin, J.R., Factors affecting permeation, sorption, and migration processes in package-product systems, in: *Food Storage Stability*, Taub, I.A. and Singh R.P. (Eds), CRC Press, Boca Raton, FL, pp. 269–330, 1998.

Although their importance has waned, phenolic resins still have significant uses. Phenolics are made by reacting formaldehyde with phenolic monomers such as phenol, cresols, xylenols and substituted phenols. The products depend on the phenol(s) used, the stoichiometric ratio of phenol to formaldehyde and the pH during the reaction. Phenolic resins are divided into two broad classes: *resole* phenolics, which are made using alkaline catalysts and high ratios of formaldehyde to phenol, and *novolac* phenolics, which are made using acid catalysts and low ratios of formaldehyde to phenol (Wicks et al., 2007). Phenolic coatings are low cost and have exceptional acid resistance and good sulfur resistance. Film thickness is restricted by their inflexibility and they have a tendency to impart off-flavor and odor to some foods.

Resole phenolic resins are used in interior can coatings and require baking using an acid catalyst to cure in short times. To enhance flexibility and adhesion, they are commonly blended with low MW poly(vinyl butyral) as a plasticizer. The films are resistant to swelling by oils, such as encountered in canned fish, and are completely resistant to hydrolysis. These resins and other heat-reactive phenolics discolor during baking due to quinone methide formation, which restricts their use to applications for which development of a yellow-brown color is acceptable (Wicks et al., 2007).

For most applications, phenolic resins are plasticized with epoxy resins with which they react to yield a cured film. A three-dimensional structure (normally golden in appearance) is formed during curing and baking, which combines the good adhesion properties of the epoxy resin with the high chemical resistance properties of the phenolic resin. The balanced properties of epoxy–phenolic coatings have made them almost universal in their application on food cans with the exception of deep multistage DRD cans. Epoxy–phenolics are among the most chemically resistant known coatings and are the predominant protective coatings used for lining the interior of metal food cans. They are made either by straight blending of a solid epoxy resin with a phenolic resin, or by the precondensation of a mixture of two resins in appropriate solvents. These resins are often polymerization products of BADGE or novolac diglycidyl ether (NOGE, also known as epoxy novolac) and the lowest MW component of NOGE is bisphenol F diglycidyl ether (BFDGE).

Vinyl coatings to improve retort resistance are based on copolymers of vinyl chloride and vinyl acetate of low MW (frequently with a small amount of a third monomer to impart special properties) dissolved in strong ketonic and aromatic hydrocarbon solvents. The vinyl acetate lowers the T_g. Vinyl chloride copolymers require stabilization to prevent thermal and photochemical degradation as they undergo dehydrochlorination in an autocatalytic chain reaction. The long carbon–carbon chains make them thermoplastic, and they can be blended with alkyd, epoxy and phenolic resins to enhance their performance. The essential qualities of vinyl coatings are adhesion, high flexibility and a complete absence of taste. Their flexibility allows them to be used for caps and closures as well as drawn cans. Their main disadvantage is their high sensitivity to heat and retorting processes, restricting their application to cans that are hot filled rather than retorted, and to beer and beverage products.

An organosol is a colloidal suspension or dispersion of very finely divided, insoluble material suspended in an organic liquid in which it cannot dissolve at normal temperatures. Vinyl organosol coatings incorporate a dispersion of high MW PVC resins in hydrocarbon solvents with a plasticizer such as dioctyl phthalate to aid film formation. Organosol have all the desirable properties found in vinyl coatings, together with better process resistance. Soluble thermosetting resins (including epoxy, phenolic, acrylic and polyesters) are added in order to enhance the film's chemical resistance, thermal stability and adhesion. BADGE and NOGE have been used as additives to vinyl organosols to scavenge the HCl formed during heat treatment in the coating procedure and they can migrate into the food during retorting if the curing process is unsuccessful.

Polyester-based coatings provide an alternative to epoxy-based resins. In these systems, the three-dimensional coating network is built up from any combination of a number of polyfunctional alcohol and carboxylic acid monomers. Polyester-based coatings can be thermoplastic, as used in sideseam stripes, or they can undergo cross-linking reactions (typically through their hydroxyl functionality) with a number of systems, such as phenolic resins, amino resins (particularly melamine formaldehyde resins) or polyisocyanates (Oldring and Nehring, 2007). It is desirable that the product arising from such modification should be free from migrating components and by-products, but possible candidates for migration include cyclic oligomers of the initial polyester resins. Among attempts to reduce this migration potential, polyester–polyurethane (PEPU) coatings were developed. Such coatings commonly contain a hardener precursor such as a polyisocyanate, resulting in coatings that develop urethane linkages during the curing process (Jiang et al., 2010).

Amino resins are based on the reaction products of urea, melamine or benzoguanamine with formaldehyde and frequently a low MW aliphatic alcohol. Their prime use in coatings for metal packaging is as a cross-linking resin for either epoxy or polyester resins. Amino resins typically undergo some degree of self-condensation reaction during their manufacture. During the curing process, they react with functionalities in the other resins present in the coating, as well as undergoing some self-condensation reactions, which can give rise to "clusters" of amino resin moieties in the cured coating (Oldring and Nehring, 2007). They are a universal coating for beer and beverage cans.

Trimellitic acid (TMA) and its anhydride are used as curing agents for the manufacture of epoxy–anhydride coatings, for example, a few percent of TMA is added to BADGE-type resins as a cross-linker. They are often based on the reaction product of trimellitic anhydride with an aliphatic glycol such as ethylene glycol and the anhydride functionality is retained. The resulting coating, typically white owing to added titanium oxide, is used in some 10% of all food cans.

As an alternative to applying coatings on metal, thermoplastic films can be laminated or extruded onto the metal and the coated metal formed into cans or can components. Films may consist of PP, PA, a PP/PA coextruded combination or PET, the latter being the most common.

PET coatings provide waterproof protection to ECCS plate, prevent physicochemical interactions with the environment, and offer resistance to surface mechanical damage during handling and transport of the metal sheets. However, the polymer-coated sheets can undergo damage during rolling and forming resulting in fracture, detachment of the polymer layer, discontinuities between coating and substrates, and the presence of surface microdeformations after these processes. All of these features are of considerable importance in determining the formability limits of ECCS plate. The PET layer can be subject to thermomechanical deformation during the processing and manufacturing of plates, such as extrusion, drawing, and molding, but during these processes, microstructural and mechanical properties of PET coatings are for the most part independent (Zumelzu et al., 2009).

Novel, highly functional biobased epoxy compounds, epoxidized sucrose esters of fatty acids (ESEFAs), have recently been cross-linked with a liquid cycloaliphatic anhydride to prepare polyester thermosets with a high biobased content (71%–77% in theory). They have excellent properties in the equivalent ratio of epoxides to anhydrides of 1:0.5. Because of the high performance achieved, they may have wide-ranging applications in areas where thermally cured materials are used such as in protective coatings (Pan et al., 2011).

Instead of using enamels, there is considerable interest in using different organic (heterocyclic) compounds that can act as cathodic or anodic corrosion inhibitors. Essential onion oil (EOO) has been proposed as a potential inhibitor of tin and chromium dissolution from tinplate sheets. The influence of EOO on the dissolution of iron and the porosity of tinplate was investigated by Grassino et al. (2010) who reported that EOO improved the protection of tinplate compared with DOS oil, and was almost as effective as epoxy–phenolic lacquer. They recommended the addition of EOO due to the lower cost of canned food production and enhanced organoleptic properties, but the storage temperature has to be lower than 36°C to avoid accelerating the corrosion process.

Sulfur-resistant enamels are used to prevent the staining of tinplate surfaces by sulfur compounds released from foods such as meat, fish and vegetables with sulfur-containing amino acids that breakdown during heat processing and storage to release sulfides. These react with tin to form black tin sulfide, or accumulate in the headspace and give out an unpleasant odor. To overcome this problem, two approaches have been used. Enamels are pigmented with zinc oxide or zinc carbonate that reacts with the sulfur compounds to form white zinc sulfide (these are known as the sulfur-absorbing enamels), or the enamels are pigmented with aluminum powder or white pigment to obscure any unsightly black tin sulfide that might form (these are known as sulfur-resisting enamels).

In the United States, most fruits and vegetables are packed in cans with an interior coating called an R enamel (from R for regular). Historically, R enamel was a phenolic varnish but now it is more commonly a phenolic resin or an epoxy–phenolic coating (a resole phenolic), with a BPA epoxy and phosphoric acid catalyst (Wicks et al., 2007). For packing vegetables such as corn that give off sulfides during retorting, fine-particle-size zinc oxide pigment is dispersed in the coating, which is called a C enamel (from C for corn). Acidic products should not be permitted to come into contact with coatings containing zinc oxide because the reaction may produce zinc salts that could destroy the continuity of the film (Oldring and Nehring, 2007).

Coatings obtain their final color in various ways. Epoxy–phenolic coatings normally generate a golden color when cured due to the chromophores in the phenolic resin; the color is a useful indicator of the degree of cure for a given system. White coatings are made by the addition of titanium dioxide, often in an epoxy–anhydride coating or sometimes an organosol, for example, vinyl organosol coatings are typically white or buff colored due to the addition of titanium dioxide. Aluminum powder is added to a coating to give a grey "aluminumized" appearance to the final film (Oldring and Nehring, 2007). Enamels pigmented with aluminum powder or other materials were described earlier as sulfur-resisting enamels, but they are also used in premium quality packs (where sulfur staining is not a problem), simply to improve the appearance of the inside can surface.

In coatings for meats such as ham, a key requirement is that the coatings permit the release of the product from the can. This requires that a release agent such as petroleum or polyamide wax be incorporated into the coating.

Two methods are used for the application of protective coatings to metal containers: roller coating and spraying, the former being the most widespread. Roller coating is used if physical contact is possible; thus, it finds use in the coating of material in sheet and coil form, and the external coating of cylindrical can bodies. Spraying techniques are used if physical contact is impossible or difficult; thus, it finds use mainly to coat the inside surface of can bodies, including two-piece D&I and sometimes DRD cans.

Because the coating is generally applied wet (i.e., the resin is suspended in a carrier such as an organic or aqueous solvent for ease of application), it must be dried after application by solvent removal, oxidation or heat polymerization. This process (known as baking or curing) is usually carried out in a forced convection oven using hot air at up to 210°C for up to 15 min. Today's resin formulations require lower temperatures and shorter curing times, and this is achieved through the use of UV radiation to accelerate polymerization. Such UV-cured resins are virtually solvent free. They contain photosensitive molecules that absorb the UV radiation and release free radicals, which polymerize or cross-link the liquid resin to form a solid coating almost instantly. Because the substrate is not heated, it can be handled immediately for further operations, and substantial savings (up to 50%) in energy and space are possible. UV-curable coatings based on low-viscosity aromatic, aliphatic and cyclo-aliphatic epoxy resins are used to coat the exterior and ends of cans.

Powder coating, where the resin is applied "dry" in the form of a fine powder under the direction of an electrostatic field, is used mainly where heavy coatings are required, such as in the protection of welded side seams where the bare metal that exists in the weld area (most of the tin is removed during the welding process) must be covered. Curing is usually by gas heating or high-frequency induction heating. Powdered coatings contain little or no volatile effluents and require low energy consumption for application and cure.

Electrophoretic deposition, a process originally developed for protecting automobile bodies, has been used for coating both two-piece and three-piece cans (Silbereis, 2009). A resin film is deposited electrically from an aqueous suspension, providing a far more even distribution than that obtained by spraying. Moreover, its throwing power enables it to coat regions inaccessible to spray. The process overcomes the current wasteful spray techniques with almost 99% coating utilization achieved.

Owing to environmental concerns and legislation concerning VOCs, the trend is for waterborne coatings to replace organic coatings that can consist of up to 70% solvent. The aqueous coatings contain only a small amount of organic solvents, and can be applied using essentially the same coating and curing equipment.

7.5.4.2 Decorative Coatings

Although the primary purpose in decorating the external surface of a metal container is to improve its appearance and assist its marketability, it also significantly improves the container's external corrosion resistance. In many respects, decoration of the external surface is similar to the process used to protect the internal surface, with the constituents generally being dispersed in volatile solvents, applied on roller coating machines (apart from the printed image) and baked in tunnel ovens.

Offset lithography (see Chapter 9 for a description) has been used for over a century for decorating sheet metal. Because metal is nonabsorbent, the coatings and prints cure by internal chemical reactions involving oxidation, polymerization or both. By adjusting the tack properties of the ink, it is possible to print one wet ink onto the previous wet ink ("wet-on-wet") without the second blanket picking off the first layer. Methods used to "set" the ink in between single color presses in tandem include high temperature air blasts, flame treatment and, more recently, the application of UV radiation to the print. The development of UV-curable resins has found application in the metal decorating industries for both printing inks and coatings that give instantaneous curing, reducing costs, space and production time. This has necessitated a new approach to ink formulation. The print process is usually carried out with sheet stock prior to slitting into can body blanks or scroll shearing into end stock. With the advent of two-piece cans, less elaborate designs are used on beer and beverage cans because of the necessity to use presses that can print completely fabricated cans.

7.6 ALUMINUM FOILS AND CONTAINERS

7.6.1 Aluminum Foil

Aluminum foil is a thin-rolled sheet of alloyed aluminum varying in thickness from about 4–150 μm. It was first produced commercially in the United States in 1913 where it was used for wrapping Life Savers™, candy bars and chewing gum. In 1921, it was laminated on paperboard for folding cartons. Household foil was marketed in the late 1920s, and the first heat sealable foil was developed in 1938. Formed or semirigid containers appeared on the market in 1949.

Foil can be produced by two methods: either by passing heated aluminum sheet ingot between rollers in a mill under pressure and then rerolling on sheet and plate mills until the desired gauge is obtained or continuously casting and cold rolling. This latter method is much less energy intensive and has become the preferred process.

Aluminum foil is available in a variety of alloys (see Table 7.4), with the alloys 1100, 1145 and 1235 most commonly used in flexible packaging and 3003 when heavier gauges are required for stiffness. In the softest temper, aluminum foil exhibits dead fold characteristics—that is, when wrapped around an object it will assume the profile of the object with no spring back. Although this is frequently advantageous, soft temper foil also wrinkles very easily, which necessitates the use of great care during handling.

Aluminum foil is essentially impermeable to gases and water vapor when it is thicker than 15 μm, but it is permeable at lower thicknesses due to the presence of minute pinholes. For example, 12 μm thick foil has a WVTR of $\leq 0.01\,\text{g m}^{-2}\,\text{day}^{-1}$, and 8–9 μm thick generally of $0.07\text{–}0.1\,\text{g m}^{-2}\,\text{day}^{-1}$ (Lamberti and Escher, 2007). These values are still far below those of most plastic films used for food packaging and, at thicknesses below 15 μm, aluminum foil is mainly used with polymers or lacquers, thus making the effect due to pores negligible.

Aluminum foil can be converted into a wide range of shapes and products including semirigid containers with formed foil lids, caps and cap liners, composite cans and canisters, laminates containing plastic and sometimes paper or paperboard where it acts as a gas and light barrier and foil lidding, the latter being sealed using inductive sealing (see Chapter 10). Processes involved may include converting, forming, laminating, coloring, printing and coating. It can also be embossed to provide textured surfaces.

7.6.2 TUBE

The collapsible aluminum tube is a unique food package that allows the user to apply the product directly and in precise amounts when required. Typical applications include condiments such as mustards, mayonnaises and sauces, as well as dessert sauces, cheese spreads and pâté.

The aluminum tube is formed by the cold impact extrusion of an aluminum slug using a plunger. To relieve the hardness, the tube is annealed in an oven at 600°C, after which the inside is enameled with an epoxy–phenolic or acrylic lacquer. Aluminum tubes are printed by a dry offset process (see Chapter 9) using either thermally or UV-cured inks. Aluminum tubes are closed by folding after the application of latex or heat sealable lacquer inside the fold area, and heat applied, which ensures a hermetic seal. Currently, the aluminum tube is relatively rare with most food tubes being made of plastic laminates.

Foil laminate tubes are sealed using a high frequency, which generates an eddy current in the aluminum, heating up the surrounding plastic layers and forming a hermetic seal. Although early plastic tubes contained aluminum foil as a barrier layer, it is now common to coextrude LDPE with EVOH to obtain a tube that provides an excellent barrier to air and moisture. Plastic tubes are also printed by a dry offset process.

7.6.3 RETORT POUCH

Developed in the 1950s, the retort pouch is a flexible package, hermetically sealed on three or four sides and made from one or more layers of plastic or foil, each layer having a specific functionality. The choice of barrier layers, sealant layers and food contact layers depends on the processing conditions, product application and desired shelf life. Typical processing conditions involve temperatures of 121°C for times of up to 30 min (60 min for the large [3.5 kg] catering packs). One of the attractions of the retort pouch compared to the metal can is the thin profile of the package (12–33 mm for 200–1000 g pouches), enabling retorting times to be reduced by up to 60%, final quality to be improved, as well as rapid reheating prior to consumption. Other advantages include the ease of carrying, reheating and serving, as well as weight and space saving. Finally, disposal of the used pouch is much simpler than for the metal can as it can be easily flattened. It is for all of these reasons that retort pouches have found wide acceptance by military forces, the U.S. military term for this type of package being "Meal, Ready-To-Eat" (MRE). NASA began using retort pouch food for space missions in the 1970s and the U.S. Army began delivering large quantities of MREs to the troops in 1981 (Lampi, 2009). The current packaging material specification for MREs (MIL-PRF-44073F, 2006) includes performance requirements for OTR $\leq$ 0.06 mL m^{-2} day^{-1} atm^{-1} and WVTR $\leq$ 0.01 g m^{-2} day^{-1}.

A typical three-layer pouch structure would consist of an outer layer of 13 μm PET for strength and toughness; a middle layer of 9–18 μm aluminum foil as a moisture, light and gas barrier and an inner layer of 70–100 μm CPP for heat sealability, strength and compatibility with all foods. An additional inner layer of 15–25 μm BON-6 is used when a longer shelf life is required. Traditionally, a three-sided seal pouch was used for MREs and other commercial products, but this has been superseded by a multilayer four-side-seal pouch. Stand-up pouch designs having a gusseted bottom have also been commercialized.

Transparent retort pouches can be produced by replacing the aluminum foil layer. Typical structures including PET-OPA-CPP, SiO_x PET-OPA-CPP, AlO_x PET-OPA-CPP, OPA-PVdC-CPP and OPA-EVOH-CPP. These materials allow the pouch to be reheated in a microwave oven.

Unlike the metal can, retort pouches are susceptible to rupture or seal separation during retorting if the internal pressure exceeds the external process pressure. This is most likely to occur at the start of the cooling cycle when the product is at its hottest. The use of superimposed air pressure to counter balance the buildup in internal pressure in the pouch and control pouch integrity is necessary. Retorts used in processing pouches can be batch or continuous, and agitating or static. It is also necessary to use trays that support the pouches and ensure uniform thickness and, thus, an adequate thermal process.

The shelf life of foods packaged in retort pouches is very dependent on storage temperature. If stored at 16°C, they will have a shelf life of about 130 months. If they are stored at 27°C, then shelf life will be 76 months; at 38°C, 22 months and at 50°C, only a month. Because of this, military MREs are stored in climate-controlled warehouses where they can be kept for up to 10 years at chill temperatures before being used.

Pouches are reverse printed on the PET layer using any of the standard plastic printing techniques (see Chapter 9). However, the highest quality printing is generally obtained using rotogravure, with the high gloss of the PET adding a reflective sparkle to the surface of the package.

A recent development has been the incorporation of zippers into the pouch to make it easier to open and reseal. Conventional zippers are made of LDPE that will not withstand retort temperatures, forcing zipper manufacturers to design zippers made from PP resins and match them with compatible pouch film. Aesthetic considerations have also had to be addressed. Because food migrates to the edges of the pouch during retorting, a secondary barrier to shield the zipper and prevent food from crusting around it had to be designed.

Laser scoring (done on either the exterior or interior surface) can withstand the conditions in a retort and maintain pouch integrity. With laser-scored packages, the laser beam “burns off” a portion of the substrate, providing a line for easy, uniform tearing of the pouch. However, the laser should only remove enough substrata to allow easy opening while not providing a route for O_2 migration through the pouch, which would decrease shelf life.

Several investigations on the effect of retorting on the O_2 barrier of packages containing EVOH have shown a significant deterioration. In a recent review, Mokwena and Tang (2012) summarized reported results. An increase in OTR of more than 10 times has been reported for a PET/EVOH/PP pouch and about 47 times for PET/PP/PA-6/EVOH/PA-6/PP pouch after retorting for 28 min at 125°C. Generally, a larger increase has been observed for film containing EVOH than for other barrier materials such as PVdC copolymer. The OTR for film containing EVOH increased by more than 60 times compared to only 1.4 times for SiO_x-coated and PVdC copolymer films under similar retort conditions. The effect of retort processing on EVOH has been explained on the basis of both plasticization of the polymer matrix and alteration in polymer morphology. An irreversible partial dissolution of EVOH crystalline regions occurs due to pressurized heated water entering the polymer and disrupting the intermolecular hydrogen bonding between EVOH chains.

In general, part of the O_2 barrier of multilayer EVOH films lost during retorting is recovered during long-term storage. Thus, while the O_2 barrier of such films decreased considerably during the first 2 months of storage, it remained relatively constant for the rest of the storage period (up to 12 months), although the preprocessing OTR values were not reached during the entire storage period. At steady-state (i.e., after 2 months), the OTR for PET/EVOH/PP film was about four times that of the initial preprocessing value, while that of PET/PP/PA-6/EVOH/PA-6/PP film was about eight times the initial preprocessing value. The OTRs for both films processed by combined microwave-hot water processing remained below 2 mL m^{-2} day^{-1} over 12 months of storage, a value that is comparable to commercially available PVdC copolymer-laminated films currently used in the United States as lidstock film for shelf stable products. Others have reported that during long-term storage of rigid containers of polyolefin/tie/EVOH/tie/polyolefin, steady-state was reached after 200 days of storage, at which time the OTR was four times higher than the preprocessing value. In contrast, others have reported that the OTR was only four times the initial value 6 days after retorting at 121°C for 20 min. In practice, the lack of full barrier recovery during storage can result in substantial additional quantities of O_2 permeating into the package, leading to possible deterioration of O_2 sensitive foods, especially during the first few weeks of storage.

Although the O_2 barrier properties of EVOH are compromised when exposed to high moisture conditions, EVOH acts as an effective O_2 barrier in rigid retort packages when used in combination with water-resistant polymers such as PP. For thin film structures (<0.254 mm), EVOH is vulnerable to the effects of high moisture and high temperature conditions encountered during retorting. Therefore, a properly designed package that incorporates both good material selection and their correct positioning in the multilayer structure is essential to achieve the optimal O_2 barrier.

7.6.4 BOTTLE

The aluminum beverage bottle (also referred to as a bottlecan) was launched by two Japanese breweries in 2000 and in the United States for energy drinks in 2001. The bottles are made by either an impact extrusion (IE) or, since 2008, a Coil-to-Can (C2C) process, resulting in a wide range of shapes and sizes. A variety of standard finishes is available including a 26 mm standard crown cap, 38 mm lug finish, 38 mm continuous thread with plastic sleeve, 38 mm ROPP and 28 mm continuous thread.

IE is a technique originally developed to produce a heavier-wall aerosol container that could withstand greater internal pressure. The process involves pushing a mandrel into a die cylinder containing an aluminum slug with up to 3.5×10^8 kg m^{-2} of force. Through the impact, the metal of the slug is forced to flow up along the inside of the die, creating a seamless can body. As IE evolved, manufacturers took advantage of the softness of the aluminum alloy to add shaping capabilities to the necking area, resulting in threaded bottle openings that have essentially brought resealable aluminum cans to the beverage market to compete with resealable PET bottles.

The key to the C2C process is combining traditional D&I beverage canmaking technology on the front end with the IE shaping capabilities on the back end. IE bottles are produced with three times the aluminum of a traditional beer can; C2C bottles use 30%–40% less aluminum than IE bottles. The 3104 alloy used for the C2C process is lighter but stronger and harder than the 1070 pure virgin aluminum alloy used for IE that is much harder to shape.

7.7 CORROSION OF METAL PACKAGING MATERIALS

7.7.1 FUNDAMENTAL CONCEPTS

7.7.1.1 Introduction

Metals are important materials for the packaging of foods, combining properties of strength, toughness, ductility and impermeability. However, the chemical structure that gives them their valuable practical properties is also responsible for their main weakness—their susceptibility to corrosion. Corrosion is the term used to describe the chemical reaction between a metal and its environment to form compounds; it is a universal process affecting all metals to some extent. Because the reaction takes place at the metal surface, the rate of attack can be reduced and controlled by modifying the conditions at the surface.

Metals are chemically reactive and can be readily oxidized by O_2 and other agents to form largely useless corrosion products. This vulnerability to oxidation accounts for the fact that with few exceptions (copper, silver and gold), metals do not occur naturally in the metallic state but are found combined with O_2 or sulfur in their ores. A considerable amount of energy is required to extract metals from their ores, and the reverse process (which releases energy) is strongly favored as the metal reverts back to its natural state. Generally, it can be said that the more difficult it has been to win the metal from its natural form, the greater will be its tendency to return to that form by corroding, but the rate of return will, of course, depend on the environment.

7.7.1.2 Electrochemical Corrosion

The reaction of metals in aqueous solutions or under moist conditions (known as wet corrosion) is electrochemical in nature, involving the transfer of electrical charges across the boundary formed by the metal surface and its environment. An electrolyte is a medium that conducts electricity by the movement of ions, the cations (e.g., Fe^{2+}) and anions (e.g., Cl^-) moving in opposite directions. When an electrode reaction takes place at a metal surface, the electron flow in the metal corresponds to an ion flow in the electrolyte.

When a metal corrodes, atoms of the metal are lost from the surface as cations, leaving behind the requisite number of electrons in the body of the metal. This dissolution of the metal is called an *anodic reaction* and takes place at a surface termed an *anode*; an anodic reaction always involves the release of electrons or electrochemical oxidation. Thus, for the case of a metal, M,

$$\underset{\text{(reduced)}}{\mathrm{M}} \rightarrow \underset{\text{(oxidized)}}{\mathrm{M}^{n+}} + n \text{ electrons} \tag{7.1}$$

Simultaneously, reagents in the electrolyte solution react with the metal surface to remove electrons left behind by the departing metal ions. This removal of electrons is termed a *cathodic reaction* and takes place at a surface called a *cathode*. The cathodic reaction always involves the consumption of electrons or electrochemical reduction.

Since practically all metals are covered with an oxide film, this must be removed before the metal can be exposed to an electrolyte. A metal covered with an oxide has different properties in solution from a bare metal, but in studying electrochemical corrosion, it is simplest to begin with the ideal case of a pure, bare metal electrode on which the only reaction occurring is metal dissolution.

7.7.1.3 Electrochemical Series

The removal of electrons from a metal to form an ion involves energy. When a metal with a high reaction energy is in an electrolyte, and is connected to one of lower reaction energy in the same electrolyte, electrons will flow from the high to the low energy level. If an infinite resistance voltmeter is placed across the system, it will show the difference in potential (E) between the two metals; this is a measure of the relative tendencies of the metals to corrode in the particular environment involved.

Because only differences in potential are measurable and not absolute values, it is desirable to have some reaction equilibrium as a datum or reference zero of potential from which other potentials could be measured. This was chosen as hydrogen gas at a pressure of 1 atm in equilibrium with hydrogen ions at pH = 0 and 25°C, and is taken as zero. Potentials measured relative to this reaction are indicated as E_H in volts. A list of equilibria and standard electrode potentials obtained from such measurements is usually called the *electrochemical series* or the *electromotive force series*, and an abridged version is shown in Table 7.6. The gold or noble end of the series is the cathodic end, and the aluminum or base end the anodic end. The further down the series a metal appears, the more readily it will give up its electrons—that is, it is more electropositive and has a greater potential to corrode.

The potentials shown in Table 7.6 refer to metals free from an oxide film. Aluminum, which covers itself with a highly protective oxide film that can be difficult to remove, commonly gives values much less negative than that indicated in Table 7.6, so that aluminum is frequently "nobler" than, for example, chromium.

While oxide films on the metal tend to shift the potential in the positive (noble) direction, the presence of salts that form complex ions containing the metal in question renders the potential abnormally negative. This is particularly important in the case of tinplate and is discussed further in Section 7.7.2.1.

In many ways, hydrogen behaves like a metal, and the chemical reduction of hydrogen ions can balance the corrosion reaction or ionization of any metal whose potential occurs below the hydrogen/hydrogen-ion equilibrium potential. Iron and tin will always tend to corrode in aqueous

TABLE 7.6
Electrochemical Series

Equilibrium Reaction	**E_H (volts)**	
Cathodic end		
$Au^{2+} + 2e^- \Leftrightarrow Au$	+1.50	↓ Increasing potential to corrode
$\frac{1}{2}O_2 + 2H^+ + 2e^- \Leftrightarrow H_2O$	+1.23	
$Fe^{3+} + e^- \Leftrightarrow Fe^{2+}$	+0.77	
$\frac{1}{2}O_2 + H_2O + 2e^- \Leftrightarrow 2OH^-$	+0.40	
$Cu^{2+} + 2e^- \Leftrightarrow Cu$	+0.34	
$2H^+ + 2e^- \Leftrightarrow H_2$	0.00 by definition	
$Pb^{2+} + 2e^- \Leftrightarrow Pb$	−0.13	
$Sn^{2+} + 2e^- \Leftrightarrow Sn$	−0.14	
$Ni^{2+} + 2e^- \Leftrightarrow Ni$	−0.25	
$Fe^{2+} + 2e^- \Leftrightarrow Fe$	−0.44	
$Cr^{3+} + 3e^- \Leftrightarrow Cr$	−0.74	
$Al^{3+} + 3e^- \Leftrightarrow Al$	−1.66	
Anodic end		

environments since the ionization or corrosion reaction can be balanced by hydrogen-ion reduction (i.e., evolution of hydrogen gas):

$$2Fe \rightarrow Fe^{2+} + 2e^- \tag{7.2}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{7.3}$$

If the concentration of hydrogen ions is increased (i.e., the aqueous environment has a lower pH), then the rate of the reaction tends to increase.

For those metals above the hydrogen/hydrogen-ion equilibrium (i.e., those metals which have a positive E_H), hydrogen-ion reduction will not give a balancing reaction for their corrosion, and some other reaction must be available if they are to corrode. The reduction of gaseous O_2 is such a reaction, except in the case of gold. If free O_2 were available, the corrosion reaction would be balanced by O_2 absorption, and, in the case of tin, the balanced reactions would be

$$Sn \rightarrow Sn^{2+} + 2e^- \tag{7.4}$$

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \tag{7.5}$$

It follows that the reduction of any available free O_2 will assist hydrogen-ion reduction in balancing the corrosion of metals that are below the hydrogen/hydrogen-ion potential (i.e., have a negative E_H). This explains why, for example, in the canning of foods, positive attempts are made to remove O_2 from the can prior to seaming on the can end.

It is important to realize that the thermodynamic approach, as embodied in the electrochemical series, has severe limitations if used as a single basis for any theory of corrosion. This is because the effect of films that may form on metals under a variety of conditions is not taken into account by theories based only on the electrochemical series. For example, since chromium and aluminum are both more basic than iron, the electrochemical series predicts that they are both more liable to corrode. This is often interpreted as implying that they would both corrode more rapidly than iron. However, it is well known that these metals are far more corrosion resistant than iron in a wide variety of practical environments. In fact, chromium is added to steel in substantial quantities as an alloying constituent to produce corrosion-resistant stainless steels.

7.7.1.4 Factors Affecting the Rate of Corrosion

7.7.1.4.1 Polarization of the Electrodes

The potentials recorded in Table 7.6 represent equilibrium values. When a current flows, there is a change in the potential of an electrode; this is known as *polarization*. As the current begins to flow, the potential of the cathode becomes increasingly negative and the anode increasingly positive. Consequently, the potential difference between the anode and the cathode decreases until a steady state is reached when corrosion proceeds at a constant rate. Thus, the corrosion current and, therefore, the corrosion rate will be affected by anything that affects the polarization of the electrodes.

The potential at which the reaction takes place changes by an amount called the *overpotential*, η, which is defined as

$$\eta = E_{\mathrm{corr}} - E_{\mathrm{i}} \tag{7.6}$$

where E_{corr} is the corrosion potential and E_{i} is the polarized potential. The anodic overpotential η_{a} drives the metal dissolution process, and the cathodic overpotential η_{c} drives the cathodic deposition process (Mannheim and Passy, 1982).

The dominant polarization term controlling the corrosion rate of many metals in deaerated water is the hydrogen overpotential at cathodic areas of the metal. The hydrogen overpotential for iron at 16°C in 1N hydrochloric acid is 0.45 V, and for tin at 20°C in 1N hydrochloric acid, it is 0.75 V. The possible significance of this difference in hydrogen overpotential as it affects corrosion of tinplate is discussed in Section 7.7.2.1.

7.7.1.4.2 Supply of Oxygen

The rate at which O_2 is supplied largely governs the rate of corrosion, because corrosion by O_2 reduction requires the presence of O_2 for the cathodic reaction to proceed (see Equation 7.5). The rate of supply is proportional to the rate at which O_2 diffuses to the metal surface, and this depends on the concentration of dissolved O_2 in solution. This is further justification for the practice of attempting to remove all the O_2 from canned foods prior to seaming on the can end.

7.7.1.4.3 Temperature

The rate of corrosion generally increases with increase in temperature, as more reactant molecules or ions are activated and are able to cross over the energy barrier. Furthermore, increasing the temperature tends to increase the rate of diffusion of molecules or ions in a solution, although the solubility of O_2 in water decreases with increasing temperature.

7.7.1.5 Passivity

In Section 7.7.1.2, the dissolution process of a metal was described as an oxidation process of the general form $M \rightarrow M^{n+} + n$ electrons. If the metal can be oxidized to an oxide that is stable in the electrolyte, then the metal is rendered passive (i.e., passivated). Passivation usually requires strong oxidizing conditions.

Thus, corrosion-resistant metals and alloys can withstand an aggressive environment because of the presence of thin films of adherent oxides on their surfaces. The oxide layer will completely stop the anodic reaction, which is the direct cause of corrosion, and if the film is insoluble in the electrolyte solution, then it will form an insulation barrier that will reduce the rate of the cathodic reaction.

For example, iron is readily attacked by dilute nitric acid, but is inert in concentrated nitric acid because a thin, protective film is formed. As a result, iron behaves in concentrated nitric acid like a much more noble metal than it actually is. Iron can also be passivated by chromate solutions, as can tinplate, the latter being a very important step in the manufacture of tinplate. Passivation of tinplate can be achieved using an aqueous solution of chromic acid, although an electrolytic treatment in a sodium dichromate electrolyte has gained widespread favor. The resultant film is composed of chromium and chromium oxides and tin oxide, and its properties vary depending on the quantity and form of these basic components.

7.7.1.6 Stress Corrosion Cracking

Stress corrosion cracking (SCC) is a type of localized corrosion that develops by way of the simultaneous action of particular media, which, in the absence of stress, may be only mildly aggressive or even nonaggressive, and a stress that is lower than that required for purely mechanical cracking. The metal may contain internal stresses due to cold working or be externally stressed. It is not possible to formulate general rules regarding the degree of susceptibility of a material to stress corrosion or the aggressive power of a food or beverage, since this type of corrosion only takes place under specific conditions.

Failure due to SCC often occurs without signs of appreciable shape deformation, which, on initial examination, gives the erroneous impression that the cracked material is intrinsically fragile. The cracks occur in a direction perpendicular to that of the maximum tensile stress and display practically no visible signs of corrosion. Depending on the metallic material and the environment, and on the extent and distribution of the stress, the cracks are predominantly intercrystalline or transcrystalline, and are often branched to varying extents (Gelati et al., 2006).

The failure of metal packaging because of SCC is a well-known phenomenon and occurs frequently in aluminum carbonated soft drink cans where the score areas of the EOEs are particularly susceptible in the presence of humid environments. The first failures from SCC of meat and fish cans in tinplate and ECCS were recorded in the early 1980s. The phenomenon of SCC seems to have been steadily increasing over the last few years and this has been attributed to the use of increasingly thin materials of high mechanical strength and lower-radius beaded profiles, the adoption of EOEs and, finally, the production of foods with complex formulations (Gelati et al., 2006). In order to maintain certain mechanical characteristics, a reduction in thickness must be accompanied by a modification in the design of the can (e.g., an increase in the number and a decrease in the radius of curvature of the beading or corrugations used to reinforce the can wall). These modifications can create deformation and residual stress that, combined with corrosive environments, can give rise to the conditions that trigger SCC.

7.7.2 CORROSION OF TINPLATE

7.7.2.1 Corrosion of Plain Tinplate Cans

7.7.2.1.1 Reversal of Polarity

The tinplate surface consists of a large area of tin and tiny areas of exposed tin–iron alloy ($FeSn_2$) and steel as a result of pores and scratches in the tin coating. Although the now obsolete hot-dipped tinplate had a substantial tin–iron alloy layer, ETP has a much thinner layer, which is electropositive to the base and also to the tin, thus acting as a chemically inert barrier to attack on the steel base. The effect of this barrier is to prevent a significant increase in the steel cathode area. Thus, the density or degree of continuity of the alloy layer has a material effect on the rate of corrosion. The alloy–tin couple test gives a good indication of the continuity of the alloy layer in tinplate.

In the case of tinplate exposed to an aerated aqueous environment, tin is noble (i.e., cathodic) to iron according to the electrochemical series. Therefore, all the anodic corrosion is concentrated on the minute areas of steel and the iron dissolves (i.e., rusts). In extreme cases, perforation of the sheet may occur. This is the process that occurs on the external surface of tinplate containers.

However, inside a tinplate can, the tin may be either the anode or the cathode, depending on the nature of the food. In a dilute, aerated acid medium, the iron is the anode and it dissolves, liberating H_2. In deaerated acidic food, iron is the anode initially, but later, reversal of polarity occurs and the tin becomes the anode, thus protecting the steel. Tin has been described in this situation as a *sacrificial anode*. This reversal occurs because certain constituents of foods can combine chemically with Sn^{2+} ions to form soluble tin complexes. Consequently, the activity of Sn^{2+} ions with which the tin is in equilibrium is greatly lowered, and the tin becomes less noble (i.e., more electropositive) than iron.

7.7.2.1.2 Rate of Tin Dissolution

Corrosion in deaerated acidic food cans comprises three stages as shown in Figure 7.9. During the first stage, the oil and tin oxide layers are removed from the can surface and the rate of tin dissolution is high. Oxygen and other depolarizers are reduced. This stage lasts from 4 to 15 days depending on the nature of the food. The mirror surface of the tin coating should change to one in which the shape of the individual tin crystals may be seen with the naked eye.

In the second stage, the corrosion rate is slow and almost constant. Continued dissolution of the tin causes enlargement of the existing pores and scratches, exposing the alloy layer and the steel. The exposed steel provides sites for cathodic reaction and the evolved H_2 is taken up by the depolarizers in the food. The area of exposed steel dictates the rate of H_2 evolution, and as the ratio between the areas of tin and steel decreases (i.e., as more steel is exposed), polarization decreases. This stage is slow and can last for over 2 years.

The third stage is characterized by a high rate of tin and iron dissolution. As large areas of steel become exposed, H_2 evolves at a faster rate and accumulates in the can causing swelling. Once the internal pressure in the can causes the ends of the can to bulge, the product is no longer saleable since consumers cannot distinguish between a swollen can caused by microbial spoilage or H_2 evolution. Moreover, the metal content of the food may have reached an unacceptable level by this stage. Therefore, this third stage is of little importance because, by this time, the food will have reached the end of its acceptable shelf life.

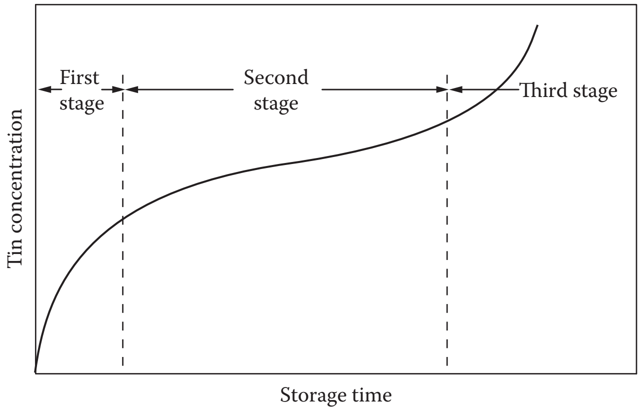

FIGURE 7.9 Schematic rate curve for tin dissolution in acidic foods. (From Mannheim, C. and Passy, N., *CRC Crit. Rev. Food Sci. Nutr.*, 17, 371, 1982.)

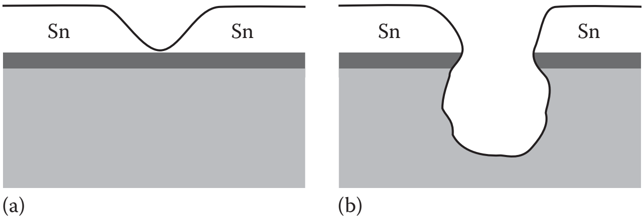

FIGURE 7.10 Schematic diagram illustrating two possible corrosion mechanisms of plain tinplate: (a) anodic tin and (b) cathodic tin.

7.7.2.1.3 Possible Tin–Iron Couple Situations

Four possible scenarios are possible in plain tinplate cans depending on the nature of the food and the presence of depolarizers.

7.7.2.1.3.1 Normal Detinning Normal detinning is an essential process in plain cans of most foods. It has already been described earlier as the second stage and leads initially to etching and later detinning of the can. In this situation, the tin is anodic to iron and affords complete cathodic protection. Tin dissolution and H_2 evolution at the exposed steel are slow, with the area of exposed steel determining the couple current. The dissolved tin forms complexes with food components and the H_2 attaches itself to the depolarizers. Food products characteristic of this type of corrosion include low pH products such as citrus, pineapple, peach and apricot packed in plain tinplate cans.

7.7.2.1.3.2 Rapid Detinning Rapid detinning occurs when the tin is sufficiently anodic to protect the steel but the couple current is high. This leads to a rapid rate of tin dissolution and hydrogen evolution as shown in Figure 7.10a. Rapid detinning is caused by the use of tinplate with a tin coating mass that is too light, or by a product that is intrinsically too corrosive or contains corrosion accelerators (also known as *depolarizers*) such as dissolved O_2 or anthocyanins, which are chemically reduced. Food products characteristic of this type of corrosion include tomato and aggressive citrus products such as lemon juice, as well as berry fruits.

7.7.2.1.3.3 Partial Detinning and Pitting With partial detinning and pitting, the tin is anodic to iron, but protection is limited because local anodes on the latter are more anodic than the tin. Early failure occurs because of H_2 swelling or perforation as a result of the exposed steel continuing to corrode. This type of behavior is associated with products such as prunes or pear nectar, or with steel of inferior quality.

7.7.2.1.3.4 Pitting Corrosion Pitting corrosion is a reversal of the normal situation, with iron being anodic to tin. Thus, the tin does not corrode, but pitting corrosion of the base steel occurs at imperfections in the tin coating as shown in Figure 7.10b. In rare cases, pitting corrosion also occurs when the tin is in fact corroding but at too slow a rate to provide sufficient electrochemical protection to the exposed steel. Pitting corrosion used to be rare, appearing in highly corrosive products such as pickles and carbonated beverages formulated with phosphoric acid. However, it is becoming more common and, for example, is the single greatest cause of failure in canned pears and pear products.

7.7.2.2 Corrosion of Enameled Cans

As discussed earlier in this chapter, food cans with enamel coatings are used to protect against excessive dissolution of tin, sulfide staining, local etching and change in color of pigmented products such as berry fruits. However, the use of enamels will not guarantee the prevention of corrosion and, in some cases, may actually accelerate it. Therefore, careful consideration must be given before selecting an enamel system for a particular canned food.

The general pattern of corrosion in enameled cans is very different from that in plain cans, and is generally more complex. It depends not only on the quality of the base steel plate, the tin–iron alloy layer and the tin coating, but also on the passivation layers and the nature of the enamel coating. The only exposure of metal in an enameled can is at pores and scratches in the enamel coating and at cracks along the side seam. Some of these discontinuities in the enamel coating may coincide with pores in the tin coating, thus resulting in exposure of the steel. Even if defects in the enamel film expose only the tin coating, the availability of all the corrosion promoters in the can for attack on the limited areas of tin ensures that steel is soon exposed. Because these areas of exposed steel are virtually unprotected either by the electromechanical action of a tin coating or by dissolved tin, corrosion may proceed at a rapid rate, resulting in H_2 swelling or perforation of the can. Thus, it is possible to actually reduce the shelf life of a canned product by using an enameled can instead of a plain one.

The effectiveness of an enamel coating is related directly to its ability to act as an impermeable barrier to gases, liquids and ions, thereby preventing corrosive action on the protected surface. The transport of ions through the enamel is governed by the electrochemical characteristics of the film. This is in contrast to the transport of gases and liquids, which involves dissolution in, and diffusion through, the enamel film under a concentration gradient. Because ions are electrically charged, their transfer through the enamel coating (actually the flow of an electric current) is complex and depends not only on their electric charge, but also on the concentration of the electrolyte. If the transport rate of cations and anions through the coating differs, the coating itself may become charged. Thus, the protection offered by the enamel coating depends on its resistance to ion transfer, which may take place even in the absence of pores, scratches or blisters.

The performance of enameled food cans is greatly affected by the thickness of the enamel coating. A thickness of 4–6 µm is sufficient for nonaggressive products such as apricots and beans, but aggressive products such as tomato paste require thicknesses of 8–12 µm, the heavier coatings having much lower porosities.

Two possible electrochemical corrosion mechanisms in enameled cans are presented in Figure 7.11. In a plain can, the product would attack the tin layer, causing it to dissolve. The presence of an enamel coating protects the surface, and tin dissolution occurs only from both sides of a scratch under the enamel or through a pore, causing anodic undermining (Figure 7.11a). Because only a very small area is in contact with the product in the can, dissolution is slow. With time, the exposed area increases, and detachment of the enamel may be observed, resulting in the appearance of enlarged pores in the enamel coating. The tin–iron alloy layer may also be visible as a grayish color. Because (in theory) the alloy layer is more passive than tin and iron, it should dissolve only after all the tin and iron. However, because of its extreme thinness and its coupling effect with the tin, the potential of the can may be nobler than that of iron, which may also go into solution. In this situation, the enamel coating may serve as the cathode due to diffusion of protons through it.

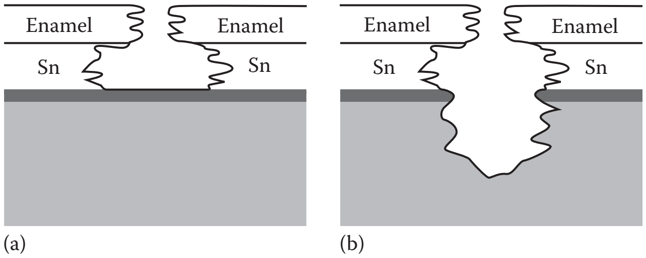

FIGURE 7.11 Schematic diagram illustrating two possible corrosion mechanisms of enameled tinplate: (a) anodic tin and (b) cathodic tin.

Mannheim and Passy (1982) used tomato concentrate as an example of the preceding scenario. Although the overall rate of tin dissolution is reduced in the presence of an enamel coating, protection of the steel by the tin is also impaired due to reduction in the ratio of exposed tin to steel areas. Corrosion is concentrated in small areas and strong local currents may occur. The presence of corrosion accelerators such as nitrates aggravates the situation.

Where the alloy and iron are more anodic than the tin (as illustrated in Figure 7.11b) the alloy layer dissolves rapidly and the iron is attacked. However, because no tin is dissolved, the alloy layer is not laid bare and, thus, has no influence on the corrosion process. Failure eventually occurs due to pinhole formation (also known as *pitting corrosion*) but there is no undermining of the enamel, with corrosion usually starting at a point of discontinuity such as a scratch or pore in the coating. Aggressive products such as beets in acetic acid and berries are responsible for this type of corrosion. The cans do not appear to be corroded, and it is only on closer inspection (usually with a hands lens) that spots of corrosion (often with deep penetration into the steel) are visible.

Failure of enameled cans is often due to a reduction in the bond between the enamel and the metal surface, resulting in eventual lifting of the enamel coating. Thus, good adhesion is required to prevent anodic reactions, to counteract forces developed under the coating due to physical or chemical factors and to ensure an aesthetic appearance.

7.7.2.3 Corrosiveness of Foods

Food products and beverages are extremely complex chemical systems covering a wide range of pH and buffering properties, as well as a variable content of corrosion inhibitors or accelerators. Factors that influence the corrosiveness of food products and beverages can be divided into two groups: intensity and type of corrosive attack inherent in the food itself, and corrosiveness due to the processing and storage conditions. All these factors are interrelated and may combine in a synergistic manner to accelerate corrosion.

The most important corrosion accelerators in foods include O_2, anthocyanins, nitrates, sulfur compounds and trimethylamine. Some typical corrosion reactions associated with these accelerators and their stoichiometric equivalents of dissolved tin are presented in Table 7.7.

From a corrosiveness point of view, it is convenient to divide foods into five classes:

1. Highly corrosive such as apple and grape juices, berries, cherries, prunes, pickles and sauerkraut
2. Moderately corrosive such as apples, peaches, pears, citrus fruits and tomato juice
3. Mildly corrosive such as peas, corn, meat and fish
4. Strong detinners such as green beans, spinach, asparagus and tomato products
5. Beverages are conveniently considered as a fifth class

TABLE 7.7
Some Corrosion-Promoting Agents and Their Mode of Reaction

Corrosion Accelerator	Reduction Product	Equivalent in Weight
Proton (H^+)	H_2	1 mL $H_2 \equiv 5.3$ mg Sn^{2+}
Oxygen (O_2)	H_2O	1 mL $O_2 \equiv 10.6$ mg Sn^{2+}
Sulfur dioxide (SO_2)	H_2S	1 mL $SO_2 \equiv 5.5$ mg Sn^{2+}
Sulfur (S)	H_2S	1 mg S $\equiv 3.7$ mg Sn^{2+}
Nitrate (NO_3)	NH_3	1 mg $NO_3 \equiv 7.65$ mg Sn^{2+}
Trimethylamine oxide (TMAO)	TMA	1 mg TMAO $\equiv 1.57$ mg Sn^{2+}

Source: Mannheim, C. and Passy, N., *CRC Crit. Rev. Food Sci. Nutr.*, 17, 371, 1982.

Although the aforementioned classification offers a broad guide, it is important to note that different lots or varieties of the same food can exhibit as much variation in their corrosiveness as may exist between different types of foods. Thus, for example, the same variety of fruit from different growing regions may vary significantly in terms of corrosiveness. The various factors that can influence the corrosiveness of food products and beverages are considered in more detail.

7.7.2.3.1 Acidity

No direct proportionality exists between the acidity of a product and the degree of corrosion of tinplate, that is, two products of the same acidity will not necessarily be equally corrosive. It also appears that pure solutions of organic acids are less corrosive than the fruit juices containing them, suggesting that fruit juices contain unidentified depolarizers that enhance the corrosive action of organic acids. It has been well established that the tendency of an acid to form a complex with dissolved tin has an important bearing on the relative polarity of tin and steel and, hence, the degree of corrosion (see Section 7.7.2.1).

7.7.2.3.2 pH

As is the case with acidity, no direct proportionality exists between pH and the degree of corrosion of tinplate. This is not surprising given that the reaction product when a metal is dissolved is not always an ionic species but often a solid oxide or hydroxide. The pH of the system also determines the relative cathodic protection given to steel. In some cases, tin is cathodic to steel over a certain pH range (in the case of acetic acid the range is pH 2.0–4.5), while in others, it offers protection up to pH 4; above that level it may accelerate corrosion.

7.7.2.3.3 Sulfur Compounds

Sulfur and sulfur compounds may be introduced into the can in a number of ways. They may be introduced in the form of spray residues from agricultural chemicals, residues from sulfur-containing preservatives or as components in sulfur-containing compounds such as proteins in meat, fish and certain vegetables. Proteins are degraded during heat processing, releasing free sulfide or hydrosulfide ions and evolving hydrogen sulfide gas into the headspace.

Trace amounts of sulfur compounds from agricultural chemicals (e.g., derivatives of thio- and dithiocarbamic acid fungicides) can lead to accelerated corrosion and failure of plain tinplate cans containing acid foods such as apricots and peaches. In addition, pitting corrosion can occur, and this has been attributed to inactivation of the tin coating by a protective film of sulfide having a more cathodic potential. Consequently, there is a significant reduction in the tin dissolution rate, and no electrochemical protection of the steel by the tin.

Sulfur dioxide may be directly reduced on the tin surface to sulfide or even to sulfur, with tin passing into solution and the development of unpleasant odors and flavors. Residual SO_2 accelerates corrosion through its action as a depolarizer, inducing a negative charge in the double layer. This repels the electrons from the electrode, thus shifting the potential in the positive direction (Mannheim and Passy, 1982). Trace amounts of SO_2 as low as $1\,mg\,kg^{-1}$ are sufficient to accelerate corrosion, but such corrosion problems may be overcome by the use of enameled cans.

There are two types of sulfide staining. One involves iron sulfide (sometimes called sulfide black) and the other involves tin sulfides. These two types of staining do not constitute a health hazard or lead to failure of the can. However, both types may cause adverse reactions from the consumer on aesthetic grounds.

Iron sulfide stains are characteristically black, and usually occur at isolated points on the can (mainly in the headspace region) during or immediately after heat processing. Iron sulfide is not formed at pH values below about 6. Thus, it is uncommon to find iron sulfide in the portion of the can in contact with the contents. However, the pH of condensed volatile matter in the headspace may be above 6. The problem may be overcome by using enameled cans or plain cans with enameled ends.

Tin sulfide staining is usually widespread throughout the can and is blue-black or sometimes brown. Two stages are believed to be involved. The first stage is an oxidation of the tin, and the second is the deposition of an insoluble tin sulfide precipitate on the surface. It occurs during, or soon after, heat processing and shows little or no increase in intensity during storage. It may be prevented by using sulfur-resistant enamels into which quantities of zinc or aluminum compounds are added before being applied to the plate surface. These react with sulfur-bearing gases to form almost invisible white metal sulfides. However, this approach is not suitable for acid products since the acids may attack the coating to produce zinc or aluminum salts, which could be harmful to health.

7.7.2.3.4 Nitrates

Nitrates are found in fruits and vegetables grown in heavily fertilized soils, and may also occur in water supplies as a result of pollution by fertilizers. Vegetables such as green beans, spinach, turnips, lettuce, beets and radishes have often been shown to contain several thousand mg kg^{-1} of nitrates. Nitrates are very efficient cathode depolarizers since they are capable of being reduced all the way to ammonia. They have been responsible for serious economic and toxicological problems in some canned foods, notably tomato products. Although nitrates and nitrites are also present as intentional additives in processed meats, they present no problem because meat products are above the critical pH (5.5) for detinning to occur via the nitrate–tin reduction system.

Nitrates act as electron acceptors, replacing the H_2 evolution reaction with the electron–nitrate two-step reduction reaction and shifting the reaction toward increased tin dissolution. The reduction reactions involved are thought to be as follows:

$$4\mathrm{Sn} \rightarrow 4\mathrm{Sn}^{2+} + 8\mathrm{e}^- \tag{7.7}$$

$$\mathrm{NO^-{}_3} + 2\mathrm{e}^- + 2\mathrm{H}^+ \rightarrow \mathrm{NO^-{}_2} + \mathrm{H_2O} \tag{7.8}$$

$$\mathrm{NO^-{}_2} + 6\mathrm{e}^- + 8\mathrm{H}^+ \rightarrow \mathrm{NH^+{}_4} + 2\mathrm{H_2O} \tag{7.9}$$

The first reduction reaction (Equation 7.8) is probably rate determining. The equations indicate that the rate of detinning depends on the nitrate concentration and pH. Nitrate does not immediately affect the corrosion rate, but begins to act after tin and iron ions have passed into solution. Although the ammonium ion is the major conversion product at pH 5 and less, above this pH other products are formed, including nitrous oxide (N_2O), nitric oxide (NO) and hydroxylamine. Oxygen present in the can at the time of processing triggers the nitrate-detinning reaction by increasing the initial rate of formation of Sn^{2+} (Equation 7.7).

Overcoming the problem by restricting the use of nitrate fertilizers has proved difficult, and instead efforts have been directed toward finding cultivars that do not accumulate high concentrations of nitrate. It is also possible to avoid the use of waters with high nitrate content for canning operations; a suggested maximum is 5 mg L^{-1} nitrate. The best solution to the problem at present is the use of enameled cans, although the development of corrosion inhibitors (the search for such substances is continuing) would offer an alternative solution.

7.7.2.3.5 Phosphates

Phosphates are naturally present in meat and are often intentionally added as polyphosphates to processed meat products such as hams to reduce the loss of water during processing. The presence of phosphates leads to increased discoloration due to iron phosphate and sulfide formation. One measure used to counter the effect of polyphosphate in cans of processed meats is the introduction of a small area of aluminum, which acts as a sacrificial anode, protecting the tin surface. This is not always completely successful, and parchment liners may be used in addition or as an alternative.

7.7.2.3.6 Plant Pigments

The anthocyanins and related pigments are among the most important potential corrosion accelerators (cathodic depolarizers) since they are easily reduced. Anthocyanin pigments can also act as anodic depolarizers through their ability to form complexes with cations, particularly those of iron and tin salts. Analysis of samples of canned fruits after a period of storage usually shows a greater amount of tin in the drained fruit than in the syrup, indicating that at least part of the tin is combined in an insoluble form with some constituent within the fruit.

The nature of the anthocyanin pigment is also important. For example, raspberries contain cyanidin glucosides that have *ortho*-dihydroxy groups in their structures. It is these groups that are involved in the formation of blue-tinted complexes with metals such as tin. The major pigment of strawberries is pelargonidin-3-glucoside, which does not possess the necessary *ortho*-dihydroxy groups for complex formation. Therefore, strawberries do not show the same shift to a blue color in the presence of tin salts as do raspberries.

Combination of metal ions with tannins has been observed in other fruits. For example, discoloration in canned cranberry has been attributed to the formation of a complex between tannins present in the fruit and tin salts. Darkening in canned maraschino cherries has been observed to be more severe when fruit of high tannin content is used, where a high tannin content is often found in unripe fruit and fruit that has been stored in wooden barrels. It should be noted that not all reactions between plant pigments and metal ions will produce undesirable colors, although this is usually the case with anthocyanin pigments.

7.7.2.3.7 Synthetic Colorings

Canned products that most commonly contain synthetic colorings are soft drinks, which consist basically of sugar-based syrups and carbonated water containing flavors, acidulants and colors. The behavior of soft drinks largely depends on the presence of azo dyes (e.g., amaranth) and the amount of residual O_2 in the filled can. Both of these components are capable of acting as corrosion accelerators and are potentially active corrosive agents. Tin dissolution may adversely affect the color of some products, and iron dissolution may lead to perforation and flavor defects. Thus, fully enameled cans are essential, it being important to obtain near-perfect coverage by the enamel.

7.7.2.3.8 Copper

Foods containing dissolved copper will deposit it when put in a metallic container, and, in acid products, this can lead to accelerated corrosion, either by tending to strip the tin or by producing local attack on the steel. The basic reason why copper accelerates the corrosion of steel is because copper catalyzes the reduction of O_2.

In the past, copper entered products by the solution of copper oxide from copper-bearing metal food contact equipment. However, with the replacement of copper equipment with stainless steel, the problem of copper in canned foods has been dramatically reduced. Another possible source of copper is from certain fungicides. In some cases, cannery water supplies may have unacceptably high copper levels.

7.7.2.4 Effects of Processing and Storage

7.7.2.4.1 Oxygen

Oxygen may be dissolved in food products as it is naturally present in food tissues such as fruit and vegetable cells and is inevitably entrained or absorbed by particulate products prior to their being filled into cans. Removal of as much of this O_2 as possible is an essential part of good cannery practice, and a variety of methods are used including hot filling, vacuum filling, exhausting, closure under vacuum, steam flow closure and vacuum syruping. In addition, positive control of the headspace volume is essential.

A larger headspace is likely to contain a higher residual O_2 concentration than a smaller one. However, the larger the headspace, the more room there is for accumulation of H_2 resulting from corrosion, and, thus, the greater the time required to form an H_2 swell. In practice, the cannery technologist has little room to maneuver the headspace if the declared weight on the can label is to be met.

Despite the aforementioned procedures, there will always be some O_2 present in the headspace of newly filled cans. The rate of O_2 consumption at this stage is quite rapid but decreases with time, the rate being a function of initial concentration, headspace volume, can vacuum, nature of the product and type of container. Oxygen acts as a depolarizer, accelerating corrosion by reacting with the H_2 formed in the can through a cathodic reaction, as shown in Equation 7.3.

7.7.2.4.2 Thermal Processing

Little is known about the effect of heat sterilization processes on corrosion rates, except that the quantity of metal dissolved during the process is very small. This is hardly surprising given the comparatively short processing times (typically 30–120 min) relative to the total shelf life of the canned product (typically 2–5 years). However, degradation products formed during thermal processing can become involved in corrosion (e.g., nonenzymic browning intermediates and sugar derivatives).

The importance of correct cooling has been emphasized, where failure to cool cans adequately (generally a target temperature of 40°C when the cans leave the retort) can lead to increased corrosion because the can center temperatures may take several days to return to ambient. On the other hand, cooling to too low a temperature may cause paneling of the can walls as well as external corrosion (see Section 7.7.2.5) because complete drying of the can exteriors will not occur.

7.7.2.4.3 Storage Temperature

The rate of a chemical reaction increases as the temperature is raised, and for many reactions, the rate doubles for each 10°C increase in temperature (i.e., the temperature quotient Q_{10} equals 2). Therefore, to minimize undesirable reactions such as nonenzymic browning in canned foods, it is preferable that storage temperatures are kept as low as practicable.

7.7.2.5 External Corrosion of Cans

Although tinplate is very durable in a dry atmosphere, it rusts readily in the presence of moisture, where rusting occurs more readily the thinner the tin coating. The presence of sulfur dioxide or oxides of nitrogen in the atmosphere accelerates the rate of corrosion since they dissolve to form acids. Chlorides (present in locations close to the sea) can also cause a rapid increase in the rate of corrosion.

The mechanism of external corrosion is complex. Under normal conditions on the outside of a can, tin is cathodic to iron, and when a galvanic cell is set up at pore sites, the attack on the iron is accelerated by the presence of tin. Rust forms as a result of corrosion of the iron. Three stages of exposure to the risk of external rusting may be differentiated: thermal processing, cooling of cans and storage.

7.7.2.5.1 Thermal Processing

The essential ingredient for rusting of cans during thermal processing is the presence of O_2 in the processing vessel (typically a steam retort). When cans are processed in water at atmospheric pressure (as is quite common for high acid, low pH products such as fruits), the risk reaches a maximum at a temperature of about 80°C. Above this temperature, the loss of dissolved O_2 counteracts the acceleration of the reaction rate at the higher temperatures. Therefore, when full boiling is not required, the water should be deoxygenated and preferably treated with corrosion restrainers.

When cans are processed in steam, it is important that proper venting of the retort occurs so that all the O_2 initially present is displaced from the retort by the steam. In addition, bleeder valves should be left open so that any residual or incoming O_2 may escape. As well as minimizing any external corrosion, the removal of air from the retort prevents pockets of air from surrounding individual cans and insulating them from the steam, the latter situation leading to underprocessing.

7.7.2.5.2 Cooling of Cans

Cans are typically cooled after thermal processing by passing water through the retort or placing the cans in cooling canals. However, in some canneries, hot cans are removed from the retort and left to cool in the air. If cans are cooled with water, it is a regulatory requirement in virtually every country that such water contain a measurable amount of bactericide (typically chlorine) when it exits the retort. In the case of chlorine, this usually means that incoming water has a free chlorine content of around 5–10 mg L^{-1}.

When cans are water cooled, they should be around 40°C when they are removed from the retort. If they are warmer than this, there is the risk of thermophilic spoilage, chemical degradation and significant internal corrosion. On the other hand, if they are cooler than this, insufficient heat will remain to evaporate any water adhering to the exterior of the can. Cans should be stacked in such a way so as to enable self-drying prior to labeling and packing.

The addition of a wetting agent to the cooling water, or the spraying of a dilute solution of a wetting agent onto the cans as they leave the cooling water, facilitates rapid drainage of the water and leaves it as a quickly evaporating thin layer rather than as isolated droplets. Accelerated drying methods such as the use of hot air, or a steam spray, or rolling cans over a sterile absorbent surface, have advantages in minimizing external corrosion of cans.

7.7.2.5.3 Storage

If corrosion is to be prevented during storage, then the atmosphere surrounding the can must be free of corrosive vapors or chemicals, and not promote condensation of moisture. In addition, packaging materials in contact with the cans (generally paperboard cartons closed with adhesives) should be as free as possible from soluble chlorides, sulfates or other salts that may promote condensation of moisture and corrosion. Cartons usually have a water content of 10%–12%, and when the air temperature rises, moisture evaporates from the cartons in the warmer outer zone and condenses in the cooler center of the stack. The time for rust to develop on wet cans held at various temperatures is presented in Table 7.8.

TABLE 7.8
Time–Temperature Profile for Rust to Develop on Wet Cans of Vegetables Held in a Saturated Moisture Atmosphere

Temperature (°C)	Storage Limits
26.7–37.8	4 h
15.6–21	1 day
10	2 days
4	4 days
0	6 days
−6.7 or below	≥90 days

Source: Yang, T.C.S., Ambient storage, in: *Food Storage Stability*, Taub, I.A. and Singh, R.P. (Eds), CRC Press, Boca Raton, FL, pp. 435–458, 1998.

The shrink or stretch wrapping of cans, while protecting them from promoters of corrosion found in the atmosphere, can cause problems of condensation. If the air inside the shrink wrap contains a considerable quantity of water vapor and the package is later subjected to a drop in temperature, condensation will occur.

Rusting can also be caused by unsuitable conditions of transport and storage where cycling of the humidity (described as "sweating") occurs (Yang, 1998). This is especially so when cans are transported from temperate to tropical areas, or temperate to temperate areas via the tropics (e.g., from Australia to North America). Attempts to prevent condensation of moisture by free movement of air have usually been unsuccessful because the center of a stack of cartons filled with cans takes a long time to respond to the external temperature change and may remain below the dew point for long periods.

7.7.3 CORROSION OF ECCS

Although the chromium/chromium oxide layer on ECCS cans is only ~1/30–1/50 the thickness of a typical tinplate coating, it transforms the base steel into an excellent canmaking material by providing rust protection, outstanding enamel coating adhesion and good resistance to underfilm sulfide staining. However, ECCS cannot be used in food packaging unless it is enameled because of its lack of resistance to corrosion. Two-piece ECCS cans have significantly lower product iron contents compared with three-piece tinplate cans.

7.7.4 CORROSION OF ALUMINUM

Unlike plain carbon steel, unalloyed aluminum has excellent corrosion resistance in natural environments. In aluminum alloys, alloying elements are not used to improve corrosion resistance as chromium does in steel, but to improve mechanical strength (Reboul and Baroux, 2011). Aluminum rapidly forms a protective oxide film when exposed to air or water:

$$4Al + 3O_2 \rightarrow 2Al_2O_3 \tag{7.10}$$

The film is extremely thin (about 10 nm) but it renders the metal completely passive in the pH range 4–9. Because aluminum oxide is amphoteric, it will dissolve in acid or alkali to give the soluble aluminum cation or anion, respectively:

$$Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O \tag{7.11}$$

$$Al_2O_3 + 2OH^- \rightarrow 2AlO^-{}_2 + H_2O \tag{7.12}$$

Although, in practice, aluminum will corrode in acid solutions (pH below 4) and alkali (pH above 9), its corrosion resistance is excellent in the neutral range of pH 4–9. Having a strongly negative electrode potential ($E_H = -1.66$), aluminum is liable to undergo severe corrosion if brought into metallic contact with copper, iron or other more positive metals in the presence of an electrolyte (e.g., fruit juice). Thus, care must be taken to ensure that situations that could lead to such corrosion (e.g., processing equipment having food contact surfaces that contain both aluminum and stainless steel parts) are avoided.

Aluminum levels are generally very low because of the very good enamel systems that prevent contact of the food with the metal. However, in certain products such as beer, even very low levels of aluminum can cause cloudiness or haze and render the product unacceptable.

Pitting corrosion of aluminum EOEs on cans of fruit juices has been experienced, with the corrosion taking place mainly along the depressed score line if the underside organic coating is torn or damaged by the scoring operation. Corrosion takes place with high chloride content products such as tomato and vegetable juices and is accelerated when the end is used with a tinplated can body. This is because the aluminum end is anodic to the can body. This problem can be overcome by reapplying enamel to the end after scoring.

Products containing brine should not be packed in aluminum as they can produce rapid and dramatic corrosion, with such corrosion becoming apparent in the form of container or end perforation within 24 h (Turner, 1998).

Although no foods have a pH greater than 8, cleaning solutions used in food processing plants frequently have pH values of 13. It is, therefore, important that these solutions do not come into contact with aluminum packaging materials, and that any package-contact surfaces that are cleaned with these solutions are thoroughly rinsed with water afterward.

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8 Glass Packaging Materials

8.1 INTRODUCTION

Glass has been defined by the ASTM (2010) as "an amorphous, inorganic product of fusion that has been cooled to a rigid condition without crystallizing." Although glass is often regarded as a synthetic material, it was formed naturally from common elements in the earth's crust long before the world was inhabited. Natural materials such as obsidian (from magma or molten igneous rock) and tektites (from meteors) have compositions and properties similar to those of synthetic glass; pumice is a naturally occurring foam glass.

Although the origin of the first synthetic glasses is lost in antiquity and legend, the first glass vessels were probably sculpted from solid blocks about 3000 BCE. In about 1000 BCE, the techniques of pouring molten glass or winding glass threads over a sand mold were developed, resulting in the formation of crude but useful glass objects. However, the real revolution in glassmaking came around 200 BCE with the introduction of the blowing iron, a tube to which red-hot, highly malleable glass adheres. Blowing through one end of the iron causes the viscous liquid to balloon at the other end, leading to the production of hollow glass objects.

By 200 CE, articles of glass were in fairly common use in Roman households. During the following 1000 years, glassmaking techniques spread over Europe. However, glass remained expensive until improved techniques in the eighteenth and nineteenth centuries brought down the price of bottles and jars to a relatively affordable level.

Mechanization of glass container manufacture was introduced on a large scale in 1892, and several important developments occurred over the next few decades. These included the first fully automated machine for making bottles, which was designed and built in 1903 by Michael J. Owens at the Toledo, Ohio, plant of Edward D. Libbey.

Added impetus was given to automatic production processes in 1923 with the development of the gob (mass or lump of molten glass) feeder, which ensured the rapid supply of more consistently sized gobs in bottle production. Soon afterward, in 1925, the Hartford Empire Company developed its IS (now generally taken to mean "individual section," but actually named after its inventors Ingersall and Smith) blow and blow (B&B) machine (Hanlon et al., 1998). Used in conjunction with the gob feeders, IS (individual section) machines allowed the simultaneous production of a number of bottles from one piece of equipment. The gob feeder–IS machine combination remains the basis of most automatic glass container production today.

Further developments have occurred, resulting in the production of a wide range of glass containers for packaging. The two main types of glass container used in food packaging are bottles (which have narrow necks) and jars (which have wide openings). About 75% of all glass food containers in the United States are bottles and approximately 85% of container glass is clear, the remainder being mainly amber. Generally, today's glass containers are lighter but stronger than their predecessors, with the weight of many bottles and jars having been reduced by 25%–50% over the last 50 years. Through developments such as this, the glass container has remained competitive and continues to play a significant but declining role in the packaging of foods.

8.2 COMPOSITION AND STRUCTURE

The basic raw materials for glassmaking come from mines or quarries and must be smelted or chemically reduced to their oxides at temperatures exceeding 1500°C. The principal ingredient of glass is silica derived from sand, flint or quartz. Silica can be melted at very high temperatures

(1723°C) to form fused silica glass which, because it has a very high melting point, is used for specialized applications including some laboratory glass.

For most glass, silica is combined with other raw materials in various proportions. Alkali fluxes (commonly sodium and potassium carbonates) lower the fusion temperature and viscosity of silica. Calcium and magnesium carbonates (limestone and dolomite) act as stabilizers, preventing the glass from dissolving in water. Other ingredients are added to give glass certain physical properties. For example, lead gives clarity and brilliance although at the expense of softness of the glass; alumina increases hardness and durability. The addition of about 6% boron to form a borosilicate glass reduces the leaching of sodium (which is loosely combined with the silicon) from glass.

As a consequence of the sodium in glass being loosely combined in the silica matrix, the glass surface is subject to three forms of "corrosion": etching, leaching and weathering. Etching is characterized by alkaline attack, which slowly destroys the silica network, releasing other glass components. Leaching is characterized by acid attack in which hydrogen ions exchange for alkali or other positively charged mobile ions. The remaining glass (principally silica) usually retains its normal integrity. Although not fully understood, weathering is not a problem in commercial glass packaging applications since it may take centuries to become apparent. However, a mild form of weathering is commonly known as surface bloom and may occur under extended storage conditions.

The most aggressive solution on glass is double-distilled water at neutral pH 7. The effect of dilute acidic solutions is much less, the main action being the extraction of sodium ions which are replaced by hydrogen ions. The result is a surface zone where the glass is depleted of sodium, this dealkalized layer forming a barrier to further ionic diffusion. It is worth remembering that the aqueous phase of almost all foods is acidic.

A typical formula for soda-lime glass is given in Table 8.1. In practice, however, the quantities vary slightly; for example, silica (SiO_2) 68%–73%, calcia (CaO) 10%–13%, soda (Na_2O) 12%–15%, alumina (Al_2O_3) 1.5%–2% and iron oxides (FeO) 0.05%–0.25%, depending on the glassmaker and the raw materials being used. The loss on ignition or fusion loss (generally the oxides of carbon and sulfur) can vary from 7% to 15%, depending on the quantity of cullet (i.e., scrap or recycled glass) used, there being less fusion loss the greater the quantity of cullet. Soda-lime

TABLE 8.1
Typical Formula for a 1 Tonne Batch of Soda-Lime Container Glass

Material	Weight (kg)	Oxides Supplied (kg)					LOI[a] (kg)
		SiO_2	Al_2O_3	CaO	Na_2O	FeO	
Sand SiO_2	300	299.3	0.2			0.3	0.5
Soda ash Na_2CO_3	100				58.3		41.7
Aragonite $CaCO_3$	90			49.0		0.02	40.7
Feldspar ($SiO_2 \cdot Al_2O_3$)	40	26.4	7.6	0.4	1.3	0.03	0.1
Salt cake NaCl	4				2.1		1.9
Cullet	460	333.7	9.2	48.8	67.2	1.03	0.1
Total	994	659.4	17.0	98.2	128.9	1.95	85.0
Yield of glass	909						
Wt% oxides		72.6	1.9	10.8	14.2	0.1	

Source: Adapted from Boyd, D.C. et al., Glass, in: *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn., Kroschwitz, J. (Ed.), Vol. 12, John Wiley & Sons, New York, pp. 555–628, 1994.

[a] Loss on ignition (also referred to as fusion loss).

glass accounts for nearly 90% of all glass produced and is used for the manufacture of containers where exceptional chemical durability and heat resistance are not required (Boyd et al., 1994). Replacement of alkali by boric oxide leads to the production of borosilicate glass which is used for glass ovenware.

Glass is neither a solid nor a liquid but exists in a vitreous or glassy state in which molecular units have a disordered arrangement but sufficient cohesion to produce mechanical rigidity. Although glass has many of the properties of a solid, it is really a highly viscous liquid. During cooling, glass undergoes a reversible change in viscosity, the final viscosity being so high as to make the glass rigid for all practical purposes. Although glass at ambient temperatures has the characteristics of a solid, it is a supercooled liquid and will flow even at ambient temperatures over long periods of time, albeit extremely slowly.

Physically, glass has a random atomic structure in that the atoms are capable of arranging themselves in different orders. The basic structural unit is the silicon-oxygen tetrahedron in which a silicon atom is tetrahedrally coordinated to four surrounding oxygen atoms. However, although the silica atoms are always surrounded by four oxygen atoms, large groupings tend to be unordered. This amorphous structure, without slip planes formed by crystal boundaries that might allow deformation, is responsible for the stiffness and brittleness of glass.

8.3 PHYSICAL PROPERTIES

8.3.1 Mechanical Properties

Because of its amorphous structure, glass is brittle and usually breaks because of an applied tensile stress. It is now generally accepted that fracture of glass originates at small imperfections or flaws, the large majority of which are found at the surface. A bruise or contact with any hard body will produce on the glass surface very small cracks or checks that may be invisible to the naked eye. However, because of their extreme narrowness, they cause a concentration of stress that may be many times greater than the nominal stress at the section containing them. Because of their ductility, metals yield at such points and equalize stress before failure occurs. Since glass cannot yield, the applied stress (when it is high enough) causes these flaws to propagate (Girling, 1999). Thus, it is the ultimate tensile strength of a glass surface which determines when a container will break. The fracture formula is

$$\text{Tensile Stress} + \text{Stress Concentrator} = \text{Fracture}$$

In practice, a stress concentrator may be a small crack or check induced in the manufacturing process, or a scratch resulting from careless container handling. Therefore, the major step taken to make glass more break resistant involves the elimination of surface flaws (e.g., microcracks) by careful handling during and after forming and annealing, since the condition of the surface has a great deal to do with its tensile properties.

The mechanical strength of a glass container is a measure of its ability to resist breaking when forces or impacts are applied. Glass deforms elastically until it breaks in direct proportion to the applied stress, the proportionality constant between the applied stress and the resulting strain being Young's modulus E. It is about 70 GPa for typical glass (Boyd et al., 1994).

The principles of fracture analysis or diagnosis of the cause(s) of glass container breakage have been described by Moody (1977) in an excellent book that is regrettably now out of print. The following four aspects are important:

1. *Internal pressure resistance*: This is important for bottles produced for carbonated beverages, and when the glass container is likely to be processed in boiling water or in pressurized hot water. Internal pressure produces bending stresses at various points on the outer surface of the container, as shown in Figure 8.1.

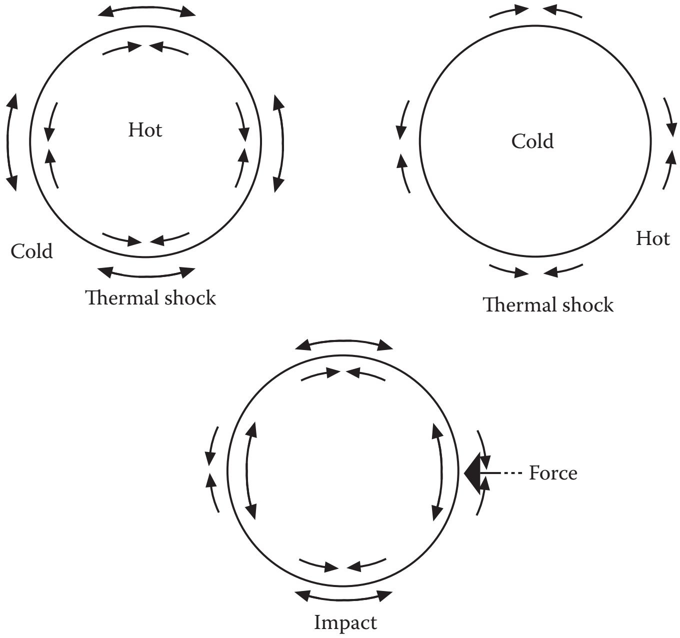

FIGURE 8.1 Cross section of a round glass container illustrating various stresses on the inside and outside surfaces.

2. *Vertical load strength*: While glass can resist severe compression, the design of the shoulder (see Figure 8.5 for details of glass container nomenclature) is important in minimizing breakage during high-speed filling and sealing operations.
3. *Resistance to impact*: Two forms of impact are important—a moving container contacting a stationary object (as when a bottle is dropped) and a moving object contacting a stationary bottle (as in a filling line). In the latter situation, design features are incorporated into the sidewall to strengthen contact points. The development of surface treatments (including energy absorbing coatings) to lessen the fragility of glass when it contacts a stationary object has been very successful. A cross section of a round bottle illustrating the ways in which tensile stresses on the inside and outside surfaces vary at various points around the bottle circumference is shown in Figure 8.1.
4. *Resistance to scratches and abrasions*: The overall strength of glass can be significantly impaired by surface damage such as scratches and abrasions. This is especially important in the case of reduced wall thickness bottles such as "one-trip" bottles. Surface treatments involving tin compounds (in conjunction with other treatments) provide scuff resistance, thereby overcoming susceptibility to early failure during bottle life.

Although the mechanical strength of a bottle or jar can increase with glass weight, this is at the expense of thermal strength which decreases with increasing glass weight. Considerable expertise is required by the glassmaker to determine the most appropriate design to satisfy the mechanical strength requirements and to balance the thermal strength demands of the finished product.

8.3.2 Thermal Properties

The thermal strength of a glass container is a measure of its ability to withstand sudden temperature change. In the food industry, the behavior of glass with respect to temperature is of major significance, because relative to other forms of food packaging, glass has the least resistance to temperature changes. The resistance to thermal failure depends on the type of glass employed, the shape of the container and the wall thickness.

When a glass container is suddenly cooled (e.g., on removal from a hot oven), tensile stresses are set up on the outer surfaces, with compensating compressional stresses on the inner surface, as shown in Figure 8.1. Conversely, sudden heating leads to surface compression and internal tension. In both situations, the stresses are temporary and disappear when the equilibrium temperature has been reached. Because glass containers fracture only in tension, the temporary stresses from sudden cooling are much more damaging than those resulting from sudden heating, since the potentially damaged outside surface is in tension. It is found in practice (Moody, 1977) that the amount of tension produced in one surface of a bottle by suddenly chilling it is about twice as great as the tension produced by suddenly heating the other surface, assuming the same temperature change in both cases.

Thermal shock resistance cannot be calculated directly because the strength of glass containers is greater under momentary stress than under prolonged load. Therefore, empirical testing procedures are used. ASTM C149 covers the determination of the relative resistance of commercial glass containers (bottles and jars) to thermal shock, and is intended to apply to all types of glass containers that are required to withstand sudden temperature changes (thermal shock) in service such as in washing, pasteurization or "hot fill" processes, or in being transferred from a warmer to a colder medium or *vice versa*. Resistance to breaking is determined by transferring glass containers which have been totally immersed in a hot water bath (typically at 63°C) for 5 min to a cold water bath (typically at 21°C) and observing the number of breakages.

8.3.3 OPTICAL PROPERTIES

Because glass has no crystalline structure, when it is homogeneous and free from any stresses, it is optically isotropic. The optical properties of glass relate to the degree of penetration of light and the subsequent effect of that transmission, transmission being a function of wavelength. The spectral transmission of glass is determined by reflection at the glass surface and the optical absorption within the glass. In silicate glasses, transmission is limited by the absorption of silica at approximately 150 nm in the UV and at 6000 nm in the IR region. Iron impurities further reduce transmission in the UV and near-IR regions (Boyd et al., 1994).

Transmission may be controlled by the addition of coloring additives such as metallic oxides, sulfides or selenides and the compounds that are frequently used are listed in Table 8.2. Most of the transition metal oxides (e.g., cobalt, nickel, chromium, iron, etc.) will give rise to absorption bands, not only in the visible but also in the UV and IR regions of the spectrum. The presence

TABLE 8.2
Coloring Agents Used in Glass

Effect	Oxide
Colorless, UV absorbing	CeO_2, TiO_2
Blue	Co_3O_4, $Cu_2O + CuO$
Purple	Mn_2O_3, NiO
Green	Cr_2O_3, $Fe_2O_3 + Cr_2O_3 + CuO$, V_2O_3
Brown	MnO, $MnO + Fe_2O_3$, $TiO_2 + Fe_2O_3$, $MnO + CeO_2$
Amber	Na_2S
Yellow	CdS, $CeO_2 + TiO_2$
Orange	CdS + Se
Red	CdS + Se, Au, Cu, Sb_2S_3
Black	Co_3O_4 (+ Mn, Ni, Fe, Cu, Cr oxides)

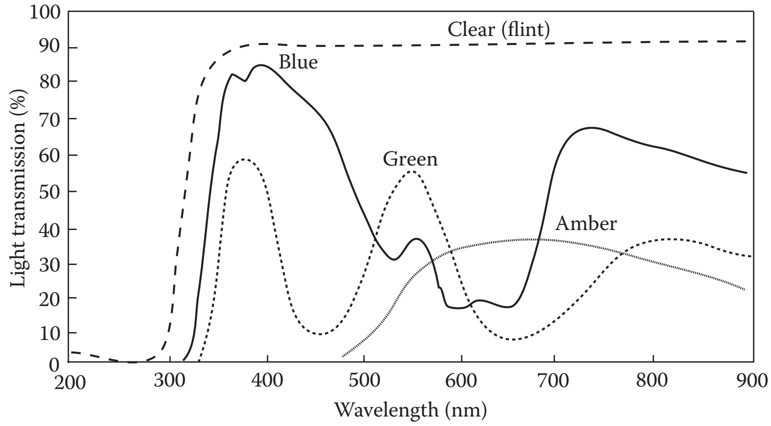

FIGURE 8.2 Typical light transmission of common container glasses.

of iron oxide in glass produces a green color owing to the absorption bands in the UV and IR regions. The three main colors of glass used to produce containers are flint or clear, amber or brown and green.

The U.S. Pharmacopoeia (2004) defines a light-resistant container as one which passes no more than 10% of incident radiation at any wavelength between 290 and 450 nm through the average sidewall thickness. Amber glass provides this degree of light protection quite economically, as shown in Figure 8.2.

Glasses and other transparent materials tend to darken and lose much of their ability to transmit light when bombarded by high energy radiations such as those used in food irradiation. There are two principal causes of this coloration of glass. First, the impact of the radiations may displace electrons, which can become lodged in holes in the structure, forming color centers. Second, changes produced in the valence of bivalent or multivalent metal oxides may result in the increased absorption of light in the visible range. This second effect forms the basis of the process to protect glass from this coloration where a metal oxide (which will change its valence under bombardment more readily than the electrons are displaced) is included in the composition of the glass. Provided that the oxide is free from serious light absorption bands in both valences, protection from discoloration may be obtained. The addition of CeO_2 (it is reduced to Ce_2O_3 by the radiations) in glasses in amounts up to 1.5% has proved an effective means of reducing coloration. Unfortunately, it is a very expensive oxide, so glass containers treated this way are significantly more costly than standard containers.

8.4 MANUFACTURE

8.4.1 Mixing and Melting

The typical composition of a soda-lime glass is given in Table 8.1. The largest constituent (68%–73%) is silica; the second largest constituent (15%–50%) is cullet, originating both as glass scrap from the factory and recycled glass from consumers (so-called *postconsumer* glass). Flint glass is the most color sensitive with a tolerance of 1% green or 5% amber cullet in the batch mix. Amber glass can tolerate 10% green cullet, while up to a 50% mixture of amber and flint cullet can be used in the production of green glass. The use of cullet can cause problems with the production of some types of glass unless there is good separation of colored glass and removal of associated material such as labels. In addition to the problem of color mixing, ceramic and metal contamination (especially aluminum bottle caps) can also limit the use of cullet in glass manufacturing. However, the use of cullet is economically desirable since less energy is required to melt cullet than new raw materials.

Cullet also reduces the amount of dust and other particulate matter that often accompanies a batch made exclusively from new raw materials (Boyd et al., 1994). Although the total primary energy use decreases as the percent of cullet rises, the maximum energy saved is only about 13% (Gaines and Mintz, 1994).

The raw materials are weighed, mixed and charged into a glass-melting furnace, which is maintained at a temperature of approximately 1500°C. Here, they are converted into molten glass that is chemically homogeneous and virtually free of gaseous inclusions (bubbles). The melting process consists of two phases: (1) changing the solids into a liquid and (2) fining or "clearing up" of the liquid. During the refining process, gases (principally CO_2, SO_2 and water vapor) produced by the chemical reaction rise to the surface of the furnace and are removed. When the molten glass becomes free of gas (seed-free), it is then ready for forming into containers. It moves from the furnace into the working end of the furnace (mistakenly called the *refiner*) where thermal homogenization and cooling of the glass to the viscosity required for the particular operation begin. At this point, the temperature of the melt has been lowered from 1250°C to 1350°C to approximately 1100°C.

The preferred energy source for glassmaking is natural gas, although alternate fuels such as oil and propane are used in some plants. With increasingly stringent environmental regulations limiting the emissions of NO_x from glass container furnaces, various systems have been introduced using natural gas and O_2 as the furnace fuel (Cavanagh, 1997). When air (78% N_2) is subjected to very high temperatures, various oxides of nitrogen are formed. By using natural gas and O_2 as the furnace fuel, there is no N_2 to be oxidized. In addition, there are improvements in energy efficiency since only two volumes of O_2 are needed to burn 1 volume of natural gas compared to 10 volumes when air is used. This reduces the total energy requirement by up to one-third (Cavanagh, 1997).

8.4.2 FORMING PROCESSES

The glass is carried from the working end of the furnace to the forming machine in a channel-like structure called a *forehearth*, which is fired by a number of small burners, the aim being to ensure uniform temperature distribution throughout the depth of the glass. At the end of the forehearth is a gob-forming mechanism consisting of a rotating sleeve and vertical plunger. The glass exits in a continuous, viscous stream which is cut by rapidly moving, horizontal steel blades to form what is known as a "gob" (i.e., a mass or lump of molten glass).

Precise control of temperature and shape during the formation of the gob is required for the high-speed production of accurately formed glass containers. Temperatures in the vicinity of 1100°C varying by no more than ±1°C are typical.

The process of converting a cylindrically shaped gob of glass into a bottle or jar is called forming, and it is essentially a controlled cooling process. While various types of forming machines are used throughout the world, the most predominant type is the IS machine. As its name implies, it consists of up to 16 sections, each one an individually functioning, hollow glass machine. It performs two basic functions: it shapes the gob into a hollow container, and simultaneously removes heat from the gob to prevent it from deforming significantly under its own weight.

Two basic types of processes are used to make containers on the IS machine: the blow and blow (B&B) and the press and blow (P&B). A closure size of approximately 35 mm is the dividing line between narrow-neck B&B containers (i.e., bottles) and wide-mouth P&B containers (i.e., jars).

8.4.2.1 Blow and Blow

Bottles are normally produced by a two-step B&B process (Figure 8.3), whereby a gob of glass, accurately sheared in terms of weight and shape, is delivered into an externally air cooled, cast iron mold from above to shape a preform (also known as a parison or body blank). Some of the glass flows

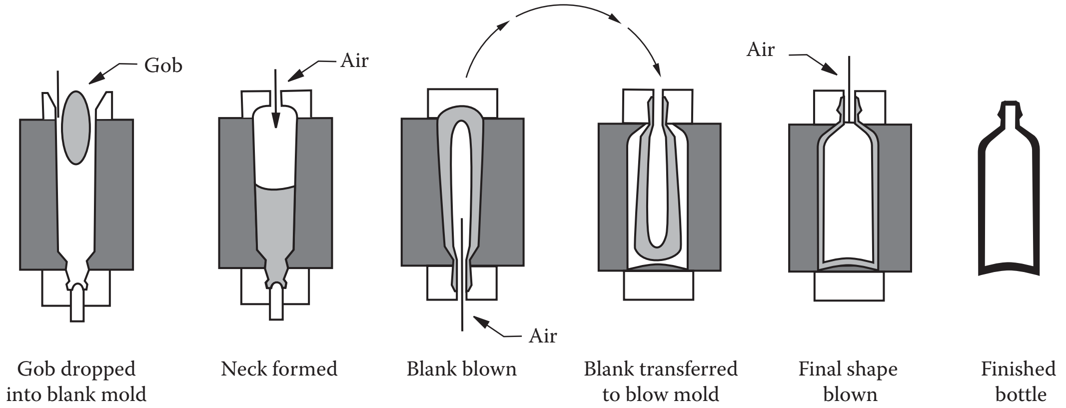

FIGURE 8.3 "Blow and blow" process for glass container manufacture.

over a plunger in the base of the mold, which is used to mold the finish (so-called because in the early days of glass manufacturing, it was the part of the container to be fabricated last) of the container by means of ring molds. Compressed air is applied to force the glass down onto the plunger to form the neck ring. Sometimes, vacuum is applied from the bottom as an alternative or additional procedure.

When the finish molding is complete, the plunger is retracted and air blown in from the bottom of the mold, enlarging the size of the bubble until the glass is pressed out against the blank mold to form a hollow, thick-walled preform or parison. This is then inverted and transferred to the blow mold where it elongates under its own weight until it nearly touches the base of the mold. Air at about 200 kPa is applied so that the glass is pressed against the metal surface of the blow mold, which is air-cooled to ensure rapid removal of heat. The mold is then opened and the fully blown parison (now at approximately 650°C) is removed and briefly held over a deadplate to allow air to flow up through the deadplate and around the container to further cool it. It is then transported to the annealing lehr.

8.4.2.2 Wide Mouth Press and Blow

In the case of jars, a two-step WMP&B process (Figure 8.4) is used. The body blank or parison is formed by pressing the gob of molten glass against the mold walls with a large plunger. When the cavity is filled, glass is then pushed down into the neck ring and the finish is formed. No baffle or

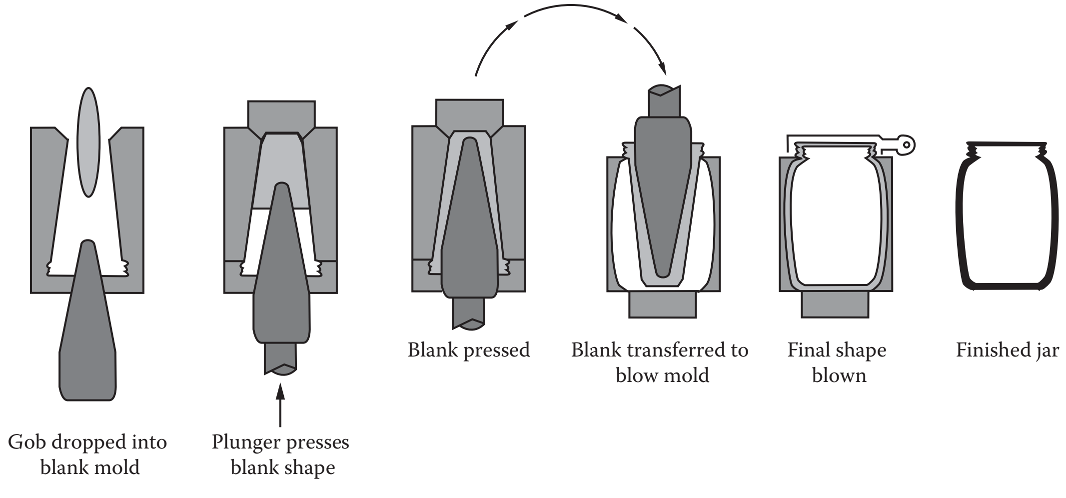

FIGURE 8.4 Wide mouth "press and blow" process for glass container manufacture.

counterblow air is used in the formation of the parison, with the operation relying on the mechanical introduction of the plunger into the glass. The rest of the steps in the WMP&B process are identical to those in the B&B process.

8.4.2.3 Narrow Neck Press and Blow

Narrow neck press and blow (NNP&B) is a more recent process for lightweight bottles, in which the gob is delivered into the blank mold and pressed by a metal plunger. The plunger and gob together have the same volume as the blank mold cavity. This enables the glassmaker to decide exactly how the glass is distributed in the parison and, hence, to be able to more accurately control the uniformity of glass distribution in the finished container. Indeed, weight savings of up to 30% can be made. The second stage is similar to the B&B process. The parison is blown to a finished container having a more uniform wall thickness and, as a result, higher strength.

The mechanical performance of lightweight glass bottles produced by the NNP&B process has been compared with the same glass bottles (regular weight 20% heavier) produced by the conventional B&B process (Jaime et al., 2002). The lightweight glass bottles had a more homogenous thickness distribution in comparison with the regular weight bottles and a better performance (about 33% improvement) in relation to the impact strength, especially in the heel. The vertical load strength of the lightweight glass bottle also indicated a superior performance to the regular weight bottle. Due to the better thickness distribution of lightweight glass bottles, they withstood a maximum temperature difference (progressive thermal shock) of 5°C–10°C higher than the regular weight bottles.

8.4.3 ANNEALING

The term annealing generally refers to the removal of stress, and the annealing temperature or point is defined (ASTM C336) as the temperature at which stresses in the glass are relieved in a few minutes. The containers are transferred from the deadplate to a large oven, known as a lehr, which is equipped with a belt conveyer. The function of the annealing lehr is to produce a stable product by removing any residual stresses resulting from nonuniform cooling rates during forming and handling. This is achieved by raising the temperature of the container to approximately 540°C (almost the softening point of the glass), holding it there for a few minutes and then cooling at a rate which is consistent with the removal of stress from a predetermined wall thickness.

The critical area of temperature is between the upper annealing point (softening point) and the lower annealing point, after which they may be cooled at a rate which enables them to be handled as they emerge from the lehr. During cooling, the inside surface is hotter than the outside; this results in compression on the outer surface but tension at the inner surface. As mentioned earlier, glass fractures only in tension and usually at the surface. Sudden cooling introduces tensile stresses into the outer surfaces and compensating compressional stresses in the interior. Poorly annealed containers may be subject to breakage if the tension is high or the inner surface is bruised (Boyd et al., 1994).

8.4.4 SURFACE TREATMENTS

The strength of a newly made glass container can be rapidly reduced by moisture or abrasion, and some form of surface treatment to increase the strength is essential, since glass is nonlubricious. Two general types of surface treatment are applied to glass containers to modify mechanical properties.

8.4.4.1 Hot-End Treatment

In hot-end treatment (typically carried out while the glass container is at 550°C), vapor containing tin or titanium (generally in the form of a tetrachloride) is brought into contact with the outside of the container, forming a thin unimolecular film of metal oxide. This treatment prevents surface damage while the container is still hot, strengthens the surface and improves the adhesion of the subsequent cold-end coating.

8.4.4.2 Cold-End Treatment

Cold-end treatment (typically carried out while the glass container is at less than 100°C) is designed to protect the container surface and assist its flow through the filling line. Typically, it involves spraying an organic material in an aqueous base containing either waxes, stearates, silicones, oleic acid or polyethylene onto the outside of the container to increase its lubricity by providing a surface with a low coefficient of friction (Cavanagh, 1997). It is important to check the compatibility of the cold-end treatment with any adhesives used to attach labels. Sometimes, only the cold-end treatment is applied.

8.4.4.3 Shrink Sleeves

Although not strictly related to surface treatment of glass containers, shrink sleeves will be considered here since they can have an important influence on the formation of imperfections leading to container breakage due to surface contact. Most shrink sleeves are made of oriented plastic films that shrink around a glass container when heat is applied. Two types of protective labels are used on glass bottles in the form of a body sleeve: one constructed from thin, foamed PS; the other is made from uniaxially oriented PVC or PS. The former offers some thermal insulation, while the latter (which can completely wrap the bottle from its neck to underneath the base if desired) contains the glass fragments and prevents shattered glass being scattered in all directions if the bottle is dropped. Shrink sleeves are discussed in more detail in Section 9.5.4.

8.4.5 Defects in Glass Containers

Some 60 defects can occur in finished glass containers, ranging from critical defects such as “birdswings” and “spikes” (long, thin strands inside the container that would probably break off when the container was filled) to minor defects such as “wavy appearance” (an irregular surface on the inside). Defects are classed as “critical” if they are hazardous to the user and make the container completely unusable, “major” if they reduce the usability of the container or its contents and “minor” if they detract from its appearance or acceptability to the consumer (Hanlon et al., 1998).

Accurate classification of defects in glass packaging and their commercial significance are areas of specific expertise and no attempt will be made to describe or catalog them here.

8.5 GLASS CONTAINER DESIGN

One of the major advantages of glass as a packaging material is its capability to be formed into a wide range of shapes related to specific end uses, customer requirements and aesthetic appeal. The commercialization of computer-aided design (CAD) and computer-aided manufacture (CAM) has made the task of designing and manufacturing new glass containers considerably easier and more rapid. This has lead to greater flexibility and resulted in considerable efficiencies through a more thorough analysis of stresses and strength/weight factors and calculation of likely mechanical performance. In particular, the application of finite element analysis (FEA) has resulted in lightweighting of glass containers with improved mechanical performance (Davis, 2009). Numerical modeling and simulations have also been applied in the production of glass containers to optimize performance (Dijkstra and Mattheij, 2008). For example, the forming process has been modeled as a coupled thermodynamic/mechanical problem with corresponding interaction between glass, air and equipment and correctly represented the flow of the glass and the energy exchange during the process. As well, simulations have helped optimize cooling conditions and increased production speeds.

8.5.1 GLASS CONTAINER NOMENCLATURE

The basic nomenclature used for glass containers is shown in Figure 8.5. Usually, the shape of the container is determined by the nature of the product, each product group having a characteristic shape. Thus, liquid products generally have small diameter finishes for easier pouring; solid products require larger finishes for filling and removing the contents. As well as filling and emptying requirements, consideration must also be given to the nature and manner of labeling the container, and its compatibility with packaging and shipping systems.

The container finish is the part of the container that holds the cap or closure (i.e., the glass surrounding the opening in the container). It must be compatible with the cap or closure and can be broadly classified by size (i.e., diameter), sealing method (e.g., twist cap, cork, etc.) and special features (e.g., snap cap, pour-out, etc.).

The finish has several specific areas including the sealing surface, which may be on the top or side of the finish, or a combination of the two; the glass lug, which is one of several horizontal, tapering and protruding ridges of glass around the periphery of the finish on which the closure can be secured by twisting; the continuous thread, which is a spiral projecting glass ridge on the finish, intended to mesh with the thread of a screw-type closure; a transfer bead, which is a continuous horizontal ridge near the bottom of the finish, used in transferring the container from one part of the manufacturing operation to another; a vertical neck ring seam resulting from the joining of the two parts of the neck ring; and a neck ring parting line, which is a horizontal mark on the glass surface at the bottom of the neck ring or finish ring, resulting from the matching of the neck ring parts with the body mold parts. Not all glass containers have transfer beads or vertical neck ring seams.

Although there are literally hundreds of different finishes used on glass containers, a series of voluntary standards containing specific dimensions, specifications and tolerances has been established for every finish designation by the Glass Packaging Institute (GPI) in the United States and equivalent bodies in other parts of the world. These voluntary standards are intended to provide a basis for achieving compatibility and interchangeability between manufacturers and users of glass containers and closures.

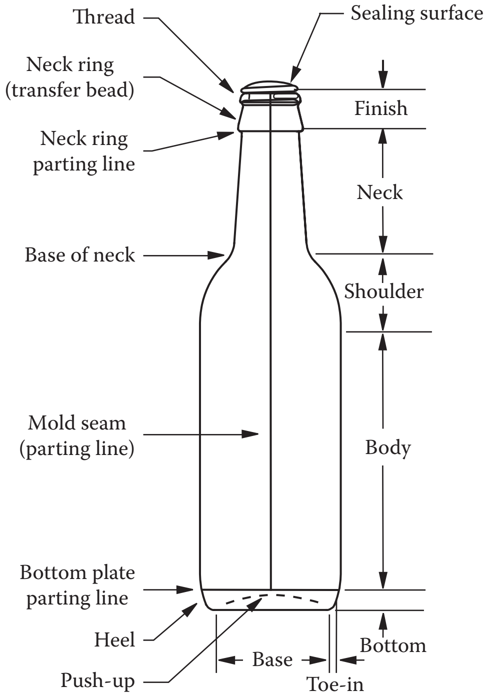

FIGURE 8.5 Glass container nomenclature.

Once a design has been accepted, the molds used in the manufacturing process must be made. They are usually constructed of cast iron and consist of three parts: a bottom plate, a body mold (divided vertically into two halves) and a neck or finish mold, which is also usually split into two parts. Because of the high cost of mold manufacture, changes to container size and shape are usually made only if large quantities of the container are required. Generally, customers select their containers from the standard range provided by glass manufacturers unless they are extremely large users, in which case the extra expense of customized designs is justified.

The GPI has established limits which are generally accepted as reasonable tolerances by most manufacturers. Allowances have been made for increases in container size as a consequence of mold wear, as well as expected process capabilities of the manufacturer. Although closer tolerances can be met, this often incurs a higher cost since molds must be replaced more frequently.

8.5.2 Glass Container Strength Factors

The shape, surface condition, applied stresses and glass weight all combine to determine the strength of a glass container (Glass container design, 1997). Sharp transitions in container shape (e.g., a rectangular cross section compared to a circular cross section) lead to high stress concentrations. Small surface imperfections formed as a result of surface contact during the manufacturing process and subsequent handling operations can influence container strength. Good design will incorporate specific contact areas (e.g., knurls or small protrusions) that concentrate abrasions where they will have minimal effect on glass strength. Surface treatments (see Section 8.4.4) also assist in reducing surface abrasions.

The forces applied to a glass container during its intended use depend largely on the function of the container. Carbonated beverages and vacuum-packed foods develop internal pressure stresses, predominantly circumferential and longitudinal. In the cylindrical part of a typical glass bottle, the circumferential stress S depends on the bottle diameter d, the glass thickness x and the pressure p as follows (Glass container design, 1997):

$$S = \frac{pd}{2x} \tag{8.1}$$

The longitudinal stress in this part of the bottle is one-half of the circumferential value S; Equation 8.1 does not hold for the noncylindrical parts of a bottle.

Typical pressures inside a carbonated beverage bottle at ambient temperatures are 400 kPa (four volumes of CO_2 gas per volume of beverage), rising to about 700 kPa at 40°C and 1000 kPa at pasteurization temperatures. Bottles for carbonated beverages have target bursting strengths well in excess of the equilibrium pressure of a carbonated beverage. The target bursting strength of a nonrefillable, one-way bottle is between 1240 and 1380 kPa, and for a returnable bottle about 1720 kPa. Willhoft (1986) presented figures which indicated that the mean bursting pressure for a brand new, untouched glass bottle was 4054 kPa, falling to 2331 kPa on delivery to the bottler and to 1524 kPa after long use.

Vertical load stresses are generated by stacking containers on top of each other or by applying a closure; these compressive forces produce tensile stresses in the shoulder and heel region of up to 690 kPa. These stresses can be lowered by decreasing the diameter difference between the neck and the body, by increasing the shoulder radius and by reducing the diameter difference between the body and the bearing surface (Glass container design, 1997).

During hot filling or pasteurizing of glass containers, the rapid temperature changes lead to the development of tension stresses on the cold surface and compression stresses on the hot surface, with additional bending stresses being generated by expansions and contractions of the container (see Section 8.3.2). Thermal stresses can be reduced by minimizing the temperature gradient from the hot to the cold side, decreasing the glass thickness, and avoiding sharp corners, especially in the heel.

Stresses caused by steady-state thermal gradients may or may not cause failure, depending on the degree of constraint imposed by some parts of the container on others, or by the external mounting. Consequently, under minimum constraint and maximum uniformity of gradient through the thickness, very large temperature differences can be tolerated (Boyd et al., 1994).

8.6 CLOSURES FOR GLASS CONTAINERS

The final, critical aspect of glass packaging is the closure which can consist of a cap, lid, cork or plug to seal the jar or bottle. Although glass is an excellent barrier to moisture vapor, gases and odors, an incorrectly designed or applied closure may negate the benefits that glass packaging offers in protecting foods from deterioration. Closures for glass containers are discussed in Chapter 10.

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9 Printing Processes, Inks, Adhesives and Labeling of Packaging Materials

9.1 INTRODUCTION

Most packaging materials are printed, so a basic knowledge of the characteristics of the main printing processes is essential. In 594 CE, the Chinese began to practice printing from a negative relief. Their method of rubbing off impressions from a wood block spread along the caravan routes to the western world and, in 1400, the technique of printing with wooden blocks arrived in Europe. The invention of paper, which was to provide the ideal surface for printing, also came from China.

In 1450, Johann Gutenberg invented the printing press in Germany by adapting the wine presses, which had been used in the Rhine Valley since the days of the Roman Empire. He used a recently perfected ink (based on linseed oil and soot) and also invented a functional metal alloy to mold the type. The printed word enabled information and knowledge, which was previously restricted to ecclesiastical establishments, to be widely disseminated and, by 1500, more than 9 million printed books were in circulation.

The basic principle of most printing processes is that ink is deposited on an engraved plate and the inked image transferred to the substrate through contact. This can be performed in several ways when packaging material is to be printed. In direct printing, the inked plate makes direct contact with the packaging substrate. In indirect printing, the engraved plate transfers ink to an intermediate rubber blanket that then transfers the image to the packaging substrate. In stencil printing (e.g., screen printing) the ink is passed through a stencil to the substrate.

There are several different methods of package printing in use today: the conventional printing methods of relief (letterpress, flexography and flexo process), gravure or intaglio, lithography (offset) or planographic and screen or porous and the digital printing methods of ink-jet and electrophotography as shown in Figure 9.1. In the conventional methods, ink is applied to a printing unit such as a cylinder or a plate and is then transferred to the substrate by direct contact.

Plastics such as LDPE, HDPE, PP, PET and EVA copolymer cannot be satisfactorily printed unless their surfaces have been pretreated so as to obtain satisfactory adhesion between the ink and the plastic. This is because their inert, nonpolar surfaces do not permit any chemical or mechanical bonding between them and the ink. Various processes are used, all aimed at oxidizing the surface in some way. These include solvent treatment, chemical treatments, flame treatment and electrical treatment and several of these processes were discussed in Section 5.3.1. In addition to removing dust, oils, greases, processing aids and so on, the surface of the plastic is activated by these processes and becomes more polar.

Photopolymers are light-sensitive plastics used to prepare letterpress, flexographic and offset printing plates. They have been available since 1974 and numerous systems have been developed for producing photopolymer plates. Basically, a photographic process is used in contrast to the photomechanical etching and molding system used to prepare most rubber plates. The photopolymer plate is formed by exposing the photopolymer to UV light through a film negative, which carries the image to be reproduced. Each photopolymer plate is an original derived directly from a negative.

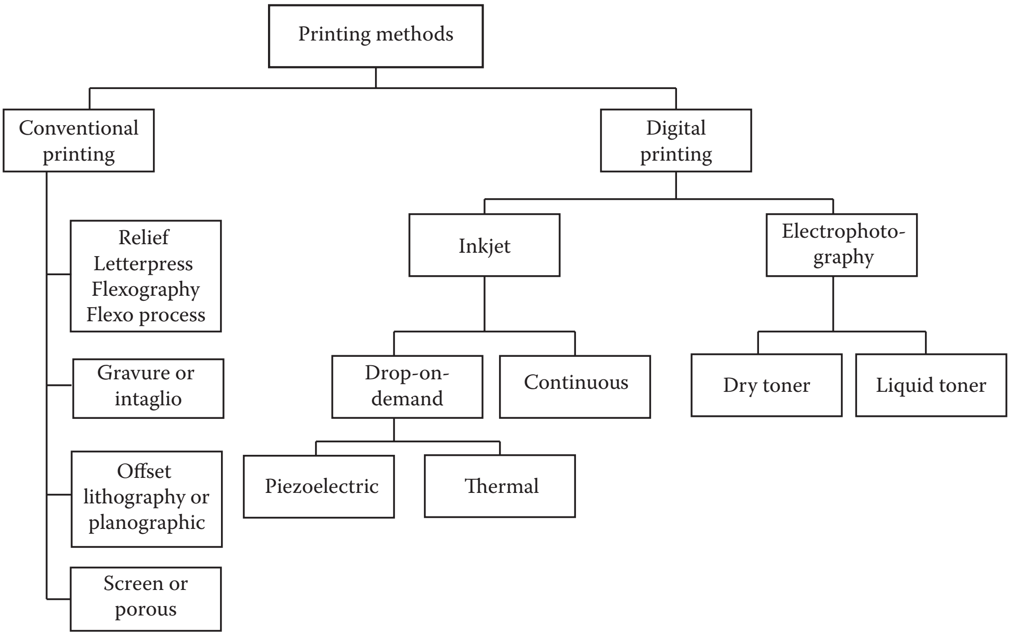

FIGURE 9.1 Classification of printing methods. (Redrawn from Heilmann, J., Digital and conventional packaging printing processes, *Second SustainPack Conference*, Barcelona, Spain, December 4–5, 2006.)

9.2 PRINTING PROCESSES

9.2.1 Relief

In this long-established process (commonly known as *letterpress*), the images or printing areas are raised above the nonprinting areas so that the ink rollers touch only the top surface of the raised areas. Originally, metal type was used, in which case the process is called *letterpress*, but this has been largely replaced by synthetic rubber or photopolymer printing plates, in which case the process is called *flexographic*.

9.2.1.1 Letterpress

Letterpress printing presses are of three types: platen, flat-bed cylinder, and rotary, the latter being by far the most common type for printing packaging materials. Plates must obviously be curved for mounting on rotary presses. They receive ink as they contact the inking rollers. An impression cylinder presses the substrate against the inked plate cylinder and transfers the image.

The inks used for letterpress printing are oil-based and slow drying, and have a pasty consistency, which makes the process a difficult one to apply to plastics films unless (like rigid PVC and RCF), they are not too susceptible to the high pressures which often have to be applied. A distinctive feature for recognizing letterpress printing is a "ghost-like" image around each character caused by the ink spreading slightly due to the pressure of the plate on the substrate. A slight embossing or denting sometimes appears on the reverse side of the surface, but the letterpress image is usually sharp and crisp. Letterpress printing is still used for the printing of folding cartons, labels and all types of bags for dry goods.

9.2.1.2 Flexography

Flexography, a relief-printing technique and variation of letterpress printing, is a high-speed method that was developed primarily for printing packaging materials. Introduced into the United States on a fairly broad scale from Germany in the early 1920s, it was known as *aniline* printing because at

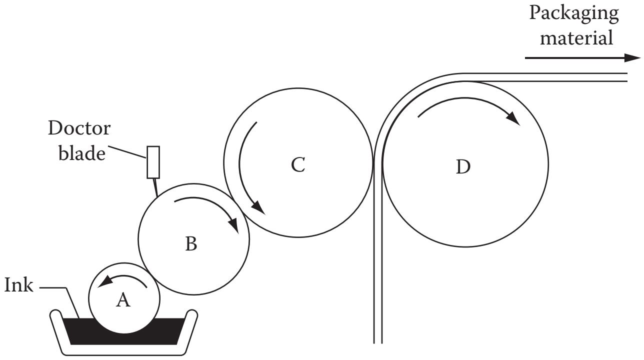

FIGURE 9.2 In flexographic printing, the fountain pan supplies ink to the rubber fountain roller A which supplies ink to the anilox roller B which transfers a uniform layer of ink to the printing cylinder C; the impression cylinder D presses the packaging material against the printing cylinder from which ink is transferred to the packaging material.

that time coal tar dyestuffs (derived from aniline oil) were used as the coloring ingredients for ink. In 1952, the name was changed to flexography. This is defined as a method of direct rotary printing using resilient, raised image printing plates, affixable to plate cylinders of various repeat lengths, inked by a roll or doctor blade wiped metering roll, carrying fluid or paste type inks to virtually any substrate.

Generally, four rollers or cylinders are used. A rubber inking roller (fountain roller) revolves in an ink reservoir and transfers ink to a cavitated metering roller (often called an *anilox roller*) which is engraved such that it can hold ink in its recesses. An optional doctor blade removes excess ink from the surface of the anilox roller so that it transfers a controlled film of ink to the printing plates, which were made of rubber and referred to as *stereos* (an abbreviation for stereotypes), but are now generally made from photopolymer material. The printing plate then transfers this layer of ink to the substrate which is supported by the impression cylinder (Figure 9.2).

Flexographic printing can be carried out with a number of printing stations in sequence: one on top of the other (stack press), with the printing rollers arranged around a central large diameter drum (central impression) or with the printing stations arranged in a straight line (in line). A stack press is used primarily for paper and laminated films, a central impression press for high-quality wide web films and an in-line press for corrugated and folding cartons (Taggi and Walker, 2009). Because the costs of producing the plates are relatively low, flexographic printing is cost effective, especially for short runs.

Thin, fast-drying, solvent-based inks are used in flexography, permitting multicolored printing to be done in one pass provided that oven drying is used. High speeds are possible. A major disadvantage was that very fine half tones were unable to be reproduced, because the inks had a low viscosity and it was difficult to get sharp images, with fine type having a tendency to fill in. However, with the introduction of photopolymer plates, this disadvantage has been overcome.

9.2.1.3 Flexo Process

For flexo process printing, a double-chambered doctor blade delivers the ink to the anilox roller in a closed system that ensures a constant flow of ink. A doctor blade removes excess ink from the anilox roller which is engraved with a very fine screen of 240–320 lines cm^{-1} (600–800 lines $in.^{-1}$). The engravings distribute a metered amount of ink to the print roller, which has printing plates mounted onto it. An impression roller presses the packaging material against the printing plate and ensures good transfer of ink to the paper (see Figure 9.3).

The quality of reproduction possible with flexo process printing has increased to the extent that it now approaches that of gravure printing. Photographic designs are able to be used.

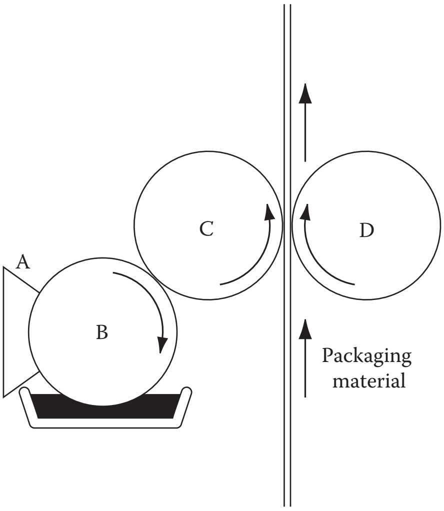

FIGURE 9.3 In flexo process printing, a chambered doctor blade A delivers ink to an anilox roller B which distributes a metered amount of ink to the printing cylinder C; the impression cylinder D presses the packaging material against the printing cylinder.

9.2.2 GRAVURE

Gravure printing was known as *intaglio* from the Italian word for incising or engraving, reflecting the fact that this technique was first practiced in Florence in 1446 by the goldsmith and engraver Finiguerra. Gravure printing (more commonly known as *rotogravure printing* by the packaging industry because cylinders rather than plates are used) consists of a printing cylinder (image carrier), an impression cylinder and an inking system, as shown in Figure 9.4. The printing cylinder (usually made with a chrome-plated copper surface) has the image area etched to form a series of small cells of varying depth so that differing amounts of ink are picked up. During printing, the image carrier is immersed in fluid ink. As the image carrier rotates, ink fills the tiny cells and covers the surface of the cylinder. A doctor blade wipes away excess ink from the nonimage surface of the cylinder. As the cylinder comes into contact with the material to be printed, an impression cylinder (generally covered with a resilient rubber elastomer) presses the material into contact with the tiny cells of the printing cylinder, causing the ink in the cells to be transferred to the material through capillary action.

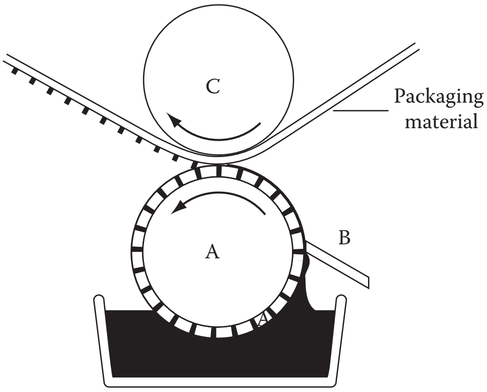

FIGURE 9.4 In rotagravure printing, an engraved cylinder A rotates through the ink, a doctor blade B removes ink from all but the etched recesses and the remaining ink leaves an imprint on the packaging material. C is a rubber impression cylinder.

As with flexographic printing, gravure can print on a wide variety of materials and has found widespread use in the printing of cartons, foils, films and papers for conversion into bags and so on. The ideal substrates are generally smooth in finish (i.e., clay coated, supercalendered papers, films and foils) because effective ink transfer depends on thorough cell contact with the substrate.

Gravure printing can easily be recognized because the entire image area is screened (usually 60 lines cm^{-1} [150 lines in.^{-1}] for normal printing but more if a higher quality is required) to produce the tiny cells in the gravure cylinder. Thus, with a normal screen, there would be 3,600 cells cm^{-2} (22,500 cells in.^{-2}).

The preparation of the printing cylinders is costly and time-consuming and gravure printing is therefore only economical for long production runs. Printing speeds are slower than those obtainable with flexographic printing processes. Despite these disadvantages, gravure printing produces high-quality, multicolor fine-detail printing.

9.2.3 LITHOGRAPHY

Lithographic printing (also known as *offset lithography* and occasionally as *planographic* printing) was invented by the Austrian artist Alois Senefelder in Munich in 1798 as a way to print musical scores more cheaply than by engraving. A lithograph is a print of a drawing done on a stone (usually a limestone). When Senefelder realized his stone-printing method could be used for many other things, he went into business with some partners to operate lithographic presses in the capitals of Europe. For 100 years, lithography was used to print packaging, cards, menus, book illustrations and labels—the first mass forms of advertising. It is still the major form of printmaking today.

Lithography involves printing from a flat surface, the image area being neither raised (as in letterpress and flexography) nor lowered (as in gravure). It is based on the principle that oil and water do not mix.

Oil-based ink is applied evenly through a series of rollers to the *offset* plate cylinder (usually made of aluminum). Water or fountain solution is simultaneously fed via rollers to the plate just before it contacts the inking rollers, as shown in Figure 9.5. Although very little moisture is required, the

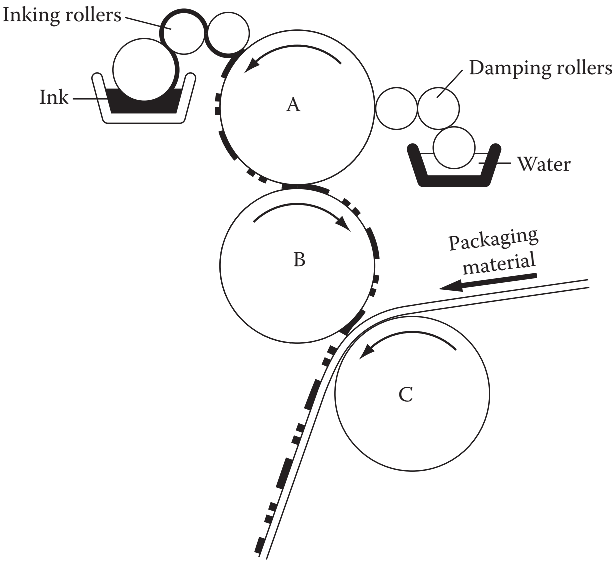

FIGURE 9.5 In offset lithography the image is neither raised nor lowered. It is based on the principle that oil and water do not mix. A is the plate cylinder, B is the offset blanket cylinder and C the impression cylinder.

film of moisture is continuous on the nonimage areas of the plate and acts as a barrier, preventing adhesion of the ink. The plate accepts ink and repels water in the image areas. The image on the plate is transferred or offset to an intermediate or blanket cylinder covered with a rubber blanket. The material to be printed picks up the image as it passes between the blanket and the impression cylinder. The soft rubber blanket creates smooth, sharp images on a wide variety of materials, and is used extensively where illustrations are required on packaging materials.

Offset lithography produces quality printing on both rough and smooth papers, although coated papers are often used as they require less ink and give more brilliance to colors. It is used for printing labels and cartons, and for decorating metal containers, but is rarely used with plastic films. Offset printing plates are cheaper than those for rotogravure and can now deliver almost equivalent print quality.

A process which combines features of both letterpress and lithographic printing methods is known as *letterset* or *dry offset* printing. The term *dry* is used to differentiate it from the standard offset system that uses the incompatibility of water and inks to dampen the surface of the plate or substrate to prevent ink transfer.

In dry offset, ink is transferred by the raised surface of the relief plate to the rubber blanket, which then prints the entire multicolor copy taken from one to as many as six plate cylinders in one operation. No chemical or water action is involved. This method has been especially developed to print round and tapered containers. Letterpress and lithographic inks can be used, with the inks being either heat set or UV cured. However, special letterset inks that provide very low odor printing for food cartons and confectionery wraps that require the use of water-miscible inks are available. Letterset is also used for printing on plastic bottles, cups and tubs and on some metal packages, primarily tubes.

9.2.4 SCREEN

Screen printing (also referred to as *serigraphy* or *porous* printing) is basically a stenciling process which uses a fine mesh screen made of silk, polyester or metal (fine wire) on which is supported a stencil. The screen is completely coated on both sides with a light-sensitive emulsion, and a positive image of the graphics to be printed is placed on the outside of the emulsion screen. On exposure to intense light, the unshielded emulsion is cured (hardens) after which the shielded, uncured emulsion can be washed away. The nonblocked mesh area of the screen allows ink to pass through the fine mesh.

Ink is forced through the screen onto a substrate by a rubber blade or squeegee. Although screen printing was originally a hand process (and still is in some applications), power-screen presses with mechanical feed and delivery are in common use. Rotary screen presses are also available.

Screen printing inks can be solvent, oil, rubber or water based, but are usually of the drying-oil type and have the consistency of thick paint. Far greater amounts of ink are applied in screen printing compared to other methods of printing, and sometimes the texture of the screen can be recognized on the final image. Extra drying time is frequently needed.

Screen printing is a very versatile printing process, capable of printing on the widest variety of substrates including rounded and irregular surfaces, for example, milk and soft drink bottles. It is ideal for short production runs and is used for imaging glass, box wraps, folding cartons and plastic containers. However, it is relatively low speed and time is required for the ink to dry between colors.

9.2.5 DIGITAL

Digital printing refers to printing from a digital source directly to a variety of substrates using large format and/or high volume laser or ink-jet printers or electrophotography. Digital printing methods do not utilize a physical master (i.e., a fixed printing plate or cylinder) because all the graphic content is in digital form from creation to output. This results in two distinct benefits. First, consecutive copies can be different from each other allowing customization and personalization for selected target groups. Second, the printing process becomes simpler and faster compared to traditional printing methods due to the elimination of master production.

9.2.5.1 Ink-Jet

Ink-jet or impactless printing is a noncontact, pressureless printing process in which tiny drops of ink are projected directly onto a surface for printing without physical contact between the printing device and the substrate. The placement of each drop is controlled electronically. The printing process is termed impactless because no high mechanical impact pressure is involved in transferring ink to the receiving surface as in letterpress printing. Because it is impactless and no platen is required to support the receiving substrate, the process can be used to print on cans, bottles and many other objects. The two main techniques used in ink-jet printers are continuous and drop-on-demand (DoD); DoD is further divided into piezoelectric DoD and thermal DoD. A DoD process uses software that directs the heads to apply between zero and eight droplets of ink per dot, only where needed.

In the continuous ink-jet (CIJ) technique, ink droplets are continually generated by pumping liquid ink to the ink chamber and creating high frequency acoustic pressure waves using a piezoelectric crystal. The wavefield forces ink droplets out from the printhead. The frequency of droplet generation can be 64,000–165,000 droplets s^{-1}. Electrodes apply an electrical charge to the droplets, and the charged droplets are steered using deflectors. Droplets can be either left uncharged or charged selectively according to the signal of the printed image. CIJ technology has been used in applications that require high volume and medium quality, for example, marking and coding of products and packaging.

In the piezoelectric DoD ink-jet technique, the droplets are formed when an electrical signal causes a piezoelectric crystal to expand, which creates a pressure wave forcing a droplet out of the printhead nozzle. The thermal DOD ink-jet, also known as a bubble jet, works in a similar manner, but the pressure wave is generated by heat and vaporizes a small quantity of ink, causing a large pressure increase that propels a droplet of ink onto the substrate. Most production ink-jet printers use piezo printheads.

This printing process has been available since the mid-1960s and has found widespread application for the labeling, coding and dating of packaged food. The tiny droplets of ink are able to be projected into various recesses on the package, which, with the use of inks that adhere to nonabsorbent surfaces, make it ideal for such applications.

9.2.5.2 Electrophotography

Electrophotography, or EP, is the oldest of the nonimpact printing technologies, and was invented by Chester F. Carlson in his Queens, New York, laboratory in 1938. The first of his 28 patents on the subject was issued in 1940 and the first EP copier was sold in 1950. EP printing is often referred to as xerography (from the Greek for "dry writing") or laser printing. Technically, the term "laser" refers to the specific light exposure technology used in the process, but the term laser printer is now generically used to describe any EP printing system (such as an LED printer), regardless of its exposure technology. EP is the printing technique used in copy machines, laser and LED printers, and is the most complex digital printing technology, as well as the most widely used, of the plateless printing technologies.

EP is based on an image carrier surface that is photoconductive and can be charged electrically (Viluksela et al., 2010). Typically, a selenium-coated, photoconductive drum is positively charged. Using a laser or LEDs, a negative of the image is beamed onto the drum, cancelling the charge and leaving a positively charged replica of the original image. Dry or liquid toner attaches to the image areas of the photoconductive surface, and electrostatic forces transfer the toner onto the substrate where it is fixed to the paper. The final stage is fusing, which uses heat and pressure, pressure alone or light to cause the toner binder to melt and permanently adhere to the paper surface.

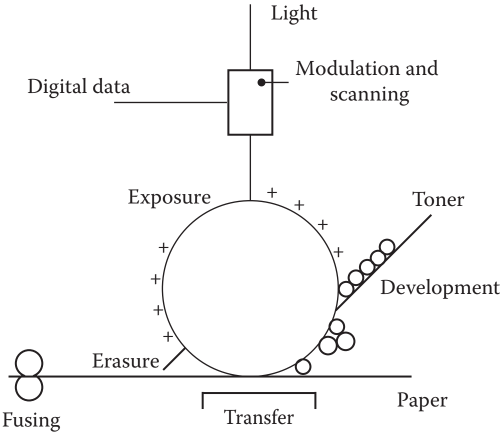

FIGURE 9.6 Principle of digital electrophotography. (Redrawn from Hakola E., Oittinen P. 2009. Principles of digital printing. In: *Print Media–Principles, Processes and Quality*. 2nd edn. Oittinen P., Saarelma H. (Eds). Papermaking Science and Technology, book 13. Paper Engineers' Association/Paperi ja Puu Oy, Helsinki, Finland, pp. 147–172.)

The photoconductive surface is cleaned mechanically and electrically, and charged for the next imaging, as shown in Figure 9.6.

The image quality of digital printing is high enough to be used for packaging. The advantages of digital printing include the possibilities of using variable data, on-demand manufacturing and cost-effectiveness within short print runs. The limitations may include a smaller color gamut compared to traditional presses, format size, productivity and lower printing speed. In addition, the variety of substrates for use is smaller than in traditional printing (Ryynänen et al., 2012).

Lahti et al. (2004) evaluated the printability of three different extrusion coatings used for packaging boards (LDPE, PET and ethylene-*co*-methyl acrylate copolymer) printed using dry toner EP. They showed that adequately high surface energy and surface–charge uniformity were necessary for uniform print quality and toner adhesion. LDPE required surface modification with corona treatment to get good toner adhesion and high print quality, whereas the other two polymer coatings had the required surface energy without corona treatment.

Since the mid-1980s, color EP printing (commonly known as laser printing technology) has been a popular choice by businesses, with high-quality laser printing rivaling more expensive offset color printing for image quality and general appearance. The suitability of digital printing for short runs in the packaging industry has been evaluated and the productivity of a digital packaging line compared with that of a standard packaging line based on an offline offset printing technique (Ryynänen et al., 2012). It was possible to achieve significant cost savings using inline digital printing and converting systems when compared with traditional offline manufacturing systems in short runs. The break-even point was estimated to be in the range of 4000–8000 packages, depending on the package and sheet sizes, with the greatest difference in price per package occurring when the runs were below 2000 packages.

9.3 INKS

9.3.1 INTRODUCTION

The major categories of printing processes are distinguished by whether the ink is held below, on or above, or passes through the surface that contacts the substrate to be printed. Recently, several *no surface* or *contactless* methods have been developed. These different geometries impose different requirements on the inks, which, in turn, largely determine the environmental impacts of each process.

9.3.1.1 Below the Surface

This includes the gravure process, using engraved plates, and the rotogravure process, using engraved cylinders. Ink is retained in depressions in the surface, and is transferred to the substrate when pressed against it. The ink needs to flow readily, and therefore has a relatively high solvent content.

9.3.1.2 On the Surface

This includes the lithographic processes that use differences in surface tension to create areas on the surface that are ink repelling and ink attracting. The type of ink used is invariably one that does not mix with water because the ink-repelling areas are water attracting, and vice versa. A water-based "fountain solution" (often containing some alcohol or equivalent solvent) is used to help keep the ink out of the ink-repelling areas. The ink needs to be somewhat higher in viscosity so that it sits on the surface without spreading. Both the hydrophobic ink solvent (often toluene) and the organics from the fountain solution can add to the environmental impacts. A relatively new process—waterless printing—is a type of lithographic printing that uses mechanical and temperature differences to accomplish the same purpose, with much lower solvent emissions.

9.3.1.3 Above the Surface

This consists of the archetypal printing processes associated with Gutenberg and the linotype machine. Raised letters and lines are inked and the ink is transferred to the substrate. The ink is low viscosity in order to spread uniformly on the ridges, and dries quickly once transferred to the substrate, thus requiring a volatile solvent. There are two major variations, depending on the nature of the plate or roller: letterpress and flexographic, as discussed earlier.

9.3.1.4 Through the Surface

This refers to the screen printing processes, in which the ink is forced through a polyester or wire mesh. A stencil is applied to the top of the mesh, and the ink passes through voids in the stencil, with the mesh regulating the flow of the ink.

9.3.1.5 No Surface

Modern electronics technology has made possible new approaches to transferring ink onto substrates in preset patterns with ink-jet and EP printing, which are now well-established techniques. The requirements for these inks are different and in some ways much more stringent than those for inks for traditional impact printing methods.

9.3.2 INK COMPONENTS

Inks are designed for each of the five main printing processes. Flexography and gravure are known as the *liquid ink* processes, and are based on volatile solvents that evaporate readily at room temperatures. Typically, the evaporative process removes about 35%–40% of the delivered ink volume. Lithography and letterpress are collectively known as the *paste ink* processes, using inks that are essentially nonvolatile at normal temperatures. Screen printing uses inks that fall between these two groups.

Printing inks are mixtures of three main types of ingredients: pigments, vehicles and additives. Pigments used in printing inks include both inorganic pigments (e.g., carbon black and titanium dioxide) and organic pigments, which are frequently dyes rendered insoluble by complexing with a metal ion. Most organic pigments are prepared from azo, anthraquinone and triarylmethane dyes and phthalocyanines. Pigments produce color by selective absorption of light but, because they are solids, they also scatter light. Lead and other toxic pigments have been eliminated from inks for food packaging.

Vehicles generally consist of a resin or polymer with a liquid dispersant, which may be a solvent, oil or monomer. Choice of the vehicle for a printing ink depends on the printing process, how the ink will be dried and the substrate on which the image is to be printed. In lithography and letterpress, where inks are dried by absorption and oxidation, vehicles are generally mixtures of mineral and vegetable oils and resins. Flexographic inks, which are designed to dry quickly by evaporation, can be based on either water or organic solvents such as ethanol, ethyl acetate, *n*-propanol or isopropanol, with a wide variety of resins. Vehicles for gravure inks, which also dry by evaporation, may contain aromatic or aliphatic hydrocarbons and ketones as solvents. Inks for screen printing use organic solvents that are somewhat less volatile than those used for flexography or gravure (e.g., higher glycol ethers and aromatic and aliphatic hydrocarbons). Additives in inks include driers, waxes and plasticizers.

Radiation-curable inks, also known as energy-curable inks, are based on reactive acrylate chemistry where the curing mechanism involves free-radical polymerization. They can be applied by any standard printing process and then cured (polymerized) in line by a brief exposure to either UV or EB (electron beam) energy to form a tough, dry film. They have become the dominant printing technology for food packaging and are used in all of the printing processes to varying degrees. Curing occurs within a fraction of a second, and printing speeds of up to ca. 400 m min^{-1} are possible during continuous printing.

In EB curing, high-energy electrons initiate and complete the curing process. However, because the energy output from a UV lamp is much less, UV-curable inks require *photoinitiators*—chemicals that absorb UV energy and decompose to form free radicals that break the acrylate double bonds to initiate the curing process. UV radiation (ranging from 180 to 400 nm) can be generated by fluorescent lamps and mercury vapor lamps (the latter are more common). The primary wavelengths needed for curing inks are around 250–365 nm.

UV-curable inks consist mainly of acrylic monomers having one to four reactive acrylic groups, although some have higher functionality. They are used as solvents because of their ability to reduce viscosity and combine with other ink components. The inks also contain oligomers such as epoxy, polyester or urethane resins that have been esterified with acrylic acid, and they determine the performance properties of the ink, such as chemical resistance, rub resistance, gloss and coefficient of friction. Significant cross-linking occurs between the monomers and oligomers as both usually contain multiple acrylate groups. The inks also include standard ingredients, including pigments, waxes and defoamers.

There is a second type of UV curing chemistry that employs cationic curing as opposed to free-radical polymerization. Although the inks are also formulated with monomers and oligomers containing reactive double bonds, the photoinitiators decompose on exposure to UV energy to form Lewis acids that initiate the polymerization. The acidic nature of the process somewhat limits the pigments and other ingredients that can be used. Cationic curing is very sensitive to humidity and is also slightly slower than free-radical polymerization. These inks are unsuitable for offset printing for technical reasons but are often used when printing labels (Aurela and Söderhjelm, 2007).

EB achieves a higher degree of cure than UV because the energy input of the EB curing unit is higher. Furthermore, because EB ink film has no residual photoinitiator residues and a lower degree of residual extractables and volatiles compared to UV print, the use of EB is favored over UV for food packaging. The advantages of both EB and UV inks include fast cure speed, room temperature operation, high-quality end products and a decrease in the use of VOCs, incinerators and/or solvent recovery units. A disadvantage is that they are more expensive than conventional inks; as well, the cured ink has a significant volume and so gives a slight relief on the surface. As a result, they are used only where performance advantages outweigh their added cost.

More than 90% of all EB inks and at least half of all UV inks are used for printing packaging materials. While UV and EB inks are mostly used in flexographic printing, new UV offset inks are also being used for UV letterpress applications.

The manufacture of inks consists of dissolving or dispersing resins in organic solvents or oils to produce the vehicle (varnish), mixing and dispersing the pigment or dye into the vehicle and then introducing any additives.

Ink may be deposited on a substrate in various ways in order to obtain the required shade and depth of color. Solid deposition produces a continuous coating of ink, where the shade and depth of color depend on the type and amount of ink deposited on the substrate. Line printing produces a series of lines or crosshatches so that the ink is discontinuous. Shade and depth of color depends on the substrate, ink type, amount of ink and the relative concentration of lines or crosshatching. Dot printing (halftone) consists of a series of ink dots spread over the printed surface. The shade and depth of color depends on the substrate, ink type, amount of ink, dot spacing, dot size and dot density.

An important phenomenon involving inks is "set-off" that can be defined as the unintentional transfer of substances used in printing inks from the external printed surface to the inner, food contact surface. There are three set-off mechanisms: *blocking* (where the ink adheres to the internal surface of the packaging material when stored on reels [printed paper, board or plastics film] or stacked [sheet stock] or nested [articles]), *rubbing* (where the ink layer suffers abrasive transfer when printed stock is stacked or nested, or when a film surface suffers longitudinal friction during the unwinding of a reeled film) and *peeling* (where the ink layer suffers a complete loss of adhesion to the printed substrate and peels away on to the food contact surface). A fourth transfer mechanism (not set-off) can also operate whereby components of the ink migrate by diffusion through the printed substrate to the food contact surface (Bradley et al., 2005).

Recently, migration of printing ink components into food has become a focus of interest following the detection of the photoinitiator isopropylthioxanthone (ITX) in baby milk, milk products and cloudy juices packaged in aseptic cartons in Europe in 2005. More recently the migration of 4-methylbenzophenone and benzophenone (also photoinitiators) from printed cartons into cereals has highlighted the fact that contamination of foods from printing inks is still a problem. This issue is discussed further in Section 22.5.3. The inks used for the major package printing methods are discussed next.

9.3.3 LIQUID INKS

9.3.3.1 Flexographic Ink

9.3.3.1.1 Solvent Based

Typically, alcohols are the solvent of choice with additions of lower esters and small amounts of hydrocarbons to achieve solubility of the vehicle resin and proper drying of the ink film at press speed (Bassemir and Bean, 2009). It is important that all the solvents used are screened to ensure that they do not interact with the printing plates and rolls. Since the 1990s, there has been a trend to phase out solvent-based inks so as to avoid the emission of VOCs, which are implicated in the formation of ground-level ozone and smog.

9.3.3.1.2 Water Based

These have become increasingly common because of environmental concerns about the use of organic solvents in inks. Despite being termed *water-based* inks, the solvent used is not usually 100% water; up to 20% of an alcohol (typically ethanol) is added to increase drying speed, suppress foaming, increase resin compatibility and aid wetting of the plastic substrates. The water-based vehicles are generally emulsions or colloidal dispersions rather than true solutions, and include acrylic emulsion, maleic resin dispersion and styrene-maleic anhydride resins (Bassemir and Bean, 2009).

9.3.3.2 Gravure Ink

9.3.3.2.1 Solvent Based

A wider range of solvents can be used in gravure inks compared with flexographic inks because metal plates are used for gravure printing. Solvents used include aromatic hydrocarbons (toluene being the most common); aliphatic hydrocarbons, alcohols; esters; ketones; chlorinated solvents; and nitroparaffins and glycol ethers, but their use is being phased out.

Technical developments have made it possible to almost completely prevent any toluene emissions in modern rotogravure printing processes. Nonetheless, the question is often asked as to whether ink containing toluene could be replaced by water-based rotogravure ink systems. However, in using water-based inks, there are considerable environmental and qualitative detriments that must be taken into consideration. Ink based on toluene is largely produced using regenerative raw material (resins), whereas water-based ink requires a production process which uses about three times as much energy. In addition, the energy required for drying the ink after the printing process is also higher, which results in increased emissions. In recycling, the color is harder to remove from paper which has been printed with water-based as opposed to solvent-based gravure inks. Finally, the quality of the colors in water-based inks does not meet today's market demands.

Regulations govern the use of toluene in ink, mainly because of the residues of the chemical left in the ink after printing, which could theoretically pose a threat to consumers. Toluene is considered to be a skin irritant, dangerous during long exposure through inhalation and a possible risk to the unborn child. It is also seen as a possible endocrine disrupter which could impair human fertility levels.

9.3.3.2.2 Water Based

These are used for printing paper, paperboard substrates and increasingly for nonpaper substrates as solvent-based inks are phased out. To assist drying of water-based inks, the gravure cylinders are usually engraved or etched with shallower cells so that a thinner ink film is applied. However, to achieve the same relative printing density as solvent-based inks, a greater concentration of pigment must be used.

9.3.3.3 Screen Ink

Relatively little packaging material is screen printed. The two major types of inks used are solvent based and plastisol, although other types including water-based, radiation-cured and two-part catalytic systems are also available (Bassemir and Bean, 2009).

9.3.3.4 Digital Ink

Inks for ink-jet printing must have a low viscosity to enable jetting of droplets, but low viscosity increases dot gain as well as ink spreading and penetration into porous substrates. The inks typically consist of a vehicle (usually 60%–90%), colorant (pigments or dyes; 1%–10%), binder, surfactants, humectants and additives (Hakola and Oittinen, 2009.)

Three types of ink-jet inks are available: (1) water based, (2) oil-nonaqueous-based and (3) hot melt. Water-based inks usually contain >70% water and small amounts of humectants such as glycols to reduce the rate of evaporation and prevent precipitation of dyes when evaporation occurs at the orifice. Biocides are also added to prevent the growth of microorganisms. Oil-nonaqueous-based inks contain more than 50% nonvolatile vehicles such as glycols and fatty acids or their esters. They have low toxicity, minimal corrosive effects and low volatility. Hot-melt inks are solid at room temperature and the printheads are kept at elevated temperature so that the ink is in the liquid state. Molten ink is ejected in discrete drops and rapidly solidifies on reaching the substrate, resulting in very fast drying times. The advantages of hot-melt inks over aqueous inks are their lack of drying at the ink-jet nozzle and excellent image quality on almost any media.

The colorant can be a pigment or dye. Soluble dye inks provide better performance with respect to jettability and nozzle clogging, but the print quality on porous substrates has been limited due to high ink absorption. Pigment-based inks have provided better print quality on porous substrates, because more of the colorant stays on the surface of the substrate. Pigment inks work better with glossy coated papers.

Water-based inks are cheaper than other liquid inks, but have problems with lightfastness and waterfastness. Solvent-based inks have low surface tension, making them well suited to nonporous substrates, and they dry quickly by evaporation. Common solvents include alcohols, ketones and glycols, but as 80%–90% of the ink evaporates, it leads to VOC emissions. Oil-based inks contain hydrocarbons or glycols and dry by absorption; they produce medium print quality. UV-cured inks are becoming popular in label, packaging and wide-format printing, and UV printing is the fastest-growing sector of ink-jet printing (Hakola and Oittinen, 2009).

Most EP printing applications utilize dry toner, that is, toner in powder form. Two-component powder toners are called developers, and consist of larger carrier particles (iron and additives, diameter about 80 µm) and smaller toner particles (pigment and resin binder, diameter 5–20 µm). In the developing station, toner particles attach to the carrier. Application rollers transfer the developer to the photoconductive drum. Toner particles are transferred onto the drum, and the carrier particles return to the developer unit. Additional toner must be added to the developing unit to replace the consumed toner (Viluksela et al., 2010).

9.3.4 PASTE INKS

9.3.4.1 Offset Lithographic Inks

Lithographic ink is basically a concentrated dispersion of pigment in a viscous oil vehicle with various additives. Because the ink comes into contact with water during printing, it must be free from any tendency to bleed or to form an ink-in-water emulsion. The formation of a water-in-ink emulsion is unavoidable, but this does no harm unless the working consistency of the ink is affected.

These inks must resist the chemicals contained in the dampening solution, which is used to keep the plate constantly wetted. A typical ink for metal decoration would consist of organic pigment (15%), acrylate oligomer (40%), acrylate monomer (30%), photoinitiator and sensitizer (8%), tack reducer (4%) and wax (3%), and be dried by simple radiation curing (Bassemir and Bean, 2009). The inks used can also be dried by an oxidative process, which may be accelerated by the use of IR or UV radiation, and, in the case of metal packaging materials, by the use of heat (>150°C) or UV radiation.

9.3.4.2 Letterset Inks

The inks used generally have the viscosity and body of letterpress inks, and are used for the decoration of metal cans and plastic preformed tubs and containers; they are generally dried using heat (metal substrates) or UV radiation.

9.3.4.3 Letterpress Inks

These inks are used primarily for printing corrugated boxes and folding cartons, and drying is essentially oxidative or absorptive. This printing method is being increasingly replaced by water-based flexography (Bassemir and Bean, 2009).

9.3.5 THERMOCHROMIC INKS

Thermochromic inks change color in response to fluctuations in temperature. They are reversible and will change color time after time with the appropriate exposure. These are highly specialized inks that combine standard ink components with one of several color-changing agents described later. Since these inks are used on a wide variety of substrates, they are offered in the typical solvent-based, water-based, plastisol and UV formulations. Depending on the application, thermochromic inks can be applied with a number of printing processes, including offset lithography, flexography, gravure and screen printing.

The two types of thermochromic inks are liquid crystals and leuco (from the Greek word *leukos* meaning white) dyes. Liquid crystal thermochromics are very difficult to work with and require highly specialized printing and handling techniques. For packaging applications, leuco dye thermochromic inks are used in a wide range of applications including product labels. In its cool state, a leucodye exhibits color, and, when warmed, it turns clear or translucent. It takes a 3°C–6°C shift to bring about a change in color.

Alkaline reduction of a dye produces the water soluble alkali metal salt or leuco form, which, on subsequent oxidation, reforms the original insoluble dye. A leucodye is a chemically reduced form of a dye, which, in most cases, is colorless or minimally colored and becomes colored by an oxidation step.

Despite the relatively well-known functionality of thermochromic leucodye-based inks, very little has been published about their colorimetric characteristics. These are significant from an application perspective, and the most important characteristics are the temperature-dependent properties of the complex thermochromic system, the degree of its reversibility and factors that influence this. Kulčar et al. (2010) studied the colorimetric properties of red, blue and black leucodye-based thermochromic inks with an activation temperature of 31°C. The color of the inks was dependent on temperature as well as the thermal history of the sample, which gives rise to color hysteresis. Four characteristic temperatures were ascribed to the two chemical reactions causing color hysteresis. The reversibility of the thermochromic effect diminished approximately linearly with the highest heating temperature.

Some products printed with leucodye thermochromic inks change from one color to another, rather than transitioning from colored to clear. This is achieved by using an ink that combines a leucodye with a permanent-colored ink formulation. For example, a green ink may be formulated by adding a blue leucodye to a yellow ink. In its cool state, the printed ink layer is green and, once warmed, reverts to yellow as the leucodye becomes clear or translucent. Leucodyes can be designed to change color at various temperature ranges, from as low as −25°C up to 66°C. A wide range of colors is also available.

The key components of most thermochromic inks used in packaging are polymer microcapsules 1–10 μm in diameter which is at least 10 times larger than the average pigment particle. The microcapsules provide protection from the components of the ink and contain three interacting chemicals responsible for the overall temperature-dependent color of an ink (Mills, 2009). The first is a leucodye such as fluoran, triphenylmethane lactone or spirolactone. In their ring-closed forms, these dyes are colorless but become highly colored in their ring-opened forms which are generated using a proton donor. The second microcapsule component is a weak acid such as bisphenol A, alkyl *p*-hydroxybenzoate and derivatives of 1,2,3-triazole and 4-hydroxycoumarin that acts as a solvent and proton donor. The third component is a polar cosolvent with a low melting point such as lauryl alcohol or butyl stearate that controls the temperature at which the color change takes place. The dye is usually protonated (i.e., highly colored) when this solvent is a solid, but colorless (i.e., in its leuco form) when it is melted (Mills, 2009). Special considerations are usually involved in printing inks with these relatively large particles because the microencapsulation process cannot completely protect the leucodye system.

Under normal conditions, thermochromic leucodye inks have a shelf life of 6 months or more. After they are printed, they function, or continue to change color, for years. The postprint functionality can, however, be adversely affected by UV light, temperatures in excess of 121°C and aggressive solvents.

As the price of thermochromic inks decreases, their use has become more widespread on food packaging. One obvious area is to indicate to the consumer when the product is at the ideal temperature for consumption and this has been used for beverages such as canned beer and bottled wine. In addition, a thermochromic ink that goes from colored to transparent can hide a warning message that will only be legible once a certain temperature is achieved and this has been used on the lids of disposable coffee cups. Fast-drying, irreversible thermochromic inks have also been formulated for the canning industry. Applied to the end of a can prior to retorting, they can provide a visual verification that the can has been retorted, changing color under the specific conditions of wet heating typical of the retort process. However, they do not indicate that an adequate F_o process has been achieved.

9.4 ADHESIVES

Adhesives are widely used in the packaging industry. The principal uses include the forming and sealing of corrugated cases and folding cartons; the winding of tubes for cores and composite cans; the labeling of bottles, jars and other packages; the lamination of paper to paper, paperboard and foil; and the lamination of plastic films.

Adhesion is the process of bonding two surfaces together, the surfaces being referred to as *adherends*. An adhesive is any substance applied as a thin intermediate layer between two adherends that holds or bonds them together. Adsorption theory states that adhesion results from intimate intermolecular contact between two materials and involves surface forces that develop between the atoms in the two surfaces. The most common surface forces that form at the adhesive-adherend interface are van der Waals forces. In addition, acid–base interactions and hydrogen bonds may also contribute to intrinsic adhesion forces.

Mechanical adhesion is where two porous materials are bonded by adhesive entering the mechanical structure (e.g., paper to paper). Porosity of the adherend will affect the degree of penetration—too little or too much porosity results in a weak bond. Materials such as paper can be coated to control penetration of adhesive or ink.

In contrast, chemical adhesion is the formation of chemical bonds between an adherent and the adhesive. Many adhesives are strongly polar (e.g., starch, PVA and casein). Paper is a polar adherend, whereas LDPE, PP, glass and metals are nonpolar adherends. Many adhesives work using both mechanisms.

The process of establishing intimate contact between an adhesive and adherend is known as *wetting*. To be effective, the adhesive must wet the surface of the adherend. For effective wetting, the surface must be clean and the surface tension of the solvent in the adhesive should be such that the adhesive will wet the surface. Wetting agents are sometimes added to improve this aspect. Polarity will also affect wetting with polar liquids wetting polar surfaces and vice versa. A continuous adhesive film across the surface improves adhesion, which is related to the surface tension and viscosity of the adhesive.

Tack is the ability to form a bond of measurable strength immediately. The elusive nature of the word (and of the concept) stems from the fact that tack results from a composite of several physical observations, parameters and concepts. Tack is the property of an adhesive that allows it to adhere to another surface on immediate contact. It is the "stickiness" of the adhesive while in a fluid or semifluid state.

Tack is not a true physical property of an adhesive, but rather a composite property that has a broad and somewhat qualitative meaning that is very useful in practice. Although there are many different ways to measure tack depending on the application, tack is simply the resistance to separation. Separation is rate and temperature sensitive and involves viscoelastic deformation of the bulk adhesive. The appropriate measurement is the work expended in separation rather than the force used.

Water-borne adhesives are the oldest and still the largest volume class of adhesive used in packaging (Kaye, 2009). Water-borne adhesives are slower drying than solvent-based adhesives, requiring about three times more heat to dry; they also need more time to achieve steady-state performance during production runs. Water-borne adhesives generally do not provide the shear or peel strength that solvent-based systems provide, and, once cured, water-borne adhesives usually do not have the moisture resistance of solvent-borne adhesives. However, water-borne adhesives can withstand wide temperature ranges, are easy and safe to handle and low in cost.

Pressure-sensitive adhesives (PSAs) develop measurable adhesion to a surface simply upon contact or by the application of light pressure. No chemical reaction generally takes place between the substrate and the adhesive, no curing of the adhesive is necessary and no solvent is lost during the adhesion process. Intimate contact between the substrate and the adhesive must be established rapidly and under slight pressure, and the energy necessary to separate the adhesive from the substrate must be sufficient for the specific application. Such a combination of properties is uniquely found in polymers above their T_g, and a balance between compliance and fracture energy is the key when tailoring the properties to a specific application (Creton, 1997).

9.4.1 NATURAL MATERIALS

Until the 1940s, only naturally derived materials were used as packaging adhesives. However, they have now been replaced by synthetic adhesives in many applications.

9.4.1.1 Starch

Starches in the form of amylose and amylopectin are obtained from plants such as wheat, potatoes and maize, and are then subjected to acid hydrolysis to produce smaller chain segments including dextrins. Plasticizers are often added, together with fillers such as kaolin clay and calcium carbonate, which modify the viscosity and reduce cost. Borax can act as a viscosity modifier, increasing tack and preventing microbial growth.

The single largest use of starch adhesives is in the manufacture of corrugated board for shipping containers. Modified starches and dextrins are used in the sealing of cartons, winding of spiral tubes, seaming and forming of bags and attaching labels to metal cans. For the labeling of glass bottles, an alkaline-treated starch adhesive with a special tacky, cohesive consistency is used.

Starch-based adhesives are easy to handle and inexpensive, but suffer from a relatively slow rate of bond formation, poor water resistance and limited adhesion to coatings and plastics.

9.4.1.2 Protein

Natural adhesives based on animal protein were once widely used, but are now used only in specific narrow areas where synthetics have been unable to match their performance. Protein-based adhesives are derived from casein, soybeans or animal hides, bones and connective tissue (collagen).

9.4.1.2.1 Casein

This is produced by the acidification of skim milk which results in the precipitation of the milk protein casein. It has high bond strength and good water resistance, and is the preferred adhesive for labeling glass beer bottles because it provides resistance to cold water immersion and can be removed by alkaline washing. It is also used as an ingredient in adhesives used to laminate aluminum foil to paper (Kaye, 2009).

9.4.1.2.2 Animal Glue

This is a water-borne solution derived from collagen extracted from animal skin and bone by alkaline hydrolysis. It has a high level of hot tack and a long, gummy tack range. It is the standard adhesive used in forming rigid setup boxes (Kaye, 2009).

9.4.1.3 Natural Rubber Latex

This is extracted from the rubber tree *Hevea brasiliensis* and finds use in a variety of self-seal applications since it is the only adhesive system that will form bonds only to itself with pressure (Kaye, 2009). This property (used, for example, in self-seal candy wraps) is called *cold seal* because heat is not required to make a bond. Cold seal adhesives are also referred to as self-seal adhesives and cohesives. The uniqueness of cold seal adhesives is that they seal only to themselves. When a substrate coated with a cold seal adhesive comes into contact with another substrate coated with the same cold seal adhesive, the bond results by using simple digital pressure.

Typically, a water-borne emulsion is printed onto a web substrate using an engraved gravure cylinder. In addition to natural rubber latex, the emulsion also contains water, ammonia, surfactants, antioxidants, antifoam agents, biocides and an acrylic component to aid adhesion to the coated surface (Durston, 2006). In the wet state, cold seal has a shelf life of around 6 months, and after printing, a shelf life of at least 6 months is guaranteed.

Unfortunately, natural rubber latex solutions suffer from limited stability on high shear, high-speed production lines as well as allergy, odor and quality variations that can be problematic. Synthetic alternatives usually do not meet the low tackiness requirements, but some acceptable alternatives are available with the required balance of desired properties while eliminating allergy, odor and consistency problems.

9.4.2 SYNTHETIC MATERIALS

9.4.2.1 Water-Borne Adhesives

These are the most broadly used class of adhesives in packaging, and are mainly resin emulsions consisting of PVA emulsions and stable suspensions of PVA particles in water. The use of EVA copolymers or acrylic esters has greatly improved adhesion capabilities (Kaye, 2009). They are used to form, seal or label cartons, tubes, bags and bottles, and can be formulated to adhere to paper, glass and most plastics and metals. Water-borne adhesives can be formulated to be very water insensitive (for immersion resistance) or water sensitive, depending on need.

9.4.2.2 Hot-Melt Adhesives

Hot-melt adhesives are 100% nonvolatile thermoplastic materials that can be melted by heat and then applied as a liquid to an adherend. The bond is formed when the adhesive resolidifies. Because of their extremely rapid rate of bond formation, they can be used successfully on high-speed packing lines. They can be formulated to adhere to almost any surface due to the wide range of polymers and modifiers used. Their major weakness is the rapid falloff in strength at elevated temperatures which is not generally a problem in food packaging applications.

A typical hot-melt sealant is composed of three primary components: polymers (30%–40%); tackifying resin (30%–40%); and petroleum wax (20%–30%) plus antioxidants, fillers, plasticizers and blowing agents to enhance other properties. The tackifying resins control viscosity as well as wetting and adhesion. The function of the wax is to lower viscosity and control set speed. Fillers are added to opacify or modify the adhesive's flow characteristics as well as to reduce cost (Pocius and Campbell, 2009).

The most widely used polymer is EVA copolymer which is normally run at 180°C. However, the availability of very low MW EVA copolymers has resulted in EVA hot melt that can be run as low as 120°C, leading to energy savings and safer running conditions (Kaye, 2009). Other polymers used include PP, PETs, PAs and polyurethanes (the latter used for adhesive lamination of films such as PP).

9.4.2.3 Solvent-Based Adhesives

Organic solvents have been used as adhesive carrier fluids and diluents, as well as for surface preparation and cleanup. Since the 1990s, environmental and workplace safety regulations on solvents have become increasingly stringent, and there has been a trend to replace solvents and solvent-based adhesives to avoid the emission of VOCs that takes place during formulation, application, drying and curing. As a consequence, the use of water-based and hot-melt adhesives has grown. Today, only a small quantity of solvent-based adhesives is used in specialized applications where water-borne or hot-melt systems do not meet the technical requirements.

9.4.2.4 Pressure-Sensitive Adhesives

PSA is one that remains permanently and aggressively tacky in the dry form and has the ability to bond instantaneously to a wide variety of materials solely by the application of light pressure. No water, solvent or heat is needed to activate these materials (Werblow and Noah, 2009). The desired properties are usually obtained by formulating a miscible blend of uncross-linked or partially cross-linked polymer, a tackifying resin, a plasticizer and various stabilizers. The tackifying resin (usually an oligomer that is fully miscible with the polymer) has the function of substantially increasing the tack of the polymer, while the plasticizer is usually added for processing purposes. The polymers used fall into four broad families, each having their own specific advantages: polyacrylates, silicone polymers, polydienes and random copolymers based on natural rubber and styrene-butadiene rubber, and block copolymers of styrene-diene (Creton, 1997).

9.5 LABELING

Labeling is a means of performing the communication function of packaging, informing the consumer about nutritional content, net weight, product use and so on. Labeling acts as a silent salesman through distinctive branding, as well as facilitating identification at check-outs through the Universal Product Code (UPC). While almost all paper-based packaging (and increasingly metal and plastics packaging) is preprinted, many glass, plastic and metal packages still require labeling.

9.5.1 Glued-On Labels

These are the simplest type and consist of sheet material (typically paper), which has been printed and cut to size. They are attached to the package with adhesive, which is applied either at the time of application, or at the time of manufacture, in which case the adhesive is activated with moisture immediately prior to application. This type of label is widely used for large volume items such as beer, soft drinks, wines and canned foods where high-speed application is required.

For returnable glass and plastic bottles, it is important that the wet strength of the paper is sufficient to ensure that the label can be removed in the bottle washer without repulping.

9.5.2 Self-Adhesive (Pressure-Sensitive) Labels

These can be made from paper, plastic or aluminum foil laminated to paper or plastic, and can be produced to adhere to a wide range of materials. They are supplied with an adhesive coated on the unprinted side and mounted on release paper, which is removed immediately before application to expose the adhesive (Werblow and Noah, 2009).

9.5.3 In-Mold Labels

In-mold labeling is a decorating technique used worldwide for blow molded bottles, as well as injection molded and thermoformed containers. It was pioneered in Europe for injection molding in the early 1970s, and in the United States for blow molding later in that decade. Printed labels can be applied to containers and lids during thermoforming, blow molding and injection molding.

The first in-mold labels (IMLs) consisted of paper, clay-coated on both sides. One side had a heat seal adhesive, and the other an inked surface with an overprint coating to provide protection. Today, such paper labels comprise approximately half the IML market. Labels made with a plastic film form the other portion of the market.

A plastic IML is typically made from HDPE/LDPE blended material and is compatible with a host of plastic containers. What differentiates IMLs from conventional glue-on labels is the heat seal coating that is applied to the back side of the IML stock during the manufacturing process.

IMLs made from film offer better heat, moisture and chemical resistance than those labels made from paper. There are also recycling advantages with film labels. However, the greatest advantage with the use of film is a decorative consideration designated the “no-label” look. This means it is possible to prepare an in-mold-labeled container that actually appears to have no label at all since the unprinted areas of the label blend into the container wall.

IML materials must be able to withstand the container manufacturing process. The heat generated during blow molding presents a challenge to most inks because pigments can change. Varnishes also face special challenges in IML use. The combination of heat and flexing as the container is shaped, followed by sudden cooling, can produce an “orange peel” effect (i.e., a deformation of the smooth surface).

During the in-mold labeling process, a label is placed in the open mold and held in place by vacuum ports, electrostatic attraction or other appropriate means. The mold closes and molten plastic resin is extruded into the mold where it conforms to the shape of the object. The hot plastic envelopes the label, making it an integral part of the molded object. The difference between glue-applied labels and IMLs is that glue-applied labels are on the surface of the object while IMLs are in the wall of the object. The high cost of molds has been a barrier to the wider adoption of in-mold labeling (Werblow and Noah, 2009).

9.5.4 SLEEVE LABELS

A wide range of containers can be sleeve labeled including glass bottles, plastic bottles (extrusion blow molded PP and HDPE bottles as well as stretch blow molded PET) and metal cans. There is almost no restriction regarding the shape of the container. Sleeve labels shrink into or stretch around contours, penetrate variable geometries (such as hourglass shapes) and conform to irregular features (grips or slender necks). Preformed, printed sleeves are slipped over the container (normally a glass or plastic bottle) on line, and then either shrunk in a heat tunnel or (provided that the container is of simple shape) the actual label relaxes onto the container itself. A complex container shape will generally require the sleeve to be shrunk to the contours of the container.

Most shrink sleeves are made of oriented plastic films that shrink around a container when heat is applied. They are used as labels, tamper-evident neckbands and safety shields. Most shrink sleeves are made from PVC or PS film that has been uniaxially oriented to give the desired degree of shrink. The inherent property of uniaxially oriented film—to conform to almost any shape when heat is applied—vastly increases the range and variety of container designs which can use shrink sleeves.

Roll-fed stretch sleeves work well with straight sided single-serve bottles, and are often used with PET bottles. Roll-fed labels are relatively easy to apply, and no heat tunnel is needed.

Shrink-sleeve labels can decorate the complete surface of the container, including the closure if necessary, to provide tamper-evident neck and cap seals while offering maximum graphic space. One limitation to the shape of the sleeved container is the amount of possible shrink; a diameter of 100 mm can be shrunk to a maximum of 40–35 mm. Shrink-sleeve material also provides a UV block.

Sleeve manufacture begins with the extrusion of the film material. This can be PVC, OPP, OPS or PET and is typically 50 μm thick. Depending on the material, up to 75% shrinkage can be achieved. Although it does not have a very environmentally friendly image in some countries, PVC offers a high transparency with a high shrink of 65% at a low temperature. In contrast, OPP (which does not suffer from environmental image problems) offers minimal distortion of the decoration but is less transparent, features a low rigidity and can shrink only 50%. OPP also goes through natural shrinkage, and the sleeve can relax after application. OPS has comparable mechanical and thermal properties. However, OPS is more transparent than OPP and has a minimum vertical shrinkage. At 75%, OPS offers the highest shrinkage, but is not very transparent and has low rigidity. PET has good mechanical properties, is highly transparent, has a high tensile strength and offers shrinkage of 70%. However, the raw material is quite expensive and shrinkage is less controllable, making it more difficult to control than PVC. After film extrusion, the material is gravure- or flexo-printed in up to 10 colors. The sleeve is positioned before the containers enter the shrink tunnel. Shrinking is effected with hot air, infrared radiant heat, steam or a combination of these.

Thin PS foams coextruded with a surface layer for printability are used on beverage bottles. A typical construction would be a foamed PS layer of 300 μm with a 20 μm surface layer. The foamed PS reduces the noise level on filling lines, eliminates partitions in secondary containers and protects glass bottles in vending machines. It also insulates the container. Surface-printed, shrinkable foam labels are used for prelabeling glass, plastic and microwavable containers.

9.5.5 HOLOGRAPHIC LABELS

Holographic labels that incorporate a *hologram* are finding increasing application in food packaging for both marketing and security reasons, specifically in the areas of anticounterfeiting (authentication) and brand protection.

Holograms (from the Greek for *whole* and *writing/drawing*) are part of a family of technologies known as diffractive optically variable devices (DOVIDs). They exhibit a variety of complex images and patterns according to the viewing angle (e.g., if they are tilted or rotated), based on the diffraction of light (International Hologram Manufacturers Association, 2011).

The two most common types of hologram are *surface relief* and *volume*. Surface relief holograms are the most familiar and exhibit a characteristic rainbow-colored pattern or image. The diffractive effect depends on the definition of the lines of tiny ridges and grooves in the surface relief pattern. To prevent damage which would diminish the diffractive effect, the hologram is always protected, either by being laid face down on the document or label, or by being coated with a protective lacquer. In addition, most surface relief holograms require a reflective layer (usually aluminum but other metals or metal oxides can also be used) to bounce light back through the pattern to reveal the image. They are mass-produced mechanically by embossing or casting the relief pattern or image into a thermoplastic film or a viscous coating on a film or paper. PET is the most common substrate but OPP, PVC and paper are also used.

Volume, or reflection, holograms have a very different appearance to surface relief holograms and are generally used for authentication. They are mass-produced through optical copying of a master hologram, so they retain more of the optical properties of that master than the mechanical process of surface relief holograms. This allows them to be used for classical holograms which are fully 3D images, and recent developments also allow the use of color in the image (International Hologram Manufacturers Association, 2011).

9.6 CODING

It has been standard practice in almost all food manufacturing and processing establishments to put a “closed” code (so called because only those with knowledge of the coding system can interpret the code) onto the packaged product. Generally, this code indicates the time of processing and packaging, for example, day and year, or shift, day and year, or hour, day and year. For many canned foods, it has long been mandatory to include such information on the end (lid) of the container in an embossed form, together with a code for the product itself to aid identification of unlabeled cans in the factory and assist in product recalls.

Dating of food products has been known to exist in the U.S. dairy industry since 1917, and in the 1930s U.S. consumers expressed a desire for an open dating regulation to indicate the freshness of their foods (Labuza and Szybist, 2001). Since the advent of the consumer movement in the early 1970s, many different types of open dating systems have been proposed as part of the consumer’s “right to know.” An open date on a food product is a legible, easily read date which is displayed on the package with the purpose of informing the consumer about the shelf life of the product.

The EU’s General Food Law (178/2002/EC) entered into force in 2005 and makes traceability compulsory for all food and feed businesses. Under EU law, “traceability” means the ability to track any food, feed, food-producing animal or substance that will be used for consumption, through all stages of production, processing and distribution. Businesses must be able to identify where their products have come from and where they are going, and to rapidly provide this information to the competent authorities on request.

ISO 22005 gives the principles and specifies the basic requirements for the design and implementation of a feed and food traceability system. It can be applied by an organization operating at any step in the feed and food chain.

GS1 is an international not-for-profit association with member organizations in over 100 countries. The GS1 Traceability Standard is a business process standard describing the traceability process independently from the choice of enabling technologies. It defines minimum requirements for companies of all sizes across industry sectors and the corresponding GS1 Standards used within information management tools.

9.6.1 BAR CODES

A *bar code* is defined as a series of parallel bars and spaces arranged according to the encodation rules of a particular specification in order to represent data (Barthel, 2009). Its purpose is to represent information in a form that is machine readable, typically by scanning devices that are programmed to analyze the structure of the bars and spaces and transmit the encoded data in electronic format to a computer. On June 26, 1974, the first barcode used in a commercial application was scanned; it was a 10 pack of Wrigley's Juicy Fruit gum which is now in the Smithsonian Institute.

Although there are more than 200 bar code symbologies, only are few are in common use with the most popular being EAN/UPC symbology. It is a continuous symbology encoding fixed-length numeric digits and several variants exist. These bar codes always carry a number that is a unique identifier of the item on which the bar code is affixed (Barthel, 2009). EAN/UPC symbology is widely used on consumer products including food and has the advantage of omnidirectional scanning capability.

Since 2005, the EAN/UPC symbology has been managed by the global organization GS1. The GS1 System of Standards are built and maintained through the GS1 Global Standards Management Process (GSMP), a worldwide collaborative forum (www.gs1.org). One of the main building blocks of the GS1 system is the Global Trade Item Number (GTIN) used to uniquely identify trade items at any point in the supply chain. Each trade item that is different from another is allocated its own separate GTIN. Consumer units (the smallest unit intended to be sold to the ultimate end user) are assigned a 12-digit number. Trade items above the consumer unit such as intermediate packs, cartons, packs containing multiple consumer units or standard mixtures of consumer units are assigned a 14-digit number. The GTIN-14 Serial Shipping Container Code (SSCC) uniquely identifies shipping containers and provides a method of linking the physical carton or shipping container to information about its contents. The familiar old GS1 BarCode now comes in a new version called GS1 DataBar (formerly known as Reduced Space Symbology) that is smaller than its predecessor but contains more information.

GS1 EPCglobal, a subsidiary of GS1, is leading the development of radio frequency identification (RFID) technology (see in the following text) by defining and supporting implementation of standards that makes RFID operational across geographies, boundaries and sectors. The Electronic Product Code (EPC) is designed as a universal identifier and is a way to uniquely identify a pallet, case or individual product and is the next generation of the standard bar code. Although it uses a numerical system for product identification, its capabilities are much greater. EPCs are not designed exclusively for use with RFID data carriers and can be constructed to be read by optical data carriers such as 1D and 2D bar codes.

The need to encode more information into a smaller space leads to the development in the 1990s of 2D symbologies and there are now over 20 different 2D symbologies available. Some (known as stacked codes of which the most common is PDF417) consist of 3–90 rows, each of which is like a small linear bar code. ISO 15438 details the specification for the PDF417 bar code symbology; the symbology consists of 17 modules each containing 4 bars and spaces; hence the number "417." The user can decide how wide the narrowest vertical bar (X dimension) is, and how tall the rows are (Y dimension). PDF417 is capable of encoding more than 1100 bytes, 1800 text characters or 2710 digits and can be read by linear scanners, laser scanners or 2D scanners. The physical size of 2D codes is scalable without affecting the amount of information. PDF417 format has been taken up by the airlines and travel industry for the printable boarding passes along with various postal services for printable stamps (Figure 9.7).

The other type are known as data matrix codes and consist of black and white "cells" or modules arranged in either a square or rectangular pattern. They use a small area of square modules with a unique perimeter pattern, which helps the barcode scanner determine cell locations and decode the symbol. Characters, numbers, text and actual bytes of data may be encoded, including Unicode characters and photos. ISO 16022 specifies the data matrix bar code symbology. Most camera-based

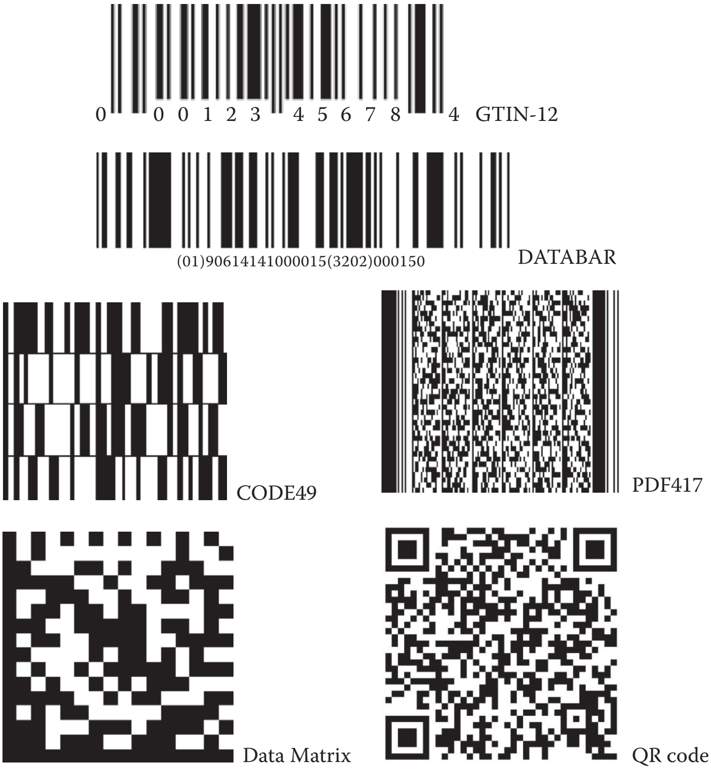

FIGURE 9.7 Examples of various bar code symbologies: GTIN12, DATABAR, CODE49, Data Matrix, PDF417 and QR.

imagers and hand-held scanners have a difficult time reading symbols that contain over 800 characters, although up to 1200 ASCII characters have been successfully encoded and read.

Another type of matrix code is the QR (for Quick Response) code that is machine readable and designed to be read by smartphones; it was invented in Japan in 1994. A QR code contains information in both the vertical and horizontal directions, whereas a bar code contains data in one direction only. As a consequence, QR code holds a considerably greater volume of information than a bar code. ISO 18004 specifies the QR bar code symbology. A company logo can be incorporated into a standard QR code.

Data Matrix from Siemens is a 2D matrix code designed to pack a lot of information (between 1 and 500 characters) on a very small space. The symbol is also scalable but the practical density is limited by the resolution of the printing and reading technology used. Data Matrix is very similar to QR codes and most software can decode both as the differences between them are negligible. The QR code is most popular in Asia whereas Data Matrix is most popular in Europe and the United States.

Several companies offer decoding software for 2D codes that can be installed into many camera phone models, simply by downloading the relevant application. Many of these mobile readers can extend the decoding to enable mobile access and interaction with websites. They are increasingly being used on packages to give consumers access to information, multimedia content, promotional opportunities, retail store locations, discounts, samples and more and can be described as “smart” labels.

A Microsoft Tag or High Capacity Color Barcode (HCCB) is a 2D barcode whose intended use is similar to that of a QR code but can be much smaller because it uses different symbol shapes in geometric patterns and multiple colors or tints to embed more information in less space. A major difference compared to QR codes is that Microsoft Tags do not actually store the information. Instead, the barcode contains a unique ID which the reader application needs to send to Microsoft's servers that then send back all the linked information. In this way, more information or a wider variety of data can be included. The disadvantages are that the reader application needs to be online and there may also be privacy concerns with this server-based approach.

An alternative to 2D codes is SnapTag™ which offers advertisers the opportunity to make their logo a branded mobile interaction point. SnapTags™ are an application-free, branded alternative to a 2D mobile barcode and are created with a brand logo or icon encircled by discrete encoding schemes. Each encoding scheme corresponds to a predetermined response. When photographed with a camera phone and sent to a predetermined phone number or email address, the SnapTag™ is decoded and returns the corresponding data or response to the phone via SMS or MMS message. Microsoft's Tag is capable of including color and can be customized to include a background image, while SnapTag™ uses a brand's identity as the centerpiece of its mobile barcode.

Virtually any printing technology can be used to print bar codes, provided it is precise enough to achieve the necessary quality level to enable accurate scanning. It is preferable that the bar code be printed in black ink on a white background. However, the Microsoft Tags require offset printing due to their small size and the possibility to use color.

9.6.2 RFID

An RFID uses radio frequencies to read information on a small device known as a *tag* or *transponder* with few problems from obstruction or disorientation (Finkenzeller, 2010). Initially, RFID tags were developed to eventually replace barcodes in supply chains. Their advantages are that they can be read wirelessly and without line of sight, contain more information than barcodes and are more robust. To date, RFIDs have been used to increase convenience and efficiency in supply chain management and traceability, being normally applied to secondary or tertiary packaging. However, they still have some drawbacks including cost of implementation, reliability, performance and potential for privacy misuse issues (McCombie and Welt, 2009). If costs can be reduced significantly, then they could find application on individual consumer packages where, in addition to supply chain management, they could also monitor food temperature and ensure food safety if they contained the appropriate sensor (Kumar et al., 2009).

Almost all conventional RFID tags contain a transistor circuit employing a microchip attached to an antenna that is packaged in a way that it can be applied to an object or package. Typically, a tag picks up signals from and sends signals to a reader (also called an interrogator) as depicted in Figure 9.8. The tag contains a unique serial number, but may have other information, such as a customers' account number. Tags come in many forms, such as smart labels that can have a barcode printed on them. The tags can simply be mounted inside a carton or embedded in plastic.

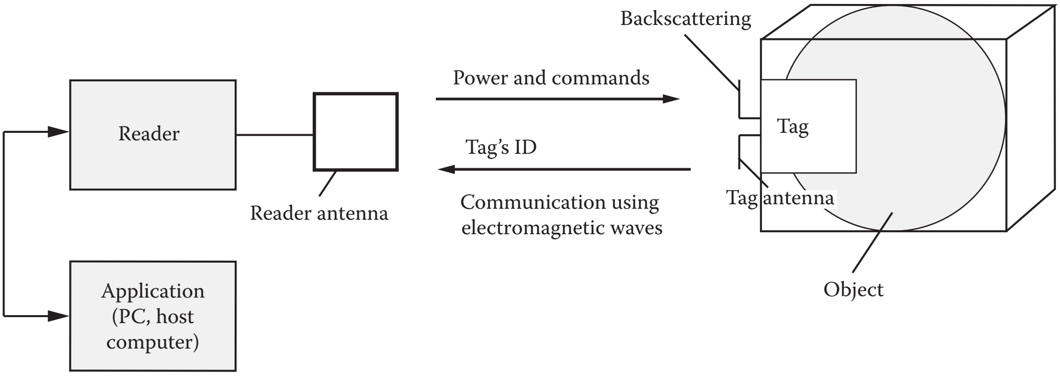

FIGURE 9.8 Key components of a passive UHF RFID system.

The potential in low-cost RFID is split between chip-based technologies and “chipless” tags (also named “RF barcodes”), which can still be interrogated through a brick wall and hold data, but are cheaper and more primitive in electronic performance than chip tags. Chipless RFID tags use material to reflect back a portion of the radio waves beamed at them and are an emerging area of RFID technology for ultra-low-cost RFID applications. However, they are currently confined to the unlicensed RF bands. Although they are less than 1% of the RFID market today, some market projections show that chipless tags will reach 60% of the RFID market before the end of this decade, owing to their low cost and great flexibility. For this reason, chipless RFID is considered the next RFID frontier (Tedjini et al., 2010).

There are three types of RFID tags: active, passive and semipassive. Active tags have an internal power source and are extremely flexible in terms of the functionality they can offer due to their onboard battery, which extends their reading range. Passive tags are not self-powered but are activated by the electromagnetic field emitted by the reader. They are deployed primarily for their low cost and ease of implementation, due to established standards, and find application in the retail supply chain, especially manufacturing, warehousing and distribution (Rida et al., 2010). Semipassive (sometimes referred to as semiactive) tags contain a power source but it is only used to power the circuitry. The radio signal is transmitted using power from the incoming radio signal. These tags are being developed primarily for reusable containers and pallets (McCombie and Welt, 2009). Compared to active or semipassive tags, passive tags have shorter reading distances, require higher power readers and are constrained in their capacity to store data. However, passive tags are simpler in structure, lighter in weight, less expensive, generally more resistant to harsh environmental conditions and offer a virtually unlimited operational lifetime.

An inlay is an RFID microchip attached to an antenna and mounted on a substrate. Inlays are essentially unfinished RFID labels. They are usually sold to label converters who turn them into smart labels. An RFID inlay is a foreign device. Unlike bar codes, which can be incorporated directly into the printed materials of the package and have no inherent volume, RFID inlays have mass, volume and other characteristics that must be considered before being incorporated into a product. Currently, the HF and UHF RFID inlay market is dominated by market segments that are strongly business to business oriented, while the consumer market potential remains almost untapped.

RFID tags fall into four regions in respect to frequency:

1. Low frequency (LF) 30–500 kHz
2. High frequency (HF) 3–30 MHz (typically 13.56 MHz)
3. Ultra high frequency (UHF) 300–950 MHz
4. Microwave (MW) 2.4–2.5 and 5.8 GHz

Each band has its own advantages and disadvantages. LF tags are cheaper than any of the higher frequency tags. Although they are fast enough for most applications, for larger amounts of data, the time a tag has to stay within range of a reader will increase. Another advantage is that LF tags are least affected by the presence of fluids or metal. The disadvantage of such tags is their short reading range (<30 cm). Frequencies for LF and HF tags are license exempt and can be used worldwide; however, frequencies approved for UHF tags differ from country to country and require a permit. The range of RFID tags is typically larger at higher frequencies (>1 m for HF and >3 m for UHF) and, therefore, most pallet-level RFID applications make use of 900 MHz or 2.4 GHz. Furthermore, since the passive components (both inductors and capacitors) are smaller at these higher frequencies, total tag size and thus cost can be reduced.

Research on passive tags, particularly UHF tags, is still very active in order to ensure interoperability, low cost and data security. The interoperability is needed since there are three frequency bands worldwide. Roughly, the operating frequency bands are 865–869 MHz for Europe, 902–928 MHz for the Americas and the United States and 952–954 MHz in most of Asia including Japan and China (Tedjini et al., 2010). Where cargo or containers are imported and exported from different regions of the world using a secure RFID system, an RFID tag is required to have sufficient bandwidth to operate globally, and this imposes very stringent design challenges for the antenna designers. The interoperability requires the development of efficient, miniaturized antenna able to cover all three RFID UHF bands.

Unfortunately, for item-level tracking, these UHF frequencies do not work particularly well, due to the presence of substantial amounts of metal (e.g., food cans) and RF-absorbing fluids (e.g., water, juice and milk). Highly dielectric materials (liquids) and conductors (metal), even in small amounts, can drastically change the properties of a tag antenna, reducing efficiency and shortening the read distance, sometimes to the point of becoming completely unreadable at any distance. Therefore, at this time, it appears that 13.56 MHz or lower is the most attractive frequency, since absorption is substantially reduced at lower frequencies. In general, therefore, the sweet spot for item-level RFID will likely exist at 13.56 MHz, though there is currently a push for developing 900 MHz solutions as well (Subramanian et al., 2005).

Recently, Singh et al. (2011) evaluated an innovative system for improving the readability of passive UHF RFID tags operating between 902.25 and 927.25 MHz in conjunction with reusable PP plastic containers (RPCs) filled to their maximum capacities with either carbonated soda packaged in aluminum cans or water in PET bottles. The system involved the inclusion of an energy transfer device (ETD) consisting of a coaxial transmission line on the bottom of the RPCs that passively transferred RF signals to interior regions of the unitized loads, thereby improving the readability of all RFID tags attached to the RPCs by nearly 97%.

Integrating sensors with RFID tags renders the whole system capable of not only tracking, but also providing real-time cognition of aspects of its status or its environment (e.g., storage conditions of perishable food). The ultimate goal is to create an easily deployable and rugged intelligent network of RFID-enabled sensors.

RFID tags are often a complement, but not a substitute, for UPC/EAN/GTIN barcodes and may not ever completely replace barcodes, due in part to the higher cost of tags and the advantage of multiple data sources on the same object. The new EPC was not designed exclusively for use with RFID data carriers, and, along with several other schemes, is widely available at reasonable cost.

Printed electronics provide a potential pathway toward the realization of ultra-low-cost RFID tags for item-level tracking of consumer goods. Ink-jet printing can be used efficiently to print electronics on paper substrates. In the design and fabrication of antennas for RFID tag devices operating in the UHF and MW range, paper substrate materials and ink-jet printing processes with conductive ink have been used to guarantee mechanical flexibility and ultra-low production costs of the antenna. Inks containing silver nanoparticles are usually selected in the ink-jet printing process to ensure good metal conductivity. After the silver nanoparticle droplet is driven through the nozzle, a sintering process is necessary to remove excess solvent and material impurities from the depositions (Rida et al., 2010).

Recently, researchers have built a 13.56 MHz-operated 1-bit RFID tag that can be printed directly onto cereal boxes and potato chip bags using a gravure printer (Jung et al., 2010). The tag uses a semiconducting ink containing carbon nanotubes that will hold an electrical charge. The current prototypes, estimated to cost 3 cents per unit, are three times the size of a typical barcode, and can only store 1 bit of information which is just enough to give either a yes or no response to an RFID reader. Improving the resolution and accuracy of the printer should allow smaller tags that carry more information. There is also a need to improve the circuit so that it emits higher power signals as at present the reader only works up to 10 cm away which is unacceptable at a checkout line.

Orecchini et al. (2011) reported the development of a new antenna design methodology to minimize the amount of both paper substrate and ink-jet conductive ink to guarantee mechanical flexibility and ultra-low cost mass production of RFID tags. Prototypes made by reducing the antenna size and removing metal material where the surface current density was negligible validated the proposed design methodology.

To qualify as intelligent packaging, RFID tags must contain an indicator that provides information about aspects of the history of the package (e.g., its temperature) or the quality of the food. Intelligent RFID tags with sensors are now being commercialized and are discussed in Section 15.4.1.4.

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10 Food Packaging Closures and Sealing Systems

10.1 CLOSURES FOR GLASS AND PLASTIC CONTAINERS

10.1.1 CLOSURE FUNCTIONS

The final, critical aspect of glass and rigid plastic packaging is the closure, which can consist of a cap, lid or cork to seal the jar or bottle (Theobald and Winder, 2006). Although glass, and to a lesser extent plastics, provide an excellent barrier to water vapor, gases and odors, an incorrectly designed or applied closure may compromise the benefits that packaging offers in protecting food products from deterioration and lead to a reduction in shelf life.

Closures are required to perform some or all of the following functions without affecting, or being affected by, the contents of the container:

1. Provide an effective hermetic (air-tight) seal to prevent the passage of solids, liquids or gases into or out of the container.
2. Provide easy opening and (when only part of the contents is used at one time) resealing of the container.
3. Provide evidence of inviolability (i.e., that unlawful access to the contents or their exposure to the atmosphere has not occurred). Roll-on tamper-evident (ROTE) closures (also referred to as roll-on pilfer-proof or ROPP closures), such as the aluminum roll-on closure used on beverage bottles, leave a tell-tale ring around the bottom of the neck of bottles after opening and are designed to deter tampering with the contents by providing visual evidence of tampering.

Many countries are experiencing rapidly aging societies in which a large proportion is likely to have relative difficulties in everyday life as a consequence of reduced strength, loss of dexterity, varying degrees of disability and cognition impairment. One specific area that stimulates a significant amount of controversy is the accessibility and functionality of product packaging, and the popular media frequently report on consumer frustration with regard to “over” packaged or poorly accessible goods. In response, researchers, designers and manufacturers have been undertaking significant work to address these concerns. Yoxall et al. (2010a) showed that although larger-diameter jars (85 mm) required much higher opening forces than smaller ones (75 mm and below), the force required to open many jars was still higher than many elderly people are able to generate.

Yoxall et al. (2006) showed that the maximum torque T_m that a consumer can theoretically apply to open a container is governed by Equation 10.1

$$T_m = \mu_{hc} N_A r_e \tag{10.1}$$

where

μ_{hc} is the coefficient of friction between the hand and the container lid surface
N_A is the minimum human grip force required for opening
r_e is the external radius of the container lid

While μ_{hc} will remain static to avoid slip between the hand and the external wall of the closure, it is necessary for a consumer to apply enough grip to avoid slip on the exterior surface of the closure. However, over a certain limit, this grip will be enough to transfer through the closure wall and add additional frictional forces to the closure/container thread interface.

Further work by Yoxall and Janson (2008) investigated the grip term in Equation 10.1 using specifically designed equipment and calculated the torques that users would then be able to apply to closures of varying diameters. The data indicated that the optimum diameter for a container lid is around 73 mm, and therefore lids of this diameter are the easiest for consumers to open. Data from Yoxall et al. (2010a) suggested that jars currently available on the market are likely to be difficult for some women and the elderly, in particular, to open. Larger sizes of jars were especially hard to open, with almost all users unable to open containers with 85 mm diameter lids. The smaller lids generally fared better, but many elderly users struggled to open all sizes of containers. Further work is required to more accurately determine the strength of consumers and the forces required to open food packaging, and to find solutions to make container lids of all diameters easier to open for all consumers.

Although various tools are available to improve the accessibility or "openability" of packaging for those who may have potential difficulty, an assessment of some of the common tools by Yoxall et al. (2010b) indicated that while some tools are effective, most offer little or no benefit, as they do not overcome issues such as loss of dexterity and strength among the aged population.

10.1.2 CLOSURE CONSTRUCTION

Closures are made from one of two materials: metal or plastic. Metal closures are stamped out of sheets of tinplate, ECCS or aluminum, generally with a thickness of about 0.25 mm. The sheets are usually coated with enamels to prevent the metal from reacting with the contents of the container and are frequently printed. Metal closures can take four forms: screw caps, crowns, lug caps and spin-on or roll-on closures.

Plastic closures are generally either compression or injection molded, the former being based on urea–formaldehyde or phenolic–formaldehyde resins, and the latter on a variety of thermoplastic polymers including PS, LDPE, HDPE, PP and PVC. Today, most closures are injection molded. Plastic closures are available in a wide range of sizes and designs and have defied several attempts at standardization over the years.

The actual sealing component of the closure is the *gasket* or *liner*, which must make intimate contact with the container finish to form an effective seal. Gaskets are made from rubber or plastisols, the latter being suspensions of finely divided resin (often PVC) in a plasticizer, which can be flowed in or molded. Flowed-in compounds are almost invariably used in vacuum closures and closures for heat processed foods.

Liners consist of a cushioning material (known as a *wad*) with a facing material, the purpose of the latter being to isolate the contents of the container from contact with the wad. Generally, the wad is made of composition cork (granules of cork bonded together with either a gelatin-type glue or a synthetic resin) or paperboard, and faced with either a coated paper, a paper faced with plastic film, a plain metal foil, a lacquered metal foil or a metal foil faced with a plastic film or coated with a layer of a wax material. Thermoplastic resins have allowed the development of "linerless" plastic closures, which rely on a variety of styles of sealing rings molded into the closures to create a liquid or hermetic seal.

10.1.3 FOOD CONTAINER CLOSURES

In general, closures that are used with food containers can be classified under four headings that are each discussed in turn.

10.1.3.1 Closures to Retain Internal Pressure

The closures for this application are generally required to contain pressures from about 200 to over 800 kPa, as typically found in carbonated drinks and beer.

10.1.3.1.1 Crown Cork

The traditional pressure-retaining closure has been the crown cork, a crimp-on/pry-off friction-fitting closure made from tinplate with a fluted skirt (angled at 15° to maintain an efficient seal) and a cork or plastisol liner. The crown cork was invented in 1891 by William Painter, an American of British descent who lived in Baltimore, Maryland, who said of his invention (so it is claimed) "this closure gives a crowning and beautiful effect to the bottle" and the name crown stuck. It was simple, economical to produce and retained gas in the bottle. Though simple in concept, the crown cork provides a friction-fit sufficient to seal pressurized beverages. The flared cap skirt, in conjunction with the smoothness of the bottle neck, provides easy access through the prying motion of a bottle opener. The crown cork of today is still much the same, except that the teeth on the skirt have been reduced from 24 to 21, ECCS is used rather than tinplate, and PVC plastisol or some type of olefinic material linings have largely replaced cork (Pitman, 1999). A relatively recent improvement has been the introduction of twist-off crown corks.

The 26 mm crown cork is used worldwide and is normally applied only to a glass finish. A crown applied to a 26 mm pry-off finish will require some type of opening device to remove the crown from the container, whereas a crown applied to a 26 mm twist finish can be removed by hand. The pry-off finish has a large solid ring of glass around the outside. The corrugations of the crown can be crimped under the ring during application to hold the crown in place and form a solid seal. The twist-off finish has four noncontinuous threads and the corrugations of the crown are crimped into the threads to form the seal. The crown can be removed from the twist container by turning it 6 mm.

The crown cork is applied to a filled container using a crowner that exerts a straight downward force on the crown to crimp it onto the finish. The crowning head compresses the crown liner to form a tight seal and bends the crown skirt downward and inward to lock it tightly under the locking ring on a pry-off finish. In the case of a twist-off finish, the knuckles between the corrugations are crimped into the threads in the bottle finish. This effectively puts threads into the inner side walls of the crown, allowing the crown to twist off.

Crowns are used in a wide range of beverage products as an inexpensive, single use seal. They are also used for hot or cold filled, pasteurized and pressurized products and for sterilized vacuum products.

10.1.3.1.2 Roll-On Tamper-Evident

A ROTE aluminum closure was first used in the 1920s as a closure on bottles of prescription drugs. It is now used where critical sealing requirements, such as carbonation retention, vacuum retention and hermetic sealing are to be met. The closure is produced as an unthreaded shell containing a liner and is applied to the proper finish on a plastic or glass container. A thread is formed in the closure matching the bottle thread. The ROTE closure is produced in a wide range of sizes (from 18 to 38 mm), and is available in two different tamper-evident styles: the vertically scored and the standard band (both with and without venting). On opening, the vertically scored band ruptures along vertical score lines and is removed as part of the closure. The standard band separates from the closure during opening and remains on the bottle. Both standard and vertically scored closures can be reclosed after the original opening by turning the threaded closure back onto the container finish.

The ROTE closure is produced from coated, light gauge aluminum, and a range of lining materials (plastics, plastisols, pulpboard and facing, etc.) are available depending on the product to be packed. The closure is coated on the inside surface for protective purposes and can be printed and decorated in various colors on the outside surface to enhance the package's appeal.

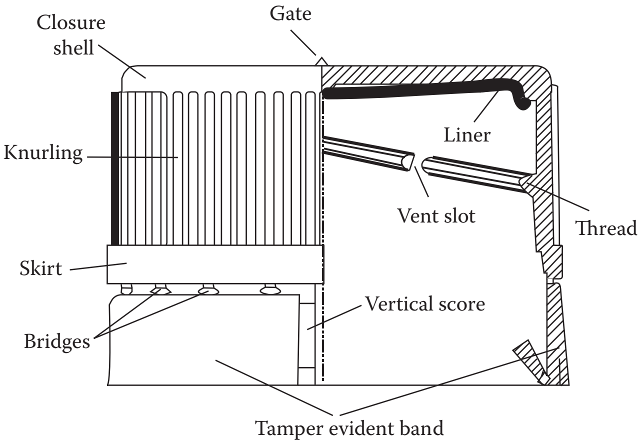

FIGURE 10.1 Nomenclature for plastic closures. (From Pitman, K., Closures for beverage packaging, in: *Handbook of Beverage Packaging*, Giles, G.A. (Ed.), CRC Press, Boca Raton, FL, 1999, p. 209.)

ROTE closures are applied to filled containers using roll-on capping machines. The capping head first applies a downward pressure that compresses the liner onto the sealing surface of the container. The capping head then forms a thread in the closure matching the container thread, while also tucking the tamper-evident band under a locking ring on the container finish.

Plastic versions of the closure are now available and used widely; nomenclature for such closures is shown in Figure 10.1. Plastic prethreaded closures can generally be characterized by their size (diameter), thread form, material (HDPE or PP), seal and type of tamper evidence (Pitman, 1999). The most common size is 28 mm although some 38 mm caps are used for carbonated beverages. The liner in two-piece closures is usually made of EVA as it is soft and easily deformable. The rolled-on or spun-on aluminum or plastic closure is especially popular for carbonated drinks in large containers where reuse is common. Generally, the same closures are applied to glass and plastic bottles.

The standard thread on PET bottles for carbonated beverages has four vertical slots to allow "venting" of CO_2 from the bottle as the cap is unscrewed; the slots in the thread on the bottle line up with the breaks in the thread on the caps to allow a gradual release of pressure from the bottle as the cap is unscrewed. This prevents a phenomenon known as "tail end blow off," tailing or missiling, which occurs when pressure inside the bottle causes caps to eject while being unscrewed as they reach the end of contact with the threads on the bottle.

10.1.3.2 Closures to Contain and Protect Contents

These closures are designed to contain and protect the contents with no internal pressure, (e.g., wine in a bottle).

The style and development of wine is strongly influenced by the choice of closure, with different closures producing different wines over time after bottling wine from the same batch, due to the different O_2 barrier properties of the closures. A key issue is whether wines require O_2 to age in the bottle. Some experts consider that wine development after bottling is a process of reduction, while others consider that some amount of O_2 benefits wine maturation after bottling, and therefore closures with different O_2 permeabilities would help to mitigate reduced off-flavors and sulfur-like odors (SLOs) and create different wine styles. According to Waterhouse and Elias (2010), a certain degree of oxidation is desirable in some wines (e.g., tannic reds, sherries and tawny ports) and undesirable in others (e.g., most whites and rosés). A recent review (Karbowiak et al., 2010) stated that while a basic understanding of key factors influencing the sensory perception of wines has been achieved, other important aspects are still not yet well understood, including the particular role of O_2. Oxidation reactions are assumed to play a dominant role in wine aging, and seem to be related to measured values of O_2 transfer through various types of closures.

The most common closure for wine has been the traditional bark cork obtained from the cork oak tree *Quercus suber*, native to southwest Europe and northwest Africa, and grown commercially for its cork mainly in Portugal and Spain. The cork stopper has been used as a closure on glass bottles for over 25 centuries and provides an incomparable friction-hold seal. With a high cellular density, cork is compressible, elastic, largely impervious to air and water and low in thermal conductivity. However, 5%–10% of all wines sealed with natural cork suffer from "cork taint," an objectionable taint caused by TCA (2,4,6-trichloroanisole) and other organohalogens, which can result in undesirable musty aromas and flavors. TCA is a naturally occurring, odorous (albeit harmless) compound that certain microorganisms produce from TCP (2,4,6-trichlorophenol); it has a very low taste threshold of 5 parts per trillion (ppt) or less depending on the sensitivity of the consumer (see Section 22.7.3).

Various approaches have been adopted to overcome the problem of cork taint in wine, a major one being the elimination of hypochlorite bleaching of corks as this was considered one of the major sources of chlorophenols. An Australian company has developed technology that reduces the likelihood of cork taint by applying a polymeric-based membrane to each end of the cork, which reduces chemicals entering the wine, regulates the passage of O_2 through the cork and retains cork moisture, resulting in less cork breakage. It is claimed that 90%–100% of the TCA in corks is prevented from entering the wine if corks with membranes are used.

The agglomerate cork, originally developed as a closure for sparkling wine, consists of small pieces or granules of clean, natural cork bound together with resin or a chemical binder into a single stopper. When one or more thin disks of intact natural cork are attached to the end intended to be in contact with the wine (and sometimes on the external end as well), it is referred to as a technical cork. An effective disinfecting or deodorizing process, which extracts volatile components from the cork prior to agglomeration, is claimed to eliminate the possibility of contaminants being retained inside the lenticels (pores through which gases are exchanged between the atmosphere and plant tissues).

In the early 1990s, many wineries tried synthetic (plastic) corks as a way to avoid cork taint. Although some synthetics were criticized for leaching a plastic flavor into wines, their use is growing and new formulations are being introduced. Two basic types of synthetic closures are currently available: injection molded and extruded closures. Extruded closures are manufactured by coextruding a long continuous length of HDPE and PP with a foamed LDPE core that is cut to size to make the individual "corks." Recently, Lopes et al. (2011) examined the sealing effectiveness of different closures on the permeation of TCA when bottled wine model solutions were stored in a contaminated environment. Natural and agglomerate corks were effective barriers as they retained high concentrations of TCA in their outer portions, whereas TCA penetrated synthetic corks and contaminated the wine.

In response to the increased use of synthetic corks, the cork industry has adopted three measures to avoid TCA and TCA precursors in corks: (a) preventing contamination of cork with chlorinated compounds, (b) avoiding microbial growth on cork and (c) corrective stripping of TCA and associated compounds from cork (Pereira, 2007). One of the world's largest cork manufacturers patented a process in 1999 that uses supercritical CO_2 for selective extraction of volatile compounds from cork, removing as much as 97% of TCA. Others use a controlled steam distillation process or microwaves to dry the cork and destroy TCA-producing microorganisms. Another process to remove the VOCs responsible for sensory problems in corks uses a carrier gas composed of water vapor and ethyl alcohol that is able to remove contaminants down to acceptable levels of $<3\,\text{ng L}^{-1}$.

The diameter of a cork on average is 24 mm, which is compressed to about 16 mm to fit into the bottleneck, after which it expands back to the average diameter of the bottleneck (ca. 18 mm). The ease of extraction depends on the structure of the cork, which affects its adhesion (friction) to the glass bottle neck. The extraction force should be >15 kg to guarantee sufficient adhesion of the cork to the bottleneck. Synthetic corks have shown a high variability of extraction force ranging from 10 to 50 kg, with values of 30 to 35 kg usually considered as optimal for uncorking, and values >45 kg indicating that the corks cannot be easily removed (Giunchi et al., 2008).

When natural cork stoppers are compressed in the bottleneck immediately after bottling, the air pressure in the cells ranges from 600 to 900 kPa and consequently air at atmospheric pressure (101 kPa) is unable to enter the bottles through the cork or between the cork–bottleneck interface. However, the extremely high internal pressure forces air out of the cork, which occurs preferentially in natural and technical corks during the first 12 and 24 months of storage, respectively, being facilitated by small openings of 60 nm diameter in the walls separating each individual cork cell (Lopes et al., 2007). Some permeation through the cork–glass interface is also possible, mainly after 12 months of storage in natural cork stoppers. Synthetic closures are permeable to atmospheric O_2, mainly after the first month of storage.

A challenge to the cork was the development in France in the late 1960s of an aluminum rolled-on closure known as Stelvin®. Research suggested that it performed better than the bark cork. The Stelvin capsule is made up of a screw cap, a long printable skirt and a liner specifically designed for contact with wine. The wad or liner consists of three or four components as shown in Figure 10.2, depending on the anticipated shelf life of the wine. For wines with a shelf life of up to 5 years, the liner consists of a central core of expanded LDPE foam to provide controlled and uniform compressibility, covered on both sides by a coextruded LDPE-PVdC copolymer-LDPE film. For wines requiring more than a 5 year shelf life, expanded LDPE is laminated to white kraft paper that is adjacent to a layer of tin foil to provide a gas barrier and a PVdC copolymer facing, which isolates the tin foil from the wine and provides an additional O_2 barrier. The Stelvin screw cap requires a special glass bottle finish know as BVS (Bague Vin Suisse) where the threads start at 2.8 mm from the top instead of the usual 1.65 mm. Stelzer (2005) reviewed many of the technical publications concerning the shelf life of wine in bottles sealed with Stelvin closures.

Reeves (2010) tabulated the reported OTRs of various wine bottle closures. Values ranged from 0.0001 to >1.0 mL O_2 closure^{-1}day^{-1} for cork, reflecting both natural variation and methodological differences. Values for synthetic cork varied from 0.007 to 0.031, and for screw caps from 0.0003 to 0.001 mL O_2 closure^{-1}day^{-1}. Karbowiak et al. (2010) presented a similar table but with units of mg O_2 closure^{-1} year^{-1} and these can be converted to mL O_2 closure^{-1} day^{-1} by multiplying by 521.6. Both tables confirm the high variability in permeability of natural cork stoppers from various origins, and even within a given batch of cork, and the very low permeabilities of screw caps. Faria et al. (2011) reported the permeability of dry, uncompressed cork to O_2, N_2, CO_2 and the refrigerant R-134a. One of their main findings was the large variability in cork permeability

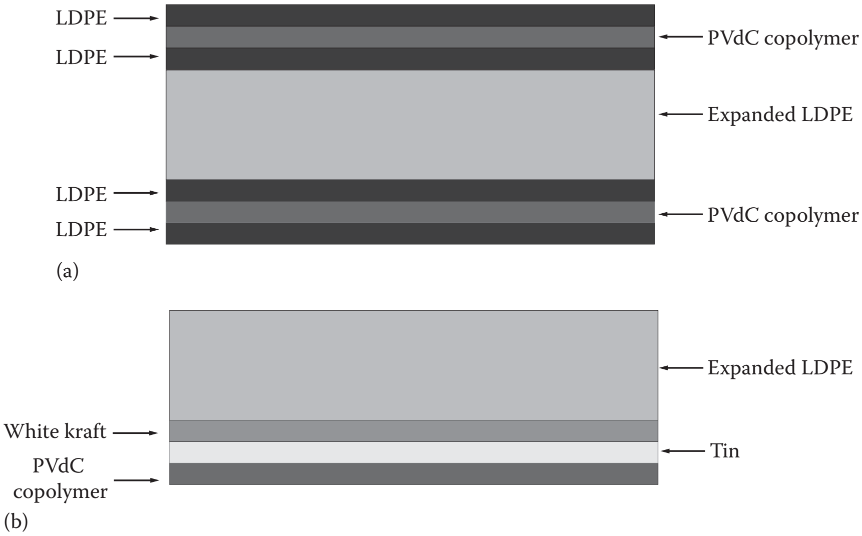

FIGURE 10.2 Composition of liners in Stelvin capsules (a) for shelf life up to 5 years and (b) for shelf life greater than 5 years.

(3 orders of magnitude), even in the absence of macroscopic inhomogeneities. Cork density and boiling processing were factors affecting the mean permeability. As their results were obtained for uncompressed cork, they are not directly applicable to cork closures. However, they provide a clear picture of the permeability of cork, as a natural material, to several gases. Overall, wine closures must be considered a unique type of food packaging, and Karbowiak et al. (2010) have suggested that it may be of interest to investigate, in a more detailed way, the relationship between a closure's permeability properties and the chemical reactions occurring in wine.

Recently, a simple, nondestructive technique for the measurement of coextruded closure OTR was presented (Diéval et al., 2011). It uses luminescence-based technology with separate sensors to measure O_2 ingress through the closure or at the interface between the closure and bottleneck. They reported values for synthetic corks ranging from 0.0171 to 0.0358 mL O_2 package^{-1} day^{-1} for 100% O_2 that converts to 0.0036–0.0075 mL O_2 package^{-1} day^{-1} for air, which is the parameter of practical interest since wine bottles are not stored under 100% O_2!

10.1.3.3 Closures to Maintain Vacuum inside Container

These closures are designed to maintain a vacuum inside glass containers that typically contain heat-processed food (Nairn and Norpell, 2009). Metal vacuum closures are frequently referred to by the following terms: the *panel* is the flat center area in the top of the closure; the *radius* or *shoulder* is the rounded area at the outer edge of the panel connecting the panel and the skirt; the *skirt* is the flat, almost vertical portion on the side of the closure, which serves as the gripping surface and may be smooth, knurled or fluted; the *curl* is the round or rolled portion at the bottom of the skirt that adds rigidity to the cap and serves to protect the cut edge of the metal; the *lug* is a horizontal inward protrusion from the curl, which seats under the thread or lug on the finish of the container, holding the closure in position.

Three types of vacuum closures are used in food processing:

1. Lug-type or twist cap. This can be removed without a tool and forms a good reseal for storage. It has three, four or six lugs and a flowed-in plastisol liner.
2. Press-on twist-off cap. This has no lugs but the finish is threaded. The gasket is molded plastisol and covers the outer edge of the panel and the curl of the cap. It is widely used on baby foods. This type of closure is held on mainly by vacuum with some assistance from the thread impressions in the gasket wall.
3. Pry-off (side seal) cap. This is still widely used on retorted products. It consists of a cut rubber gasket held in place by being crimped under the curl. As with the preceding closure, the pry-off (side seal) cap is also mainly held in place by vacuum with slight assistance from the friction of the rubber gasket against the side of the container finish.

All the earlier-mentioned closures are made of metal (tinplate or ECCS) and are fitted either with flowed-in liners, gaskets or rubber rings.

Vacuum closures often have a safety button or flip panel that consists of a raised, circular area in the center of the panel that serves two purposes. First, it provides a visual indicator to the consumer that the package is properly sealed (containers with these types of closures usually have instructions on the closure warning consumers not to purchase or consume the product if the flip panel is up). Second, in the processing plant, the flip panel aids in automatic online detection (using a "dud" detector) of low vacuum or no vacuum containers.

10.1.3.4 Closures to Secure Contents inside Container

Some closures are designed only to secure the contents inside the container (e.g., peanut butter). They are frequently screw caps with a minimum thread engagement of three quarters of a turn. They are made either from metal or plastic, and typically have either a plastic-coated paperboard wad inside or may be of the linerless plastic style.

10.2 HEAT SEALING

Heat sealing involves welding thermoplastic polymer surfaces together in order to produce seals or joints of sufficient strength to withstand stresses in the distribution and consumer environment (Aithani et al., 2006b). A seal can be nonpeelable (tearable) or peelable (so-called easy open) and the latter are discussed in Section 10.3. The heat sealability of a packaging film is one of its most important properties when considering its use, and the integrity of the resultant seal is of paramount importance to the ultimate integrity of the package, as seal failure inevitably leads to food deterioration and a reduction in shelf life. Heat sealability is a property of the materials that are being heat sealed and at a given thickness is a function of the material composition, average MW, MW distribution and thermal conductivity (Aithani et al., 2006b).

Heat sealable films are considered to be those films that can be bonded together by the normal application of heat, such as by conductance from a heavy heat-resistant metal bar containing a heating element. Non-heat-sealable films cannot be sealed this way, but they can often be made heat sealable by coating them with heat sealable coatings (HSCs). In this way, the two facing coated surfaces become bonded to each other by application of heat and pressure for the required dwell time.

There are two types of seals (Figure 10.3). A *fin* seal is formed when the inside surface of the film is sealed against itself; it is commonly used to form the top and bottom seals on horizontal or vertical form-fill-seal machines. A *lap* seal is formed when the inside surface of the film is sealed against the opposite (outside) surface of the film; it is commonly used to form the longitudinal or back seal on vertical form-fill-seal machines.

The basic heat sealing process involves fusing two polymers to one another through the application of heat and pressure. As the sealant layer begins to melt, more intimate contact or wetting of the sealing surfaces occurs. Given sufficient time, molecular segments diffuse across the interface forming entanglements, and thus the seal strength increases.

A number of factors influence the quality of a heat seal and they can be conveniently summarized under three headings:

1. Machine factors: dwell or clamp time, temperature and pressure
2. Resin factors: density, MW, MWD and additives in the resin
3. Film factors: thickness, style or form (e.g., whether gusseted or not) and any treatment for printing such as corona discharge

All of these factors tend to interact in a complex way. For example, the amount of heat available may be limited by the capacity of the heating elements, by the rate of heat transfer of the sealing bar and its coating or the type of product being packaged. Increasing the dwell time (i.e., the time during which heat is applied, typically a second or less) will increase the heat available, but this may prove to be uneconomical since fewer units will be able to be handled per minute on the production line. The interfacial temperature and dwell time are the primary factors that control the heat

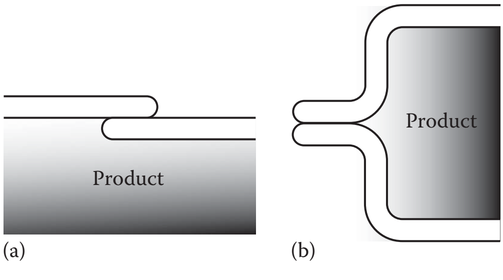

FIGURE 10.3 Two major types of heat seals: (a) lap seal and (b) fin seal.

seal strength. In practice, it is usually the surface of the heat generator rather than the interfacial temperature that is measured and controlled, resulting in problems of either overheating or improper cooling. Pressure normal to the seal surface has little effect above the level required to flatten the webs for good contact (Theller, 1989). Corona discharge treatment of LDPE and LLDPE has been reported to cause an increase in seal initiation temperature of 5°C–17°C and change the seal failure from normal tearing to peelable mode. A reduction in seal strength has also been reported when films were contaminated with oleic acid, low MW polymer fractions, additives such as antioxidants and slip agents and external processing aids such as mold release agents.

10.2.1 CONDUCTANCE SEALING

Conductance (also known as *resistance* or *bar*) sealers are the most common type of heat sealers in commercial use and typically consist of two metal jaws or bars (often patterned or embossed to give the seals extra strength), one of which is electrically heated, the temperature being controlled thermostatically. The second or backing jaw is often covered with a resilient material such as rubber to distribute pressure evenly and aid in smoothing out the film in the sealing area. Frequently, the unheated jaw is water cooled, although in some situations it may be heated to the same temperature as the first jaw to enable sealing through sheets of film in exactly the same way each time. The edges of the jaws are often rounded to avoid puncturing the packaging material. A simple conductance heat sealer is shown in Figure 10.4.

Conductance sealers are used for a range of packaging materials including RCFs and laminated materials such as foil or paper with an HSC (commonly LDPE or LLDPE). However, they are not suitable for unsupported materials such as LDPE film, which would simply melt and stick to the jaws. Serrated jaws can be used to ensure that the two webs are stretched into intimate contact with high local pressure; they also improve appearance. For all sealing jaws, a nonstick coating is desirable; PTFE is commonly used, either as a cloth-reinforced film or, in the case of serrated jaws, as a powder bound in a heat-resistant vehicle.

Dwell time should be able to be controlled to fractions of a second and be easily adjustable as it needs to be changed when different materials are heat sealed. Likewise, the pressure between the jaws should also be easily adjustable.

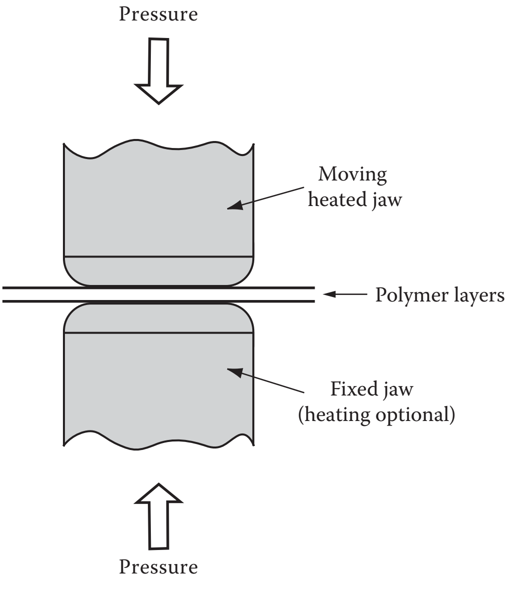

FIGURE 10.4 Conductance or bar sealer.

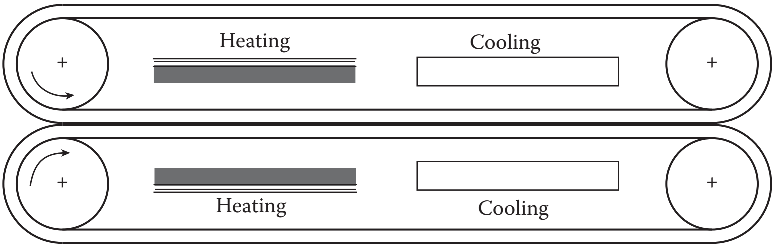

FIGURE 10.5 Band sealer.

A variation on this type of sealer is the band sealer, where the films travel between two endless bands of metal that are pressed together by heated bars (Figure 10.5). The heat passes through the bands and seals the films. The bands are then pressed together by chilled bars to withdraw heat from the seal. Band sealers are widely used for sealing pouches and have the advantage of being continuous.

Mihindukulasuriya and Lim (2012) studied the effects of liquid contaminants on the heat seal strength of three different LDPE film–film interface conditions: (1) no contaminant, (2) water contaminant and (3) vegetable oil contaminant. In the presence of liquid contaminant, jaw pressure played an important role in displacing the liquid from the seal area to form intact seals. Short dwell time (0.3 s) and low jaw temperature (150°C) was not favorable for forming intact seals in films contaminated with water or vegetable oil. The optimum jaw temperature and dwell time required to produce intact seals for oil-contaminated films was 180°C and 0.3 s, whereas a combination of 165°C jaw temperature and 1 s dwell time was required to form intact seals for water-contaminated films. Interface temperatures of 130°C–140°C resulted in optimum seal strength for both water-contaminated and clean film specimens. Above 140°C, a weakening of seal strength was observed, presumably because of the change in melt flow characteristics and possible initiation of thermal degradation of the polymer.

10.2.2 IMPULSE SEALING

In this method, the films (usually unsupported materials) are clamped between two cold metal bars and then fused by applying an impulse current of 20–50 A through a nichrome resistance wire or ribbon (typically 2–5 mm wide and 0.1–0.15 mm thick) on one or both sealing jaws for a short time (0.2–3.0 s); cooling occurs under pressure (Hishinuma, 2009). Although impulse sealers have the same general configuration and mechanical construction as conductance sealers, much lighter jaws are used (Figure 10.6).

Generally, the current in the resistance wire is kept constant and the amount of heating is changed by adjusting the energizing time in the resistance wire (Hishinuma, 2009). Dwell time of the heating impulse must also be controlled, as must the length of the cooling period. Thus, two timers are often found on impulse sealers, with the second timer controlling the cooling of the resistance wire to allow the film to harden under pressure and prevent deformation of the film in the sealed area. If very heavy films are to be sealed, both jaws may contain resistance wires. Water is recirculated through a tube behind the impulse ribbon to prevent excess heating and promote rapid cooling of the heat seal, thus permitting the sealing of unsupported thermoplastic materials.

To prevent the film from sticking to the heated jaws, it is usual to cover them with a layer of thin heat-resistant material such as silicone-rubber-coated fiberglass, PTFE-coated fiberglass or PTFE-coated polyimide film (Morris and Darby, 2009). Generally, the seals produced by impulse sealing are of excellent quality and tend to be narrower than those produced by conductance sealing. The main drawback is the high maintenance costs as the nichrome wire and release coverings require frequent replacement.

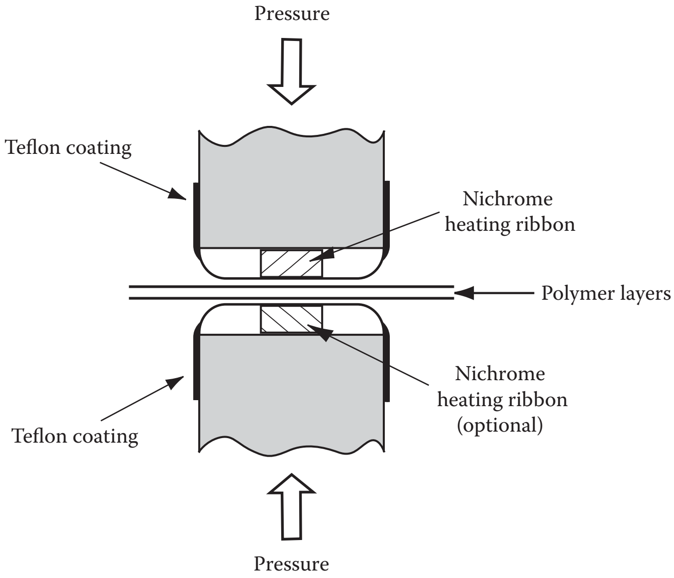

FIGURE 10.6 Impulse sealer.

10.2.3 DIELECTRIC SEALING

In dielectric sealing (also known as radio frequency [RF] sealing), a high frequency (HF) generator transforms low frequency electrical energy from the alternating current network into HF electrical energy (typically 50–80 MHz), which is then passed through two or more layers of film (Figure 10.7). The dipoles in the polymers oscillate in response to the alternating electric field and molecular resistance generates heat to melt the polymer. The electrodes (usually made of brass) are the top and bottom jaws and the latter is the ground of the circuit. The pressure that the jaws exert on the films helps to bring about thorough fusion and bonding.

Dielectric sealing is only applicable to materials that are polar and capable of forming a dipole moment, that is, have a dielectric loss factor approaching 0.01 or higher. Such materials include EVA, EVOH, PA, PET, PVC, PVdC and composite materials. The main advantages of dielectric sealing are that only the desired area is heated and the sealing instrument remains cool. It is used principally with PVC and nylon 6,6 films as they are difficult to heat seal by direct means because they tend to degrade at temperatures close to their softening point.

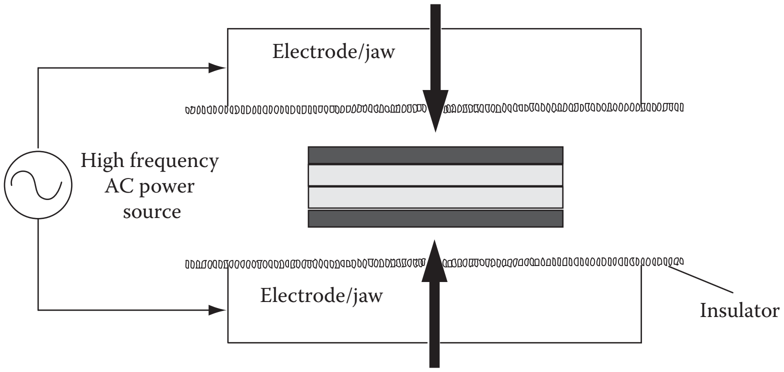

FIGURE 10.7 Dielectric sealing.

10.2.4 Induction Sealing

Induction sealing is a noncontact method of heat sealing made by exposing a metal (generally aluminum foil) coated with a thermoplastic sealant to a HF, electromagnetic field generated by passing an alternating current of 20–30 kHz through a coil. The field induces circulating eddy currents (also called Foucault currents), which generate precise amounts of localized heat in the foil, melting the sealant layer without any physical contact between the coil and the package. The basic components of an induction heating system are an AC power supply and an induction coil (Figure 10.8).

The original concept and method for induction sealing was conceived and proven by Jack Palmer from the FR Corporation of New York as a means of solving liquid leakage from polyethylene bottles during shipment; he was issued with U.S. Patent 2937481 in May 1960. Modern advances in solid state technology have made induction heating a remarkably simple and cost-effective sealing method.

Induction sealing is used to heat seal diaphragms or inner seals to bottles and jars. An induction seal provides tamper evidence and a hermetic seal when used as an inner seal beneath a normal threaded closure. The torque of the cap holds the seal in place during the induction heating process. The operating frequency of the power supply determines the heating pattern of the electromagnetic field. Higher frequency results in heat concentration on the outside edge of the inner seal, which is beneficial for one piece type liners. As the frequency is lowered, the heating tends to be more uniform across the inner seal.

Induction sealing is also widely used to heat seal both the longitudinal and transverse seals of laminated paperboard cartons containing aluminum foil. Tetra Pak was awarded U.S. Patent 4637199 in 1987 for an "*Induction apparatus and method for sealing of thermoplastic coated packing material*." A number of nonconductive sealing jaws, each containing a secondary induction coil, are mounted on an endless chain opposite corresponding rigid pressure jaws also mounted on an endless chain. After the sealing pulse is terminated, there is a cooling time that enables the LDPE to resolidify as a single layer, guaranteeing a strong and tight seal. The jaw pressure must be kept for sufficient time to allow suitable sealing and cooling, in order to ensure a tight closure of the package. In continuous transverse sealing, the pressure jaws include a knife to sever the seals.

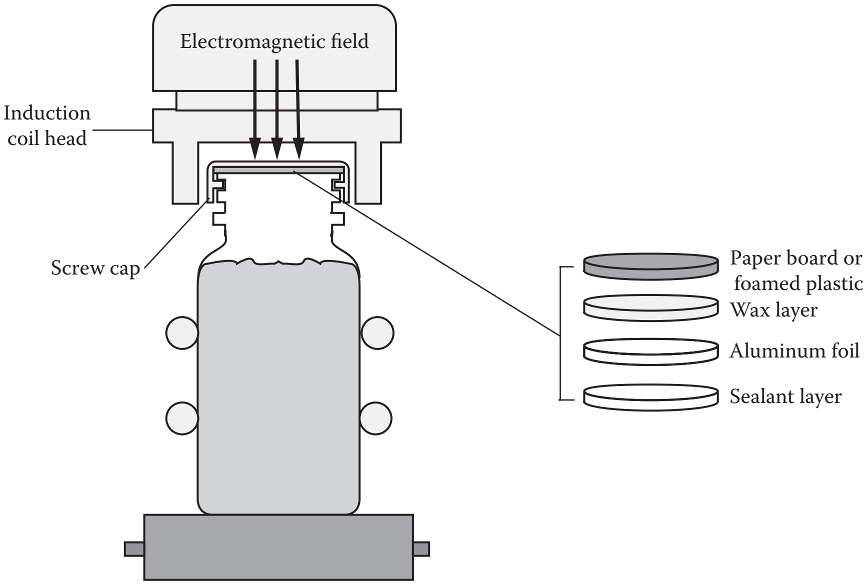

FIGURE 10.8 Induction sealing.

The great advantage of induction sealing is its applicability to almost all thermoplastic materials. Placing an electroconductive layer such as aluminum foil close to the thermoplastic material allows the sealing of composite materials with a thick heat-insulating layer, which are usually unsealable using other methods. Unlike ultrasonic sealing, the mechanical stress on the material is unimportant.

10.2.5 ULTRASONIC SEALING

In this method of sealing, a generator feeds a 20–40 kHz signal into a transducer that transforms electrical energy into mechanical vibrations of the same frequency. The mechanical energy is converted into heat at the interface and produces an almost instantaneous weld. Little overall heating is produced, thus enabling oriented films to be sealed without any change in dimensions. Ultrasonic sealing is also useful to seal materials that are too thick to permit conductive heat transfer through them for sealing (Morris and Darby, 2009).

An ultrasonic horn acts as a focusing tool for the vibrations that pass through the film to an anvil (Figure 10.9). Any gap between the two surfaces to be sealed weakens the transmission of the ultrasonic vibrations. Therefore, to ensure transmission and energy dissipation, the horn presses the films against a counter tool called the anvil that also functions as an energy director. The heating is initiated by starting the vibration of the horn and is stopped by switching off the ultrasound (Bach et al., 2012). The pressure, along with temperature and dwell time (expressed in terms of the rate at which the film is fed between the welding head and anvil), are adjusted to get optimum seal quality. The biggest disadvantage of ultrasonic sealing is its cost (Morris and Darby, 2009). Ultrasonic sealing has particular advantages for longitudinal seam sealing in horizontal form-fill-seal machines for confectionary products such as chocolate as the cool tools prevent melting of the product. It has

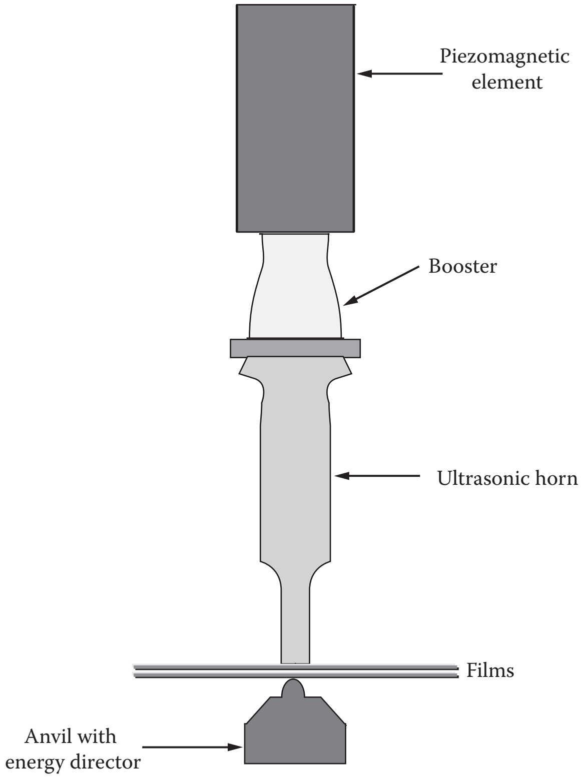

FIGURE 10.9 Ultrasonic sealing.

been suggested that ultrasonic sealing may be a useful alternative to cold sealing processes and help reduce packaging material costs (Bach et al., 2012).

Ultrasonic sealing is useful for sealing materials that are too thick to permit conductive heat transfer through them as in conventional sealing methods. Resistance to contamination in the seam area is often mentioned as one of the biggest advantages of ultrasonic sealing, because of the expulsion of the contamination due to the vibrations. Three expulsion mechanisms have been identified: (1) expulsion because of the static sealing force in combination with shaped sealing tools, (2) expulsion because of the vibration of the ultrasonic horn and (3) expulsion because of the squeezing out of melted sealing material. Bach et al. (2012) concluded that ultrasonic vibrations of the horn mainly influence the expulsion of loose materials by inducing a vibration of the films. For fluids and pasty goods, expulsion by the static force combined with the tool's shape and expulsion by melted sealing material dominated.

10.2.6 HOT-WIRE AND HOT-KNIFE SEALING

Hot-wire and hot-knife sealing use a thin wire or strip of metal with a radiused edge (knife) mounted in or on the surfaces of a bar heated with a low voltage current. The relatively small surface area of contact causes all of the force of sealing to be transmitted through a small area, resulting in a high pressure in the seal area (Morris and Darby, 2009).

This method has found application for the manufacture of polyethylene bags and pouches in tubular form, with the sealing and cutting operations carried out in one step. It is only applicable to thermoplastic films that can tolerate high temperatures for a short time and also have a low viscosity in the fused stage. When unsupported films are trim sealed by this method, they tend to form a strong bead in their seal areas due to surface tension and orientation. This method is also used to a limited degree with laminated materials.

There is a tendency with this method of sealing to get what is known as "angel hair"—fine strands of polymer protruding from the seal area. This can be controlled with the use of proper temperatures and times. Generally, films thicker than 0.05 mm are difficult to seal through, especially if they have gusseted structures.

10.2.7 TESTING OF HEAT SEALS

Seal strength is a quantitative measure for use in process validation, process control and capability. Seal strength is not only relevant to opening force and package integrity, but also to measuring the ability of the packaging processes to produce consistent seals. Seal strength at some minimum level is a necessary package requirement, and at times it is desirable to limit the strength of the seal to facilitate opening. *Hot tack* refers to the strength or peel resistance of a seal while it is still hot following heat sealing.

Testing the strength of heat seals between thin films is generally determined by measuring the force required to pull apart at a constant rate the pieces of film that have been sealed together, either in a dynamic load test or a static load test. The latter test tends to be qualitative whereas the dynamic test (usually performed on some type of tensile testing equipment) is quantitative. The *seal strength* ($N\ m^{-1}$) is defined as the maximum (peak) force required to separate the seal divided by the film width (typically 15–25 mm). At sufficiently high extension, failure of the test piece occurs. The elongation of the test piece at failure (*seal elongation*) and the area under the force/distance curve (*seal energy*) are commonly taken as indicative of the toughness of the seal.

The ASTM F88 standard test method for determination of the seal strength of flexible barrier materials describes the procedures to be followed, along with the equipment to be used and the methods to be employed, thus enabling useful comparisons to be made between the seal strength of different materials and/or different sealing methods. This test method measures the force required to separate a test strip of material containing the seal. It also identifies the mode of specimen failure.

ASTM F2029 details standard practices for making heat seals for determination of heat sealability of flexible webs as measured by seal strength. These practices apply primarily to webs intended to be used on commercial machines employing reciprocating sealing jaws, such as most form-fill-seal packaging machines, platen heat sealers and so forth. Conditions of dwell time and sealing pressure on machines of this type are typically different from those on rotary machines. This standard is restricted to sealing with a machine employing hot-bar jaw(s). Impulse, high-frequency and ultrasonic heating methods are not included. Determination of heat sealability as judged by seal continuity, typically measured by air-leak, dye penetration, visual examination, microorganism penetration or other techniques is not covered by this standard.

In form-fill-seal operations, sealed areas of packages are frequently subject to disruptive forces while still hot. If the hot seals have inadequate resistance to these forces, breakage can occur during the packaging process. ASTM F1921 measures hot seal strength (hot tack) and can be used to characterize and rank materials in their ability to perform in commercial applications where this quality is critical. This test method is restricted to instrumented hot tack testing, requiring a testing machine that automatically heat seals a specimen and immediately determines strength of the hot seal at a precisely measured time after conclusion of the sealing cycle.

For many small and odd shaped packages, the seal strength cannot be measured by standard means. The upper force limit for each individual package can be determined by applying a constant force and maintaining it for a predetermined time. By placing the package within restraining plates during pressurization, the dimensional stability of the package is maintained in a manner that results in stresses applied more uniformly along the perimeter of the package, where seals are normally placed. This allows the test to have a higher probability of detecting the weakest area of the seal and provides a measurement of the pressure required to “burst” open the package. This test only applies to flexible packages with seals placed around the perimeter of the package (i.e., pouches).

Test method ASTM D3078 covers the determination of gross leaks in flexible packaging containing a headspace gas. The package is submerged in a transparent container filled with a mixture of water and dye. Vacuum is created inside the container and maintained for a specific length of time. When the vacuum is released, any leaks will draw in dye revealing an imperfect seal. Test sensitivity is limited to 1×10^{-3} kPa m^3 s^{-1} or even less, and small leaks may not be detected. Positive pressure inside the pouch after the vacuum is drawn may force the product to plug small leaks. The size of the leak that can be detected depends on the products contained, the nature of the packaging material and the test parameters selected.

Test method ASTM D1876 is primarily intended for determining the relative peel resistance of adhesive bonds between flexible adherends by means of a T-type specimen using a tension testing machine. The bent, unbonded ends of the test specimen are clamped in the test grips of the tension testing machine and a load of a constant head speed is applied to give force as a function of elongation. The peel force, defined as the average force between 20% and 80% of the elongation at break, is determined.

Two tests are commonly used to assess the seal integrity of aseptic laminated paperboard cartons. The electrolytic test is based on the principle that a tight plastic container is an electrical insulator. By introducing an electric potential across a brine-filled package that is partially immersed in a brine solution as shown in Figure 10.10, the existence of holes in the package can be determined. Any defect in the package that allows current to flow out of the package results in a positive test. However, the electrolytic test is not a conclusive test since it is possible for tight packages to give positive results. Therefore, all positive tests should be followed with a dye test.

In the dye test, after rinsing the filled and sealed carton with water and drying, a solution of 0.5% Rhodamine B in isopropanol is applied to the critical areas of the package including the longitudinal and transverse seals. The carton is then allowed to develop for 5 min and dried in a warm cabinet overnight. The flaps of the package are unfolded and the dye-coated paper removed and examined for ink penetration. Any signs of the pink dye indicate the presence of holes in the polyethylene layers.

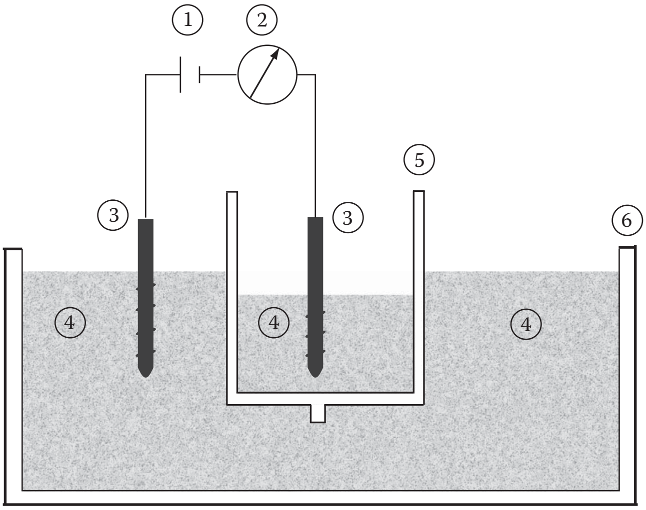

FIGURE 10.10 Electrolytic test for presence of pinholes in an aseptic carton package: (1) 9 V battery, (2) ampere meter, (3) electrode, (4) saline solution, (5) aseptic package and (6) bath.

High voltage leak detection (HVLD) is an emerging technology for fully automated detection of package leaks and tampering (Song, 2009). It is capable of detecting pinholes less than 10 µm in diameter. Although nondestructive, it may further damage defective packages by enlarging pinholes 5–10 fold due to the high voltages involved.

Many other less formalized methods of testing heat seals are widely used in the food industry. For example, polarized light can be used with transparent materials, with the birefringence patterns providing a visual guide to the consistency of the seal and highlighting any gaps or stresses.

10.3 PEELABLE SEALS

The technology of easy-open, peelable seal packaging has been used in the food industry since the concept was developed in the late 1960s. Peelable seal technology provides retention of package integrity yet allows consumers to access the contents without tearing or otherwise destroying the package. Seals can be made peelable either by using peelable films or HSCs, or by controlling the sealing temperature (Aithani et al., 2006a). Seal strength as a function of interfacial temperature is shown in Figure 10.11.

There are three basic peel mechanisms for achieving peelable heat seals (Dodrill, 2005).

10.3.1 Adhesive Peel

An adhesive peel separates between the interface of the two webs being heat sealed together as shown in Figure 10.12. As a result, it provides a relatively poor seal indicator with no transfer to the opposite web, but is desirable for applications such as lidding for a food tray. The seal strength of materials with adhesive peels tends to be more sensitive to temperature, pressure, and/or dwell time fluctuations, because seal strength is greatly affected by surface mechanics.

10.3.2 Cohesive Peel

With a cohesive peel, the sealant splits when peeled with some of the sealant transferring to the opposing web while some remains with the original sealant web as shown in Figure 10.13. Sealants designed to provide cohesive peels are usually created by blending a contaminant (usually an

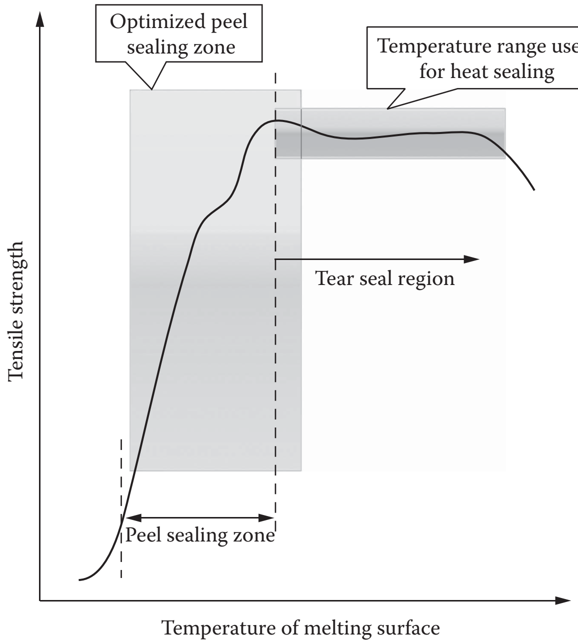

FIGURE 10.11 Tensile strength of heat seals as a function of interfacial temperature.

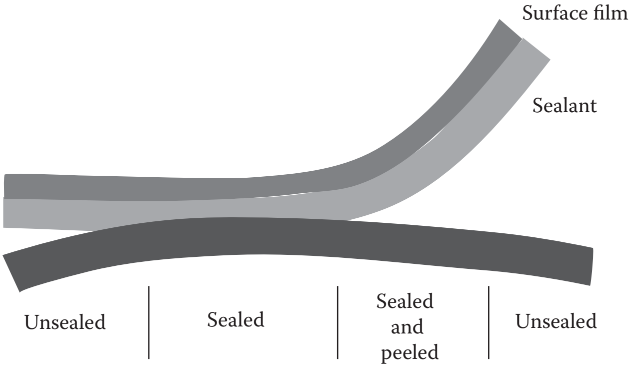

FIGURE 10.12 Adhesive peel. (From Dodrill, D., *Advances in Peelable Sealant Technology*, Rollprint Packaging Products, Inc., Addison, IL, 2005. With permission.)

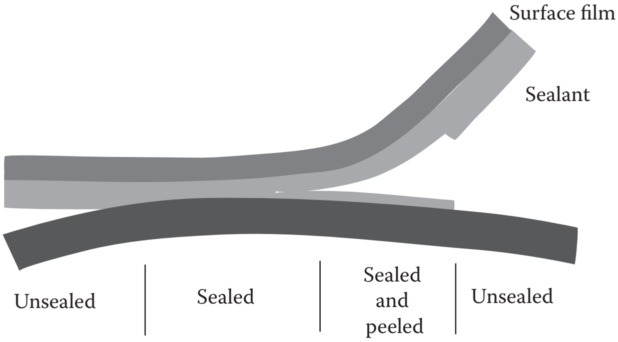

FIGURE 10.13 Cohesive peel. (From Dodrill, D., *Advances in Peelable Sealant Technology*, Rollprint Packaging Products, Inc., Addison, IL, 2005. With permission.)

incompatible resin that will not solubilize in the base resin, thus disrupting the resin matrix) into a base resin. The sealant splits when peeled because the strength of the seal interface (the bond between the two webs) is stronger than the internal bond of the sealant layer.

The seal strength of a cohesive peel is controlled by varying the amount of contaminant blended into the sealant, resulting in sealants with a very wide operating window. Because the sealant splits when peeled, cohesive peel sealants are more prone to stringing (sometimes called angel hair) than adhesive peel sealants.

The key to creating a sealant with a cohesive peel is selecting two (or more) resins that are incompatible. Sealants based on polybutene-1 have long been the standard for providing peelable seals to polyolefins where the incompatibility between polybutene-1 and polyethylene causes weak bonding. The failure mechanism is cohesive and propagates through the sealed layer, resulting in uniform separation of the substrate layers. Seal strength is dependent on the thickness of the polybutene-1 blend layer; as the thickness of the sealant layer increases, so does the seal strength. Recently, EAA ionomer resins have been used in blends with LDPE resins, plastomers or PP resins to create tailor-made cohesive seals that resist aging. A thin layer of EAA ionomer resins, coextruded with HDPE resins, can provide the desired burst peel.

10.3.3 DELAMINATION PEEL

The delamination or interlaminar peel is designed to fail at the interface between the sealant layer and the material to which it is being sealed as shown in Figure 10.14. The strength of the bond between the sealant layer and the surface film is greater than that at the interface, which is why it peels by delamination. In order for a delamination peel to open, the user must break through or tear the sealant layer from the substrate to initiate the peel. As a result, stringing and webbing are a much greater concern for this peel mechanism.

10.3.4 HEAT SEAL COATINGS

HSCs have a very long history and were the original way to achieve peelable seals. They are based on the cohesive failure of the adhesive, which is less than the bond strength between adhesive and sealed material. Today, there is a tremendous variety of HSC options available to provide peelable seals to most substrates. HSCs based on resins and additives are traditionally applied to a web as solutions and are often more expensive than other types of peelable sealants (Dodrill, 2005).

Solution-applied HSCs have long been the standard for providing peelable sealants to PP for retort applications. The sealant must withstand typical retort temperatures of 120°C and above and

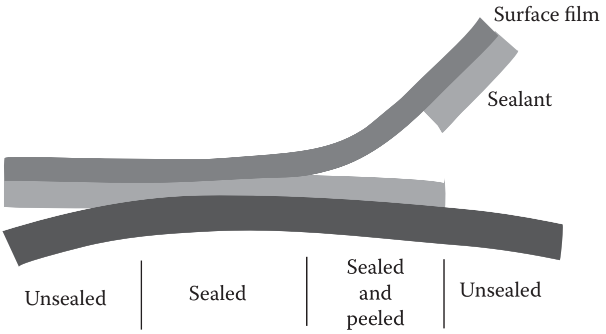

FIGURE 10.14 Delamination peel. (From Dodrill, D., *Advances in Peelable Sealant Technology*, Rollprint Packaging Products, Inc., Addison, IL, 2005. With permission.)

must seal and peel to PP. In addition, the peelable seal must not creep when exposed to the forces created by any pressure differential between the inside and outside of the package. The PP extrusion coated sealants consist of a three-layer coextrusion of a modified PP designed to promote adhesion, a bulk layer of PP and a thin peelable PP sealant layer. These sealants can be coated by coextrusion onto PET, aluminum foil and other heat-stable webs.

10.3.5 Seal Interface Temperature

A relatively new technique referred to as MTMS (method for measuring temperature of melting surface) has been used to predict the strongest peelable seal on various commercial packaging films (Aithani et al., 2006b). The MTMS system consists of three components: a temperature control unit to control the temperature of both sealing jaws, a manually-operated heat sealing unit and a time–temperature recorder unit (Hishinuma, 2009). The temperature of the seal interface is measured using a thermocouple to generate a time–temperature profile from which the inflection point (also called the fusion point) is identified. This inflection point is associated with a physical change in the state of the material being sealed. The highest peelable seal strength was achieved at a temperature close to the fusion point but below the melting point. Seals made above the fusion temperature resulted in weld seals. The key temperatures for producing peelable seals for some common polymer films are presented in Table 10.1.

10.3.6 Nanocomposite Heat Sealants

Nanocomposite heat sealants based on LLDPE/LDPE blends reinforced by a combination of EVA copolymer and organically modified MMT were reported by Manias et al. (2009). These materials yielded hermetic but peelable heat seals characterized by almost constant seal strength, which was largely independent of sealing temperature. This novel performance was ascribed to a synergy between the EVA copolymer and the MMT nanofillers, which have an interfacial adhesion that is strong enough to promote mixing and maintain the sealant integrity, but is weak enough to dictate paths of easy crack propagation on seal peeling. This synergy resulted in a general cohesive failure of the nanocomposite sealant and consequently in the formation of a broad range of peelable seals.

TABLE 10.1
Key Temperatures for Producing Peelable Seals for Some Common Polymer Films

Film Composition	Thickness (µm)	Melting Temperature by DSC (°C)	Interface Temperature (°C)	Inflection Point/Fusion Temperature (°C)
Copolymer of 90% PE/10% LLDPE	35.6	123.6	140.0	112.6–113.0
Coextruded HDPE/EVA	50.8	131.7	140.0	126.7–128.0
Cast PP with heat-sealable coating	71.1	164.8	175.0	142.9–143.1
Black pigmented LDPE	50.8	111.0	119.0	104.4–104.5
Coextruded LLDPE/EVA	58.4	102.7	120.0	95.7–96.7

Source: Adapted from Aithani, D. et al., *Packag. Technol. Sci.*, 19, 245, 2006b.

10.4 COLD SEALS

For the packing of heat-sensitive foods such as chocolate, chocolate-coated biscuits, certain confectionary and ice cream, significant product damage can result from heat sealing. Therefore, cold seal technology that requires only mechanical pressure to bond two layers together is used as an alternative to heat sealing. Although there is some use of cold seals in vertical FFS packaging, the main application is in horizontal FFS or flow wrap bar lines and overwraps. Compared to heat sealing, cold seals are much less sensitive to sealing dwell time and more tolerant to variations in packaging line speed (Durston, 2006). Cold seal adhesives differ from pressure-sensitive adhesives discussed in Section 9.4.2.4 in that the latter are permanently tacky and must be covered with release paper to prevent adhering to anything until the final use. The uniqueness of cold seal adhesives is that they seal only to themselves.

Cold seal adhesives consist of a water-based emulsion of which the key component is natural rubber latex, which offers a unique combination of adhesion and cohesive strength in the required range but without tackiness; other ingredients include water, ammonia, surfactants, antioxidants, antifoam agents, biocides and an acrylic component to aid adhesion to the coated surface (Durston, 2006). In recent years a synthetic version of cold seal adhesives based on EVA copolymers has been developed. The emulsion is printed onto the desired seal areas of the inner surface of a web substrate using an engraved gravure cylinder at a coating rate of 2–6 gsm depending on the application. A release lacquer consisting of polyamide resin is applied to the outer printed surface to permit easy unwinding of the reel. Alternatively, a release film such as low surface tension plain OPP can be laminated over the print.

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11 Deteriorative Reactions in Foods

11.1 INTRODUCTION

The principal aim of this chapter is to provide a brief overview of the major biochemical, chemical, physical and biological changes that occur in foods during processing and storage and show how these combine to affect food quality. Knowledge of such changes is essential before a sensible choice of packaging materials can be made, because the rate and/or magnitude of such changes can often be minimized by selection of the correct packaging materials.

The deterioration of packaged foods—which includes virtually all foods because very few foods are currently sold without some form of packaging—depends largely on transfers that may occur between the internal environment inside the package and the external environment which is exposed to the hazards of storage and distribution. For example, there may be transfer of moisture vapor from a humid atmosphere into a dried food or transfer of an undesirable odor from the external atmosphere into a high fat food. In addition to the ability of packaging materials to protect and preserve foods by minimizing or preventing such transfers, packaging materials must also protect the product from mechanical damage and prevent or minimize misuse by consumers (including tampering).

Although certain types of deterioration will occur even if there is no transfer of mass (or heat, since some packaging materials can act as efficient insulators against fluctuations in ambient temperatures) between the package and its environment, it is often possible to prolong the shelf life of food through the use of packaging.

It is important that food packaging not be considered in isolation from food processing and preservation, or indeed from food marketing and distribution. All of these factors interact in a complex way, and concentrating on only one aspect at the expense of the others is a surefire recipe for commercial failure.

The development of an analytical approach to food packaging is strongly recommended; and to achieve this successfully, a good understanding of food safety and quality is required. Without question, the more important of these is food safety, which is the freedom from harmful chemical and microbial contaminants at the time of consumption. Packaging is directly related to food safety in two ways.

First, if the packaging material does not provide a suitable barrier around the food, microorganisms can contaminate the food and make it unsafe. However, microbial contamination can also arise if the packaging material permits the transfer of, for example, moisture or O_2 from the atmosphere into the package. In this situation, microorganisms that are present in the food, but present no risk because of the initial absence of moisture or O_2, may subsequently be able to grow and present a risk to the consumer. Second, the migration of potentially toxic compounds from some packaging materials to the food is a possibility in certain situations, which gives rise to food safety concerns. In addition, migration of other components from packaging materials, while not harmful to human health, may adversely affect the quality of the product.

The major quality attributes of foods are texture, flavor, color, appearance and nutritive value, and these attributes can all undergo undesirable changes during processing and storage; a summary of such changes is given in Table 11.1. With the exception of nutritive value, the changes that can occur in these attributes are readily apparent to the consumer, either prior to or during consumption. Packaging can affect the rate and magnitude of many of the quality changes shown in Table 11.1. For example, development of oxidative rancidity can often be minimized if the package is an effective

TABLE 11.1
Classification of Undesirable Changes That Can Occur in Foods

Attribute	Undesirable Change
Texture	a. Loss of solubility
	b. Loss of water-holding capacity
	c. Toughening
	d. Softening
Flavor	Development of
	e. Rancidity (hydrolytic or oxidative)
	f. Cooked or caramel flavors
	g. Other off-flavors
Color	h. Darkening
	i. Bleaching
	j. Development of other off-colors
Appearance	k. Increase in particle size
	l. Decrease in particle size
	m. Nonuniformity of particle size
Nutritive value	Loss, degradation or altered bioavailability of
	n. Vitamins
	o. Minerals
	p. Proteins
	q. Lipids
Safety	Generation of toxic substances

Source: Adapted from Fennema, O.R. et al., Introduction to food chemistry, in: *Fennema's Food Chemistry*, 4th edn., Damodaran, S., Parkin, K.L., and Fennema, O.R. (Eds), CRC Press, Boca Raton, FL, pp. 1–14, 2007.

O_2 barrier; flavor compounds can be absorbed by some types of packaging material and the particle size of many food powders can increase (i.e., clump) if the package is a poor moisture barrier. This chapter outlines the major biochemical, chemical, physical and biological changes that occur in foods during processing and storage and shows how these combine to affect food quality. This chapter addresses the issue of shelf life, which is very clearly related to food quality.

11.2 DETERIORATIVE REACTIONS IN FOODS

Knowledge of the kinds of deteriorative reactions that influence food quality is the first step in developing food packaging that will minimize undesirable changes in quality and maximize the development and maintenance of desirable properties. Once the nature of these reactions is understood, knowledge of the factors that control their rates is necessary, in order to fully control the changes occurring in foods during storage (i.e., while packaged). The nature of the deteriorative reactions in foods is reviewed in this section, and the factors which control the rates of these reactions are discussed in the following section.

11.2.1 ENZYMIC REACTIONS

Enzymes are complex globular proteins that can act as catalysts, accelerating the rate of chemical reactions by factors of 10^{12}–10^{20} over that of uncatalyzed reactions. An understanding of the biological mechanisms for controlling enzymic activities, and the biochemical mechanisms of enzyme action, can provide the food technologist with the means of effectively exploiting enzymes in food processing. From a food packaging point of view, knowledge of enzyme action is fundamental to a fuller understanding of the implications of one form of packaging over another. The importance of enzymes to the food processor is often determined by the conditions prevailing within and outside the food. Control of these conditions is necessary to control enzymic activity during food processing and storage. The major factors useful in controlling enzyme activity are temperature, a_w (water activity), pH, chemicals that can inhibit enzyme action, alteration of substrates, alteration of products and preprocessing control.

Three of these factors are particularly relevant in a packaging context. The first is temperature, where the ability of a package to maintain a low product temperature and thus retard enzyme action will often increase product shelf life. The second important factor is a_w because the rate of enzyme activity is dependent on the amount of water available; low levels of water can severely restrict enzymic activities and even alter their pattern of activity. Finally, alteration of substrate (in particular, the ingress of O_2 into a package) is important in many oxygen-dependent reactions that are catalyzed by enzymes.

11.2.2 CHEMICAL REACTIONS

Many of the chemical reactions occurring in foods can lead to deterioration in food quality (both nutritional and sensory) or the impairment of food safety. The more important classes of these reactions are listed in Table 11.2 and are discussed fully in standard textbooks on food chemistry. In the present context, it is noteworthy that such reaction classes can involve different reactants or substrates depending on the food and the particular conditions for processing or storage. The rates of these chemical reactions are dependent on a variety of factors amenable to control by packaging including light, O_2 concentration, temperature and a_w. Therefore, in certain circumstances, the package can play a major role in controlling these factors and thus indirectly the rate of the deteriorative chemical reactions.

11.2.2.1 Sensory Quality

The two major chemical changes that occur during the processing and storage of foods, leading to deterioration in sensory quality, are lipid oxidation and nonenzymic browning (NEB). Chemical reactions are also responsible for changes in the color and flavor of foods during processing and storage.

TABLE 11.2
Some Chemical, Biochemical and Physical Reactions That Can Lead to Food Quality Deterioration

Example	Type	Consequences
Nonenzymic browning	Chemical reaction (Maillard reaction)	Color, taste and aroma, nutritive value, formation of toxicologically suspect compounds (acrylamide)
Fat oxidation	Chemical reaction	Loss of essential fatty acids, rancid flavor, formation of toxicologically suspect compounds
Fat oxidation	Biochemical reaction (lipoxygenase)	Off-flavors, mainly due to formation of aldehydes and ketones
Hydrolysis	Chemical reaction	Changes in flavor, vitamin content
Lipolysis	Biochemical reaction (lipase)	Formation of free fatty acids and peptides, bitter taste
Proteolysis	Biochemical reaction (proteases)	Formation of amino acids and peptides, bitter taste, flavor compounds, changes in texture
Enzymic browning	Biochemical reaction of polyphenols	Browning
Separation	Physical reaction	Sedimentation, creaming
Gelation	Combination of chemical and physical reaction	Gel formation, texture changes

Source: Adapted from van Boekel, M.A.J.S., *Compr. Rev. Food Sci. Food Safety*, 7, 144, 2008.

11.2.2.1.1 Lipid Oxidation

Autoxidation is the reaction, by a free radical mechanism, of molecular O_2 with hydrocarbons and other compounds. The reaction of free radicals with O_2 is extremely rapid, and many mechanisms for initiation of free radical reactions have been described. Autoxidation is a major cause of food deterioration; the crucial role that this reaction plays in the development of undesirable flavors and aromas in foods is well documented.

As well as being responsible for the development of off-flavors in foods, the products of lipid oxidation may also react with other food constituents such as proteins, resulting in extensive cross-linking of the protein chains through either protein–protein or protein–lipid cross-links.

Factors that influence the rate and course of oxidation of lipids are well known and include light, local O_2 concentration, high temperature, the presence of catalysts (generally transition metals such as iron and copper, but also heme pigments in muscle foods) and a_w. Control of these factors can significantly reduce the extent of lipid oxidation in foods.

11.2.2.1.2 Nonenzymic Browning

NEB is one of the major deteriorative chemical reactions which occur during storage of dried and concentrated foods. The NEB or Maillard reaction can be divided into three stages: (1) early Maillard reactions, which are chemically well-defined steps without browning; (2) advanced Maillard reactions, which lead to the formation of volatile or soluble substances and (3) final Maillard reactions, leading to insoluble brown polymers.

The initial reaction involves a simple condensation between an aldehyde (usually a reducing sugar) and an amine (usually a protein or amino acid) to give a glycosylamine. The glycosylamine then undergoes an Amadori rearrangement to form an Amadori derivative. The formation of Amadori compounds accounts for the observed loss of both reducing sugar and amine during the Maillard reaction. Although the early Maillard reactions forming Amadori compounds do not cause browning, they do reduce nutritive value.

The final step of the advanced Maillard reaction is the formation of many heterocyclic compounds such as pyrazines and pyrroles, as well as brown melanoidin pigments. These pigments are formed by polymerization of the reactive compounds produced during the advanced Maillard reactions. The polymers are relatively inert and have a molecular weight greater than 1000.

11.2.2.1.3 Color Changes

Acceptability of color in a given food is influenced by many diverse factors, including cultural, geographical and sociological aspects of the population. However, regardless of these many factors, certain food groups are only acceptable if they fall within a certain color range. The color of many foods is due to the presence of natural pigments. The major changes that these can undergo are briefly described; a more detailed discussion can be found elsewhere (Schwartz et al., 2007).

11.2.2.1.3.1 Chlorophylls The name *chlorophyll* describes those green pigments involved in the photosynthesis of higher plants. The major change which chlorophylls can undergo is *pheophytinization*—the replacement of the central magnesium atom by hydrogen and the subsequent formation of dull, olive-brown pheophytin. Because this reaction is accelerated by heat and is acid catalyzed, it is unlikely to be influenced by the choice of packaging.

Almost any type of food processing or storage causes some deterioration of the chlorophyll pigments. Although pheophytinization is the major change, other reactions are possible. For example, dehydrated products such as green peas and beans packed in clear glass containers undergo photo-oxidation and loss of desirable color.

11.2.2.1.3.2 Heme Pigments Meat is an important part of many diets, and the color of red meat is due to the presence of the heme pigment *myoglobin*. Myoglobin is a complex muscle protein contained within the cells of the tissues where it acts as a temporary storehouse for the O_2 brought by the hemoglobin in the blood. The protein moiety is known as *globin* and the nonpeptide portion is called *heme*.

The color cycle in fresh meats is reversible and dynamic, with the three pigments—oxymyoglobin, myoglobin and metmyoglobin—constantly interconverted. In cured meat products, nitrite reacts with these pigments to form additional heme-based compounds. These reactions are discussed in more detail in Chapter 17. At this stage, it is sufficient to note that packaging has an extremely important influence on meat pigments. For example, at low partial pressures of O_2 (i.e., an almost impermeable package), the formation of brown metmyoglobin is favored. If the package is completely impermeable to O_2, the heme pigments are fully reduced to the purple myoglobin.

11.2.2.1.3.3 Anthocyanins Anthocyanins are a group of more than 150 reddish water-soluble pigments that are very widespread in the plant kingdom. An anthocyanin pigment is composed of an aglycone (an anthocyanidin) esterified to one or more of five sugars (in order of relative abundance glucose, rhamnose, galactose, xylose and arabinose). The rate of anthocyanin destruction is pH dependent, being greater at higher pH values.

Of interest from a packaging point of view is the ability of some anthocyanins to form complexes with metals such as Al, Fe, Cu and Sn. These complexes generally result in a change in the color of the pigment (e.g., red sour cherries react with tin to form a purple complex) and are, therefore, undesirable. Because metal packaging materials such as cans could be sources of these metals, they are usually coated with special organic linings (enamels) to avoid these undesirable reactions (see Chapter 7).

11.2.2.1.3.4 Carotenoids The *carotenoids* are a group of mainly lipid-soluble compounds responsible for many of the yellow and red colors of plant and animal products. Carotenoids include a class of hydrocarbons called *carotenes* and their oxygenated derivatives called *xanthophylls*. Carotenoids can exist in the free state in plant tissue or in solution in lipid media such as animal fatty tissue.

The main cause of carotenoid degradation in foods is oxidation. The mechanism of oxidation in processed foods is complex and depends on many factors. The pigments may autoxidize by reaction with atmospheric O_2 at rates dependent on light, heat and the presence of pro- and anti-oxidants.

11.2.2.1.3.5 Miscellaneous Natural Pigments There are a number of other groups of compounds which are responsible for some of the colors in foods. These include *flavonoids* (yellow compounds with chemical structures similar to the anthocyanins), *proanthocyanidins* (these are colorless but contribute to enzymic browning reactions in fruits and vegetables) and *tannins* (which contribute to enzymic browning reactions, but their mechanisms of action are not well understood).

11.2.2.1.4 Flavor Changes

The term *flavor* has evolved to a usage that implies an overall integrated perception of the contributing senses of smell and taste at the time of food consumption. Specialized cells of the olfactory epithelium in the nasal cavity are able to detect trace amounts of volatile odorants. Taste buds located on the tongue and back of the oral cavity enable humans to sense sweetness, sourness, saltiness, bitterness and umami, and these sensations contribute to the taste component of flavor.

In fruits and vegetables, enzymically generated compounds derived from long-chain fatty acids play an extremely important role in the formation of characteristic flavors. In addition, these types of reactions can lead to important off-flavors. Enzyme-induced oxidative breakdown of unsaturated fatty acids occurs extensively in plant tissues, and this yields characteristic aromas associated with some ripening fruits and disrupted tissues (Lindsay, 2007).

Fats and oils are notorious for their role in the development of off-flavors through autoxidation. Aldehydes and ketones are the main volatiles from autoxidation, and these compounds can cause painty, fatty, metallic, papery and candle-like flavors in foods when their concentrations are sufficiently high. However, many of the desirable flavors of cooked and processed foods derive from modest concentrations of these compounds (Lindsay, 2007). The permeability of packaging materials is important in retaining desirable volatile components within packages and for preventing undesirable components permeating through the package from the ambient atmosphere.

Many flavor compounds found in cooked or processed foods occur as the result of reactions common to all types of foods regardless of whether they are of animal, plant or microbial origin. These reactions take place when suitable reactants are present and appropriate conditions such as heat, pH and light exist. Packaging can play an important role in these reactions.

11.2.2.2 Nutritional Quality

As well as the chemical changes described earlier, which may have a deleterious effect on the sensory properties of foods, there are other chemical changes which can affect the nutritive value of foods. As these reactions are discussed fully in standard textbooks, only a brief review of some of these reactions is presented here to illustrate the potential role of packaging in minimizing nutrient degradation in foods.

The four major factors that impact on nutrient degradation and can be controlled to varying extents by packaging are light, O_2 concentration, temperature and a_w. However, because of the diverse nature of the various nutrients, as well as the chemical heterogeneity within each class of compounds and the complex interactions of the aforementioned variables, generalizations about nutrient degradation in foods are necessarily broad.

11.2.2.2.1 Vitamins

The chemical conversion of vitamins to biologically inactive products during storage of foods has been the subject of extensive research. A generalized summary of vitamin stability is presented in Table 11.3, although it is important to note that exceptions exist and invalid conclusions could be reached on the basis of these generalizations.

Ascorbic acid is the most sensitive vitamin in foods; its stability varies markedly as a function of environmental conditions such as pH and the concentration of trace metal ions and O_2. The nature of the packaging material can significantly affect the stability of ascorbic acid in foods. The effectiveness of the material as a barrier to moisture and O_2, as well as the chemical nature of

TABLE 11.3
General Stability of Vitamins to Environmental Effects

Nutrient	Oxygen	Light	Temperature
Vitamin A	U	U	U
Vitamin B_6	S	U	U
Vitamin B_{12}	U	U	S
Biotin	S	S	U
Vitamin C	U	U	U
Carotenes	U	U	U
Choline	U	S	S
Vitamin D	U	U	U
Folic acid	U	U	U
Inositol	S	S	U
Vitamin K	S	U	S
Niacin	S	S	S
Pantothenic acid	S	S	U
Riboflavin B_2	S	U	U
Thiamin B_1	U	S	U
Tocopherols	U	U	U

U, unstable; S, stable.

the surface exposed to the food, are important factors. For example, problems of ascorbic acid instability in aseptically packaged fruit juices have been encountered because of O_2 permeability and the O_2 dependence of the ascorbic acid degradation reaction. In addition, because of the preferential oxidation of metallic tin, citrus juices packaged in cans with a tin contact surface exhibit greater stability of ascorbic acid than those in enameled cans or glass containers. The aerobic and anaerobic degradation reactions of ascorbic acid in reduced-moisture foods are highly sensitive to a_w, with the reaction rate increasing in an exponential fashion over the a_w range of 0.1–0.8.

11.2.2.2.2 Proteins

The nutritive value (and sometimes the wholesomeness) of proteins can be modified by heating and oxidation. Oxidation of proteins results in the formation of degradation products, which are known to detract from protein nutritive value. Proteins can also react with lipids to form complexes that can affect food texture and, to a minor extent, protein nutritive value. In addition, the Maillard reaction can result in loss of nutritional properties, primarily from losses in the amino acid lysine.

11.2.2.2.3 Lipids

Lipids, especially when unsaturated, undergo many kinds of chemical changes during processing, and some of these changes can affect their nutritional value and wholesomeness. Peroxidizing lipids exert negative effects on the nutritive value of foods by their chemical interaction with proteins and vitamins. Oxygen often plays an important role in lipid degradation, and packaging can play an important role in limiting or preventing O_2 ingress.

11.2.3 PHYSICAL CHANGES

The physical properties of foods can be defined as those properties that lend themselves to description and quantification by physical rather than chemical means. Their importance stretches from product handling, through processing, packaging and storage, to consumer acceptance. Physical properties include geometrical, thermal, optical, mechanical, rheological, electrical and hydrodynamic properties (Sahin and Gulum, 2006). Geometrical properties encompass the parameters of size, shape, volume, density and surface area as related to homogeneous food units, as well as geometrical texture characteristics. The latter can be sub-divided into two classes: those referring to particle size and shape (e.g., gritty and grainy) and those referring to particle shape and orientation (e.g., fibrous and cellular).

Although many of these physical properties are important and must be considered in the design and operation of a successful packaging system, the focus here is on undesirable physical changes in packaged foods. The way in which some of these changes can be affected by the nature of the packaging is now outlined.

Food powders are a diverse group and represent a large proportion of the total processed food in the world; they can be categorized in a number of ways (Onwulata, 2005). On the basis of major chemical components, powders may be classified as starchy (e.g., wheat flour), proteinaceous (e.g., soy isolate), crystalline (e.g., sugars, salts and organic acids), amorphous (e.g., dehydrated fruit juices) and fatty (e.g., soup mix). Powders may also be classified according to their particle size, although many food powders exhibit a range of several orders of magnitude in this parameter. They may also be classified according to their moisture sorption pattern, ranging from extremely hygroscopic (in the case of dehydrated fruit juices) through hygroscopic (in the case of spray dried coffee) to moderately hygroscopic (in the case of flours). Finally, powders can be classified as free flowing (e.g., granular sugar), moderately cohesive (e.g., flour) and very cohesive (most food powders after absorbing moisture).

A major undesirable change in food powders is the sorption of moisture as a consequence of an inadequate barrier provided by the package, resulting in caking. This can occur either as a result of a poor selection of packaging material in the first place or failure of the package integrity during storage.

Caking is the uncontrolled agglomeration of food powders (especially those containing soluble components or fats) and occurs when they are exposed to moist atmospheres or elevated storage temperatures. The phenomenon can result in anything from small soft aggregates that break easily to rock hard lumps of variable size or solidification of the whole powder. In most cases, the process is initiated by the formation of liquid bridges between the particles that can later solidify by drying or cooling. The size of such bridges determines the flow properties of the powder. The increase of the sinter bridges during caking has been modeled, and the calculated sinter bridge diameter correlated with the strength of the caked powder bulk (Hartmann and Palzer, 2011).

The agglomeration of amorphous particulate material is a major problem in the food industry. Currently, the glass transition temperature (T_g), which depends on water content, is used as a fundamental parameter to describe and control agglomeration. Although models are available that describe the kinetics of the agglomeration process as a function of the distance of the material from T_g (i.e., $T - T_g$), they are often not applied because they assume that the powder is instantly in equilibrium with the ambient humidity and that solid mobility only occurs at $T > T_g$. Renzetti et al. (2012) showed that the water migration mechanism is controlled by relaxation phenomena when the amorphous material is still far from the glass–rubber transition. The $T - T_g$ at which the relaxation phenomena occur depends on the material and could describe the onset of agglomeration, independently from the material properties. They concluded that matrix relaxation occurring far below T_g did not affect the onset of agglomeration.

Flow conditioners or anticaking agents are very fine powders of an inert chemical substance that are added to powders with much larger particle size at concentrations up to 2% in order to inhibit caking and improve flowability. Most conditioners are insoluble in water, but many of them can absorb a considerable amount of water owing to their very large surface areas. The main food-grade commercial conditioners generally consist of silicon dioxide, silicates, phosphates, salts of stearic acids, talcum starches and modified carbohydrates such as maltodextrins (Intipunya and Bhandari, 2010).

Studies on sucrose and onion powders showed that at ambient temperature, caking does not occur at a_ws of less than about 0.4. However, at higher activities ($a_w > 0.45$), the observed time to caking is inversely proportional to a_w, and at these levels, anticaking agents are completely ineffective. It appears that although they reduce interparticle attraction and interfere with the continuity of liquid bridges, they are unable to cover moisture sorption sites.

For foods containing solid carbohydrates, the largest change in physical properties results from sorption of water, especially for the recrystallization of amorphous carbohydrates. Such changes can occur in boiled sweets (leading to stickiness or graining) and milk powders (leading to caking and lumpiness). In addition, lactose crystallization in milk powders can lead to protein insolubility, increased free fat through rupture of fat globules and accelerated flavor deterioration.

11.2.4 BIOLOGICAL CHANGES

11.2.4.1 Microbiological

Microorganisms can make both desirable and undesirable changes to the quality of foods, depending on whether or not they are introduced as an essential part of the food preservation process (e.g., as inocula in food fermentations) or arise adventitiously and subsequently grow to produce food spoilage. In the latter case, they only reach readily observable proportions when they are present in the food in large numbers. Because the initial population or microbial load is usually small, observable levels are only reached after extensive multiplication of the microorganism(s) in the food.

The two major groups of microorganisms found in foods are bacteria and fungi, the latter consisting of yeasts and molds. Bacteria are generally the fastest growing, so that in conditions favorable to both, bacteria will usually outgrow fungi. The phases through which the two groups pass are broadly similar: a period of adjustment or adaptation (known as the *lag* phase) is followed by accelerating growth until a steady, rapid rate (known as the *logarithmic* phase since growth is exponential) is achieved. After a time, the growth rate slows until growth and death are balanced and the population remains constant (known as the *stationary* phase). Eventually, death exceeds growth and the organisms enter the phase of decline.

Foods are frequently classified on the basis of their stability as nonperishable, semiperishable and perishable. An example of the first classification is sugar; provided it is kept dry, at ambient temperature and free from contamination, it should have a very long shelf life. However, few foods are truly nonperishable, and an important factor in determining their perishability is packaging.

For example, hermetically sealed and heat processed (e.g., canned) foods are generally regarded as nonperishable. However, they may become perishable under certain circumstances when an opportunity for recontamination is afforded following processing. Such an opportunity may arise if the can seams are faulty, or if there is excessive corrosion resulting in internal gas formation and eventual bursting of the can. Spoilage may also take place when the canned food is stored at unusually high temperatures where thermophilic spore-forming bacteria may multiply, causing undesirable changes such as flat sour spoilage.

Low moisture content foods such as flour, dried fruits and vegetables and baked goods are classified as semiperishable. Frozen foods, though basically perishable, may be classified as semiperishable provided that they are properly stored at freezer temperatures.

The majority of foods (e.g., flesh foods such as meat and fish; milk, eggs and most fruits and vegetables) are classified as perishable unless they have been processed in some way. Often, the only form of processing, which such foods receive, is to be packaged and kept under controlled temperature conditions.

The species of microorganisms which cause the spoilage of particular foods are influenced by two factors: the nature of the foods and their surroundings. These factors are referred to as intrinsic (compositional) and extrinsic (environmental) parameters and are listed in Table 11.4 and discussed further in Sections 11.4 and 11.5. The intrinsic parameters are an inherent part of the food with most microorganisms growing best at pH values around 7.0, while few grow below pH 4.0. Bacteria tend to be more fastidious in their relationships to pH than molds and yeasts, with the pathogenic bacteria being the most fastidious. The minimum a_w values reported for growth of some microorganisms in foods are presented in Table 11.5. It is noteworthy that yeasts and molds grow over a wider a_w range than bacteria.

In order to grow and function normally, microorganisms require several nutrients including water, a source of energy, a source of nitrogen, vitamins and related growth factors and minerals. The availability of water is related directly to the a_w of the food. The primary source of nitrogen utilized by microorganisms is amino acids. Growth factor and vitamin requirements tend to be specific to individual groups of microorganisms. Some foods contain certain naturally occurring substances that have been shown to have antimicrobial activities, thus preventing or retarding the growth of specific microorganisms in those foods.

TABLE 11.4
Intrinsic and Extrinsic Parameters Influencing Microbial Growth in Foods

Intrinsic Factors	Extrinsic Factors
pH	Storage temperature
a_w	Relative humidity of environment
E_h	Presence and concentration of gases in the environment
Nutrient content	
Antimicrobial constituents	
Biological structures	

TABLE 11.5
Approximate Minimum a_w Values for the Growth of Microorganisms of Importance in Foods

Organism	Minimum a_w
Most spoilage bacteria	0.90
Most spoilage yeasts	0.88
Most spoilage molds	0.80
Halophilic bacteria	0.75
Xerophilic molds	0.61
Osmophilic yeasts	0.61

The extrinsic parameters of foods are those properties of the storage environment that affect both the foods and their microorganisms. The growth rate of the microorganisms responsible for spoilage primarily depends on such extrinsic parameters as storage temperature, RH and gas composition of the surrounding atmosphere. The temperature of storage is particularly important, and several food preservation techniques (e.g., chilling and freezing) rely on reducing the temperature of the food to extend its shelf life.

Although there is a very wide range of temperatures over which the growth of microorganisms has been reported (–34°C to 90°C), specific microorganisms have relatively narrow temperature ranges over which growth is possible. Those that have an optimal temperature for growth at about 15°C or lower, a maximal temperature for growth at about 20°C and a minimal temperature for growth at 0°C or lower are referred to as *psychrophiles* or *psychrotrophs*. Those that grow well between 20°C and 45°C with optima between 30°C and 40°C are referred to as *mesophiles*, and those that grow well at and above 45°C with optima between 55°C and 65°C are referred to as *thermophiles*. Molds are able to grow over a wider range of temperature than bacteria, with many molds being capable of growth at refrigerator temperature. Yeasts grow over the psychrophilic and mesophilic temperature ranges but generally not within the thermophilic range. The approximate lowest limits of a_w, pH and temperature for growth of some microorganisms of importance in foods are shown in Table 11.6.

The RH of the ambient environment is important and can influence the a_w of the food unless the package provides a barrier. Many flexible plastic packaging materials provide good moisture barriers, but none are completely impermeable, thus limiting the shelf life of low a_w foods.

The presence and concentration of gases in the environment has a considerable influence on the growth of microorganisms. Increased concentrations of gases such as CO_2 are used to retard microbial growth and thus extend the shelf life of foods (see, in particular, Chapters 16 and 17 for a full discussion of this topic). Moreover, vacuum packaging (i.e., removal of air, and thus O_2, from a package prior to sealing) can also have a beneficial effect by preventing the growth of aerobic microorganisms. This type of packaging (known as *modified atmosphere packaging* [MAP]) raises certain safety issues, which are discussed in Chapter 16. Most food pathogens do not grow at refrigeration temperatures, and CO_2 is not highly effective at nonrefrigeration temperatures. Therefore, most MAP food is usually held under refrigeration. Temperature abuse of the product (i.e., holding at nonrefrigerated temperatures) could allow the growth of organisms (including pathogens), which had been inhibited by CO_2 during storage at lower temperatures. For these reasons, it is difficult to evaluate MAP safety solely on the growth of certain pathogens at abusive temperatures.

Microbial growth in perishable foods can typically be represented as a function of time as shown in Figure 11.1 with the curve usually divided into lag, exponential and stationary phases. The four

TABLE 11.6
Approximate Lowest Limits[a] of a_w, pH and Temperature for Growth of Some Microorganisms

Organism	Lowest a_w Limit	Lowest pH Limit	Lowest Temperature Limit (°C)
Bacteria			
Bacillus cereus (mesophilic)	0.93	4.9	10
B. cereus (psychrotrophic)	0.93	4.9	5
Brochothrix thermosphacta	0.94	4.6	0
Campylobacter spp.	0.98	4.9	30
Clostridium botulinum (nonproteolytic)	0.97	5.0	3.3
Clostridium botulinum (proteolytic)	0.94	4.6	10
Clostridium perfringens	0.96	4.5	5
Escherichia coli	0.95	4.4	7
Lactobacillus spp.	0.93	3.0	4
Most lactic acid bacteria	0.95	3.5	5
Listeria monocytogenes	0.92	4.3	0
Pseudomonas spp.	0.97	5.0	−2
Salmonella spp.	0.95	4.0	5
Staphylococcus aureus	0.86	4.0	7
Molds			
Aspergillus flavus	0.78	2.0	3
Most molds	0.80	1.5	<0
Yeasts			
Most yeasts	0.87	1.5	−5
Saccharomyces cerevisiae	0.90	2.3	0

Source: Lee, D.S., Packaging and the microbial shelf life of food, in: *Food Packaging and Shelf Life*, Robertson, G.L. (Ed.), CRC Press, Boca Raton, FL, pp. 55–79, 2010.

[a] Values may vary with food type and microbial strain.

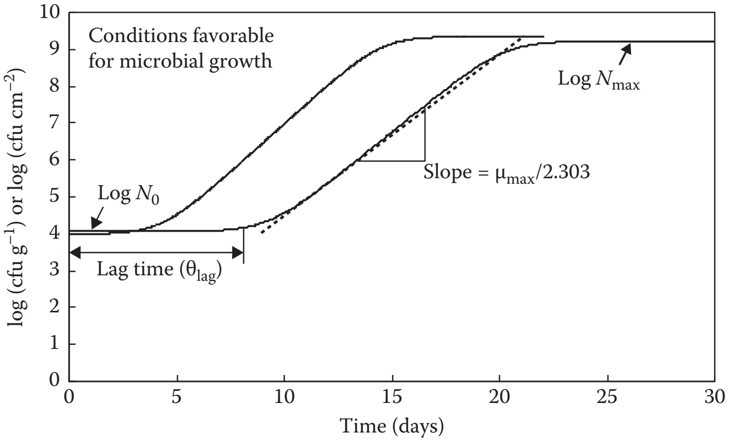

FIGURE 11.1 Typical pattern of bacterial growth on perishable food stored under constant environmental conditions. (Lee D.S., Packaging and the microbial shelf life of food, in: *Food Packaging and Shelf Life*. Robertson G.L. (Ed). CRC Press, Boca Raton, FL, pp. 55–79, 2010.)

key parameters log N_o, θ_{lag}, $\mu_{\max}$ and log $N_{\max}$ describe the progress of microbial growth with time under certain defined conditions. The parameter log N_o is determined by the initial contamination level of the food, which is dictated by raw materials and food manufacturing conditions, whereas log $N_{\max}$ represents the maximum cell density attainable under given conditions and is usually beyond the acceptable limit of quality (Lee, 2010). Lag time (θ_{lag}) and maximum specific growth rate ($\mu_{\max}$), depending on environmental conditions, directly affect the time to reach a certain critical level of microbial density corresponding to acceptable quality. Therefore, in dealing with the effect of packaging conditions on microbial shelf life, these two parameters are most often employed. The maximum specific growth rate, $\mu_{\max}$, can be assumed to represent the main part of the exponential growth. With this simplified treatment, the time (θ_s) to reach a critical limit cell density of N_c located on the exponential growth phase is the shelf life and can be calculated by

$$\theta_s = \theta_{\text{lag}} + \frac{1}{\mu_{\max}} \ln \frac{N_c}{N_o} \tag{11.1}$$

The protection of packaged food from contamination or attack by microorganisms depends on the mechanical integrity of the package (e.g., the absence of pinholes and seal imperfections) and on the resistance of the package to penetration by microorganisms. Metal and glass packaging cannot be penetrated by microorganisms, and extensive studies on a variety of plastic films and metal foils have shown that molds, yeasts and bacteria cannot penetrate these materials in the absence of pinholes. In practice, thin sheets of packaging materials such as aluminum and plastic do contain pinholes. However, because of surface tension effects, microorganisms cannot pass through very small pinholes, unless the microorganisms are suspended in solutions containing wetting agents and the pressure outside the package is greater than that within.

11.2.4.2 Macrobiological

11.2.4.2.1 Insect Pests

The common insect pests of fresh (unpackaged) food are flies (from the order Diptera), and cockroaches. They are attracted by food odors regardless of whether the food is fresh or beginning to decay. Any insect in food is a pest since not only does the food become contaminated with their bodies and excreta, but they are also capable of transmitting pathogens, including food poisoning organisms.

In contrast, the main insect species important as pests of stored (packaged) foods are entirely from the orders Lepidoptera (moths) and Coleoptera (beetles). They regularly damage and destroy large quantities of stored foods around the world every year. The number of species involved is not large and includes weevils, various other beetles and the larvae of several moths. Most stored product insects are cosmopolitan in that any given species is, for the most part, found worldwide in areas with similar climatic conditions. Warm humid environments promote insect growth, although most insects will not breed if the temperature exceeds about 35°C or falls below 10°C. Also, many insects cannot reproduce satisfactorily unless the moisture content of their food is greater than about 11%.

Moths and beetles are generally found in dry storage areas. They are able to survive on very small amounts of food, and thus can persist on food residues in improperly cleaned premises or equipment. Good ventilation, the use of cool storage areas and rotation of stock assists in keeping these pests at bay. Basic to effective control of insect pests is an understanding of their life cycles and feeding habits.

In common with many insects, moths pass through four stages during their development: the egg, the larva (caterpillar), the pupa (chrysalis) and the adult moth. Food is consumed only in the larval stage. The presence of larvae can be recognized by a characteristic mixture of silken threads and frass (droppings) that they produce. Beetles have the same four life stages as moths, but they differ in that the adult beetle is a considerably harder-bodied insect than the moth and may live and feed for months or even years. Cockroaches are larger, more robust insects, which are highly mobile. Their young are like small versions of the adult and, unlike beetles and moths, cockroaches do not inhabit packaged foods. Ants are a highly specialized group of insects, which form nests, normally outside buildings. Worker ants may travel considerable distances and collect almost any type of food (especially sweet or high-protein foods) and take it back to the nest.

Mites, which sometimes occur in stored foods, are not insects but are closely related to spiders, having eight legs. They are minute in size, requiring a lens to see them, and are primarily pests of cereals and other foods with a moisture content of at least 12%. Mites are so small that the presence of a few would pass unnoticed; they produce a sour odor in the food. Typically eggs and some other life stages are cold tolerant and development can proceed at lower temperatures than required by insect stored product pests, but low humidities prevent development (Bell, 2011).

The main categories of foods subject to pest attack are cereal grains and products derived from cereal grains, other seeds used as food (especially legumes), dairy products such as cheese and milk powders, dried fruits, dried and smoked meats and nuts. As well as their possible health significance, the presence of insects and insect excreta in packaged foods may render products unsalable, causing considerable economic loss, as well as reduction in nutritional quality, production of off-flavors and acceleration of decay processes due to the creation of higher temperatures and moisture levels.

Unlike microorganisms, some insect species (penetrators) have the ability to bore through one or more of the flexible packaging materials in use today and take up residence inside. Other species (invaders) usually do not enter packages unless there is an existing opening. However, such openings need not be very large; for example, the adult saw-toothed grain beetle can enter an opening less than 1 mm in diameter (Highland, 1991). Newly hatched larvae can enter much smaller openings; holes only 0.1 mm in diameter are sufficient to admit immature mites and the larvae of some insects. Thus, package seal quality is critical in protecting foods from insect infestations.

Unless plastic films are laminated with foil or paper, insects are able to penetrate most of them quite easily, where the rate of penetration is usually directly related to film thickness. In general, thicker films are more resistant than thinner films, and oriented films tend to be more effective than cast films. The looseness of the film has also been reported to be an important factor, with loose films being more easily penetrated than tightly fitted films.

Generally, the penetration varies depending on the basic resin from which the film is made, on the combination of materials, on the package structure, and on the species and stage of insects involved. The relative resistance to insect penetration of common flexible packaging materials is given in Table 11.7; where no thicknesses are given, the estimations are based on thicknesses commonly used in food packaging. Absolute values are difficult to determine because resistance to penetration is influenced by factors such as package configuration and the presence or absence of folds, tucks and other harborage sites. Therefore, after appropriate packaging materials have been selected, they must be evaluated in situ for insect resistance (Highland, 1991).

AACC (2001) has approved a method to determine the characteristics of insects chewing on food packaging materials to differentiate between exit and entrance holes. However, in mature infestations with multiple stages, insects often enlarge entry holes for exit and reentry. The method is applicable to various types of packaging materials. Typically, different types of commercially prepared packages are exposed to five species of insects (the red flour beetle, the saw-toothed grain beetle, the Indianmeal moth, the cigarette beetle and the warehouse beetle). These species represent a good cross section of both penetrators and invaders and are generally representative of the most common insect pests associated with packaged foods. At periodic intervals, packages are checked for infestation. Penetration holes (entry or exit) and obvious flaws in the seams and closures are noted. After the outside is examined, the commodity inside the package is examined,

TABLE 11.7
Resistance of Various Materials to Insect Penetration

	Excellent	Good	Fair	Poor
Polycarbonate	x			
Poly(ethylene terephthalate)	x			
Cellulose acetate		x		
Polyamide		x		
Polyethylene (0.254 mm)		x		
Polypropylene (biaxially oriented)		x		
Poly(vinyl chloride) (unplasticized)		x		
Acrylonitrile			x	
Poly(tetrafluoroethylene)			x	
Polyethylene (0.123 mm)			x	
Regenerated cellulose film				x
Corrugated paperboard				x
Ethylene vinyl acetate copolymer				x
Ionomer				x
Kraft paper				x
Paper/foil/polyethylene laminate pouch				x
Polyethylene (0.0254–0.100 mm)				x
Poly(vinyl chloride) (plasticized)				x
Poly(vinylidene chloride) copolymer				x

Source: Adapted from Highland, H.A., Protecting packages against insects, in: *Ecology and Management of Food-Industry Pests*, Gorham, J.R. (Ed.), Association of Official Analytical Chemists, Arlington, VA, pp. 345–350, 1991.

the insects of each species are identified and counted, and the numbers are recorded. After each test, a report is prepared and suggestions are made. The manufacturer can use this information to improve the performance of future package designs. Packaging studies have been conducted on a variety of commodities, including dry pet foods, breakfast cereals, baby foods, rice products, military rations and raisins (Mullen and Mowery, 2006).

A study by Wong et al. (2005) discussed the development of a bioassay for the evaluation of insect-repellent packaging, the use of paperboard coatings as carriers of insect repellents and the persistence with which citronella-treated cartons deter beetle infestation. Of five commercial plant extracts (citronella, garlic oil, neem extract, pine oil and pyrethrum), it was found that citronella was effective in deterring the infestation by red flour beetles of cartons containing muesli and wheat germ. The chemical components were applied as part of a coating on the carton board and reduced beetle infestation to approximately 50% of the level observed in control cartons. The insect-repellent effect persisted for at least 16 weeks. Navarro et al. (2007) reviewed the use of turmeric oil, neem and pyrethrum incorporated into packaging materials to repel insects.

The development of alternative treatments for pest control in foods is an increasing plea from the food industry, as consumers demand reduced use or elimination of pesticides. The use of CO_2 at high pressure is one of the most rapid options for pest control among current commercial treatments, offering complete control within hours. Riudavets et al. (2010) established the efficacy of this option against different stages of several insect and mite pests, and achieved a high level of control for most species and development stages when treated with CO_2 at 2000 kPa for 60 min.

11.2.4.2.2 Rodents

The rodents rats and mice are among humanity's most cunning and capable enemies. They have highly developed senses of touch, smell and hearing, and can identify new or unfamiliar objects in their environment. Rats can wriggle through openings the size of a quarter; a mouse needs a hole only as large as a nickel to gain access. Rats and mice carry disease-producing organisms on their feet and/or in their intestinal tracts and are known to harbor salmonellae of serotypes frequently associated with foodborne infections in humans. In addition to the public health consequences of rodent populations in close proximity to humans, these animals also compete intensively with humans for food.

Rats and mice gnaw to reach sources of food and drink and to keep their teeth short. Their incisor teeth are so strong that rats have been known to gnaw through lead pipes and unhardened concrete, as well as sacks, wood and flexible packaging materials. Obviously, proper sanitation in food processing and storage areas is the most effective weapon in the fight against rodents, because all packaging materials apart from metal and glass containers can be attacked by rats and mice.

11.3 RATES OF DETERIORATIVE REACTIONS

As discussed in the preceding section, a number of deteriorative chemical, biochemical and microbiological reactions can occur in foods. The rates of these reactions depend on both intrinsic and extrinsic factors. As well as understanding the nature of these reactions, it is also important to have an appreciation of their rates, so that they can be controlled. Control of deteriorative reactions requires a quantitative analysis based on knowledge of the kinetics of food deterioration. Fortunately, simple chemical kinetics can be applied to such reactions (van Boekel, 2009).

Quantitative analysis of the deteriorative reactions which occur in a food during processing and storage requires the existence of a measurable index of deterioration; that is, a chemical, physical or sensory measurement or set of measurements that may be used reproducibly to assess the changes occurring. An increase or decrease in the index of deterioration must correlate with changes in food quality. For quantitative analysis of quality changes, the index must be expressed as a function of the conditions existing during processing and storage so that the changes can be predicted or simulated. Thus, calculation of quality losses requires a mathematical model that expresses the effect of intrinsic and extrinsic factors on the deterioration index.

The general equation describing quality loss may be written as

$$\frac{-dC}{d\theta} = f(I_i, E_j) \tag{11.2}$$

where

$-dC/d\theta$ is the rate of change of some index of deterioration C with time θ; a negative sign is used if the concentration of C decreases with time

I_i are the intrinsic factors ($i = 1, \ldots, m$)

E_j are the extrinsic factors ($j = 1, \ldots, n$)

Because the quality of foods and the rate of quality changes during processing and storage depend on intrinsic and extrinsic factors, it is possible in many cases to correlate quality losses with the loss of a particular component such as a vitamin or pigment. The conversion of a single component or quality factor A to an end product B (e.g., conversion of chlorophyll to pheophytin, or conversion of ascorbic acid to brown pigments) may be written as

$$A \rightarrow \text{intermediate products} \rightarrow B \tag{11.3}$$

The absolute concentrations of A or B need not be measured. For example, the production of brown pigments in foods is often measured as the increase in absorbance at 420 nm of an alcoholic extract of the food, and the change in absorbance used as an indicator of the extent of the reaction. Such quality loss can be represented as being proportional to the power of the concentration of the reactant or product:

$$\frac{-dA}{d\theta} = kA^n \tag{11.4}$$

or

$$\frac{dB}{d\theta} = kB^n \tag{11.5}$$

where
A and B are the concentrations of quality factor measured
θ is the time
k is the rate constant (dependent on extrinsic factors)
n is a power factor called the order of the reaction, which defines whether or not the rate is dependent on the concentration of A. The value of n can be a fraction or a whole number
$dA/d\theta$ and $dB/d\theta$ is the change in concentration of A or B with time

Equation 11.5 implies that extrinsic parameters such as temperature, a_w and light intensity are held constant; if they are not, then their influence on the rate constant k must be taken into account in evaluating the equation. For most quality changes in foods, the reaction order n has generally been shown to be either 0 or 1.

From a packaging point of view, it is often useful to know the concentration of A or B at which the product is no longer acceptable, for example, when the concentration of a vitamin or pigment has fallen below some level (e.g., 50% reduction in concentration), or the concentration of some undesirable brown color has risen above some level. In these situations, the shelf life of the food (θ_s) is the time for the concentration of A (or B) to reach an undesirable level (A_e or B_e).

11.3.1 ZERO-ORDER REACTIONS

When $n = 0$, the reaction is said to be pseudo zero-order with respect to A. Equation 11.5 can then be simplified to:

$$\frac{-dA}{d\theta} = k \tag{11.6}$$

Equation 11.6 implies that the rate of loss of A is constant with time and independent of the concentration of A. Rearranging and integrating Equation 11.6 between A_o, the concentration of A at $\theta = 0$, and A, the concentration of A at time θ:

$$\int_{A_o}^{A} dA = -k\int_{0}^{\theta} d\theta \tag{11.7}$$

yields

$$A = A_o - k\theta \tag{11.8}$$

or

$$A_o - A = k\theta \tag{11.9}$$

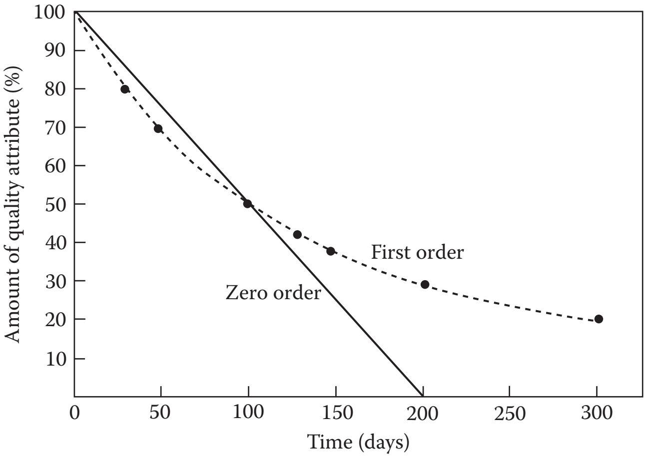

FIGURE 11.2 Change in quality versus time showing the effect of order of the reaction on extent of change.

or

$$A_e = A_o - k\theta_s \tag{11.10}$$

where

A_e is the value of A at end of shelf life
θ_s is the shelf life in days, months, years and so on

For a zero-order reaction, a plot of the amount of A remaining versus time yields a straight line (Figure 11.2) with the slope equal to the rate constant k in units of [concentration] [time^{-1}]. In other words, the loss of quality per day is constant when all extrinsic factors are held constant.

Typical pseudo zero-order deteriorative reactions include NEB (e.g., in dry cereals and powdered dairy products), lipid oxidation (e.g., development of rancidity in snacks foods, dry foods and frozen foods) and enzymic degradation (e.g., in fresh fruits and vegetables, some frozen foods and some refrigerated doughs).

It is important to appreciate that the order of the reaction (i.e., n) is strictly an empirical concept. Thus, a pseudo zero-order reaction does not imply that the mechanism is a monomolecular breakdown independent of the concentration of the reacting species. On the contrary, pseudo zero-order reactions are always an indication that a complex reaction is occurring involving a number of steps. All that a pseudo zero-order reaction suggests is that there is a high correlation between A and time.

Example 11.1

Orange juice was aseptically filled into hermetically sealed glass jars and laminated plastic/alufoil/paperboard cartons and held at 25°C. The extent of browning (expressed as optical density [OD] at 420 nm) measured over a period of weeks gave the following results:

	Browning (OD at 420 nm)	
Time (Days)	**Carton**	**Jar**
0	0.100	0.100
10	0.123	0.114
20	0.147	0.127
30	0.171	0.141
40	0.195	0.155

Analyze the data to see if the browning reaction follows a pseudo zero-order reaction, and calculate the shelf life of juice in the two containers if the juice is unacceptable when browning exceeded 0.250 OD.

This problem involves an increase in product (browning) with time, so Equation 11.5 is appropriate; this can be integrated for $n = 0$ to give

$$k = \frac{B - B_o}{\theta}$$

Carton	**Jar**
At $\theta = 40$ days,	
$k = \frac{(0.195 - 0.100)}{40}$	$k = \frac{(0.155 - 0.100)}{40}$
$= 2.38 \times 10^{-3}$ OD days^{-1}	$= 1.38 \times 10^{-3}$ OD days^{-1}
At $\theta = 20$ days,	
$k = \frac{(0.147 - 0.100)}{20}$	$k = \frac{(0.127 - 0.100)}{20}$
$= 2.38 \times 10^{-3}$ OD days^{-1}	$= 1.35 \times 10^{-3}$ OD days^{-1}

Because the rate constants for juice in each type of container agree closely after two time periods, there is some justification in treating the reaction as pseudo zero-order.

To calculate the shelf life of the juice, the following form of the aforementioned equation is appropriate:

$$\theta = \frac{B - B_o}{k}$$

Carton	**Jar**
$\theta = \frac{(0.25 - 0.10)}{2.365 \times 10^{-3}}$	$\theta = \frac{(0.25 - 0.10)}{1.365 \times 10^{-3}}$
$= 63$ days	$= 109$ days

Thus using these data, the shelf life of the orange juice packaged in a glass jar is 46 days longer than juice packaged in a laminated carton.

11.3.2 FIRST-ORDER REACTIONS

In general, foods that do not follow a pseudo zero-order reaction deteriorate according to a pseudo first-order ($n = 1$) reaction in which the rate of loss is dependent on the amount left. In this case, the solution of Equation 11.4 for $n = 1$ is

$$\int_{A_o}^{A} \frac{dA}{A} = -k \int_{0}^{\theta} d\theta \tag{11.11}$$

and

$$\ln \frac{A}{A_o} = -k\theta \tag{11.12}$$

(where ln = natural logarithm) or

$$\ln A = \ln A_o - k\theta \tag{11.13}$$

or

$$A = A_o e^{-k\theta} \tag{11.14}$$

or

$$A_e = A_o e^{-k\theta s} \tag{11.15}$$

A plot of first-order data as the concentration of A versus time gives a curved line as shown in Figure 11.2. However, if the data are plotted as the base 10 logarithm of A versus time, a straight line is obtained, the slope of which is equal to $-k/2.303$. The unit of k for a first-order reaction is [time^{-1}].

Typical pseudo first-order deteriorative reactions include NEB (e.g., loss of protein quality in dry foods), lipid oxidation (e.g., development of rancidity in salad oils and dry vegetables), vitamin loss in canned and dry foods and microbial production of off-flavors and slime in flesh foods.

Example 11.2

Lemon juice at a concentration of 9° Brix is stored at 10°C and the concentration of ascorbic acid measured over a period of weeks to give the following results:

Time (Weeks)	Ascorbic Acid (mg 100 mL^{-1})
0	52.9
4	45.1
8	38.3
12	32.9
16	26.7

Determine the rate constant for the loss of ascorbic acid assuming that the reaction is pseudo first-order and calculate the time for the ascorbic acid concentration in the juice to reach 20 mg 100 mL^{-1}.

From Equation 11.13,

$$k = \frac{(\ln A_o - \ln A)}{\theta}$$

After 16 weeks,

$$k = \frac{(\ln 52.9 - \ln 26.7)}{16} = 0.043 \text{ weeks}^{-1}$$

After 8 weeks,

$$k = \frac{(\ln 52.9 - \ln 38.3)}{8} = 0.040 \text{ weeks}^{-1}$$

To calculate the shelf life of the lemon juice,

$$\theta_s = \frac{(\ln A_o - \ln A_e)}{k} = \frac{(\ln 52.9 - \ln 20)}{0.0415} = 23 \text{ weeks}$$

Thus, the concentration of ascorbic acid will have fallen to 20 mg 100 mL^{-1} after 23 weeks at 10°C.

11.3.3 MICROBIAL GROWTH AND DESTRUCTION

11.3.3.1 Microbial Growth

Microbial growth has been described by a variety of mathematical models. Their properties and how well they fit and predict experimental growth data are discussed in numerous research articles, reviews and book chapters (e.g., van Boekel, 2009; Peleg and Corradini, 2011).

During the exponential (or logarithmic) growth phase, a microbial culture mimics a first-order chemical reaction, i.e., the rate of increase in cells is proportional to the number of microbes present at that time. Therefore, Equation 11.12 can be rewritten in the form

$$\ln\frac{A}{A_o} = \mu_{\max}\theta_{\text{doub}} \tag{11.16}$$

where

A_o is the initial number of microorganisms when $\theta = 0$

$A = 2A_o$ (i.e., the number of organisms has doubled)

$\mu_{\max}$ is the maximum specific growth rate constant (analogous to k in chemical reactions)

θ_{doub} is the time for number of organisms to double (i.e. the generation or doubling time)

On substituting $2A_o$ for A,

$$\ln 2 = \mu_{\max}\theta_{\text{doub}} \tag{11.17}$$

and

$$\mu_{\max} = \frac{0.693}{\theta_{\text{doub}}} \tag{11.18}$$

or

$$\theta_{\text{doub}} = \frac{0.693}{\mu_{\max}} \tag{11.19}$$

This enables calculation of the generation or doubling time if $\mu_{\max}$ is known, or vice versa. In shelf life studies, it is of interest to know the time to reach a critical upper limit of cells. In this case, Equation 11.16 can be rewritten to include a lag time θ_{lag} as

$$\theta_s = \theta_{\text{lag}} + \frac{1}{\mu_{\max}}\ln\frac{N_c}{N_o} \tag{11.20}$$

where

N_o is the initial number of microorganisms when $\theta = 0$

N_c is the critical or maximum permitted number of microorganisms

θ_s is the time for number of microorganisms to reach critical level (i.e., microbial shelf life)

Example 11.3

Beef is to be packaged in plastic film and stored at chill temperatures. The initial level of contamination of the beef immediately after packaging is 10^3 microorganisms per cm^2, and the maximum permitted level of microorganisms is 10^8. Assuming that the microorganisms are solely *Pseudomonas fluorescens*, which has a generation or doubling time of 8.5 h at 5°C, calculate the time for which the beef can be stored before the maximum permissible level of microorganisms is reached assuming no lag time.

From Equation 11.18:

$$\mu_{\max} = \frac{0.693}{8.5} = 0.0815\,h^{-1}$$

Substituting into Equation 11.20,

$$\theta_s = \frac{1}{\mu_{\max}} \ln\frac{N_c}{N_o} = \frac{1}{0.0815} \ln\frac{10^8}{10^3} = 141.5\,h$$

If this shelf life were insufficient, the storage temperature could be lowered. Given that the generation time at −2°C is 19 h, calculate the shelf life of the beef:

$$\mu_{\max} = \frac{0.693}{19} = 0.0365\,h^{-1}$$

and

$$\theta_s = \frac{1}{0.0365} \ln\frac{10^8}{10^3} = 315.4\,h$$

If further extension of the shelf life were required, the package could be flushed with CO_2 and the new shelf life calculated, provided of course that the generation time for *Pseudomonas fluorescens* at −2°C in a CO_2 atmosphere was known.

11.3.3.2 Microbial Destruction

For the kinetics of microbial destruction by heat and irradiation, the food industry uses a modified time term—the decimal reduction time or D value. This is defined as the time at constant temperature to reduce the population of microorganisms by 90%. Mathematically, at time $\theta = D$, $A = 0.1A_o$.

Substituting into Equation 11.12,

$$\ln\frac{A_o}{0.1A_o} = kD$$

Because ln 10 = 2.303,

$$D = \frac{2.303}{k}$$

If the logarithm of the D value is plotted against the corresponding temperature, a straight line is obtained, the slope of which is designated by the term z. This can be defined as the temperature change necessary for a 10-fold change in the D value or reaction rate. Mathematically,

$$\frac{k_T}{k_{T-z}} = 10 \tag{11.21}$$

11.4 INTRINSIC FACTORS CONTROLLING THE RATES OF DETERIORATIVE REACTIONS

11.4.1 Water Activity

11.4.1.1 Definitions

Water activity (a_w) is defined as the ratio of the water vapor pressure of a material to the vapor pressure of pure water at the same temperature. Mathematically,

$$a_w = \frac{p}{p_o} \tag{11.22}$$

where

p is the vapor pressure of water exerted by the food
p_o is the saturated vapor pressure of pure water at the same temperature

This concept is related to equilibrium relative humidity (ERH) in that ERH = 100 × a_w. However, while a_w is an intrinsic property of the food, ERH is a property of the atmosphere in equilibrium with the food. As Reid and Fennema (2007) have stressed, the equality in Equation 11.22 is based on the assumption of thermodynamic equilibrium, which is generally violated with foods, and therefore the equality should be replaced with an approximation.

The a_w of most fresh foods is above 0.99. At subfreezing temperatures, a_w is defined as the vapor pressure of ice divided by the vapor pressure of supercooled water at the same temperature. Thus, the a_w of frozen foods depends only on their temperature and not their composition; at −20°C, $a_w = 0.825$; at −10°C, 0.905; and at −5°C, 0.953 (Reid and Fennema, 2007).

As mentioned earlier in the definition of a_w, the temperature must be specified, since a_w values are temperature dependent. The temperature dependence of a_w can be described by a modified form of the Clausius–Clapeyron equation:

$$\frac{d \ln a_w}{d(1/T)} = \frac{-\Delta H}{R} \tag{11.23}$$

or

$$\ln \frac{a_{w2}}{a_{w1}} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{11.24}$$

where

a_{w1} is the water activity at temperature T_1 (K)
a_{w2} is the water activity at temperature T_2 (K)
ΔH is the isosteric net heat of sorption at the moisture content of the food (J mol^{-1})
R is the gas constant (8.314 J mol^{-1} K^{-1})

Thus, from Equation 11.23, a plot of ln a_w versus $1/T$ at constant moisture content should be linear. Such plots are not always linear over wide temperature ranges, and they exhibit sharp breaks with the onset of ice formation (Reid and Fennema, 2007).

11.4.1.2 Isotherms

When a food is placed in an environment at a constant temperature and RH, it will eventually come to equilibrium with that environment. The corresponding moisture content at steady-state is referred to as the equilibrium moisture content. When this moisture content (expressed as mass of water per unit mass of dry matter) is plotted against the corresponding RH or a_w at constant

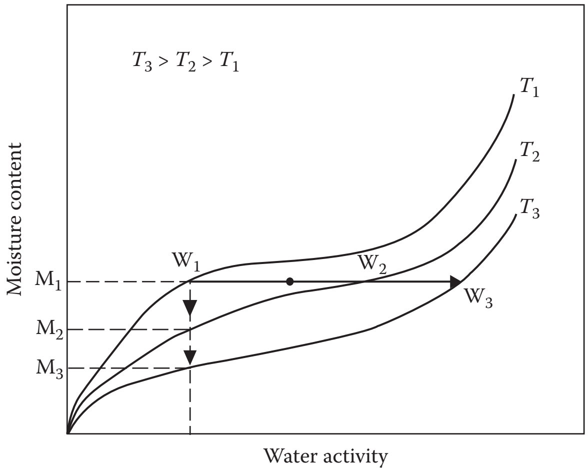

FIGURE 11.3 Schematic of a typical moisture sorption isotherm showing the effect of temperature.

temperature, a moisture sorption isotherm (MSI) is obtained (see Figure 11.3). Such plots are very useful in assessing the stability of foods and selecting effective packaging.

One complication is that a MSI prepared by the addition of water to a dry sample (resorption) will not necessarily be superimposable on an isotherm prepared by removal of water from a wet sample (desorption). This lack of superimposability is referred to as *hysteresis*. Typically, at any given a_w, the water content of the food will be greater during desorption than during resorption. This has important implications with respect to food stability, in that foods adjusted to the desired a_w by desorption rather than resorption may deteriorate more rapidly because of their higher moisture content.

Another complication occurs with some sugars. Crystalline sugars generally have completely different MSIs from those for amorphous sugars, where the equilibrium moisture content is much lower for the crystalline form at any particular a_w. The amorphous form is often present when the food has been dried quickly (e.g., spray drying of milk often results in the formation of amorphous lactose); during storage, it may slowly revert to the crystalline form. This results in a distinct break in the MSI, because the sugar releases moisture at constant a_w (see Figure 19.5).

Because a_w is temperature dependent, it follows that MSIs must also exhibit temperature dependence. Thus, at any given moisture content, a_w increases with increasing temperature, in agreement with the Clausius–Clapeyron equation (Equation 11.23) and shown in exaggerated form for illustrative purposes in Figure 11.3. This can have large consequences for the stability of the food when it is subjected to temperature fluctuations.

Many relationships have been derived relating the a_w of a food to its moisture content and a comprehensive review of the most widely used models has been presented by Basu et al. (2006). For many years, the most used relationship for food was the Brunauer–Emmett–Teller (BET) Type 2 sigmoid isotherm which took the form

$$\frac{m}{m_o} = \frac{C_b a_w}{(1 - a_w)(1 + C_b a_w - a_w)} \tag{11.25}$$

or

$$\frac{a_w}{m(1 - a_w)} = \frac{1}{m_o C_b} + \frac{C_b - 1}{m_o C_b} a_w \tag{11.26}$$

where

m is the moisture content (dry weight basis) at water activity a_w
m_o is the moisture content of the monolayer (dry weight basis)
C_b is a dimensionless parameter related to the heat of sorption of the monolayer region

The BET equation gives a good fit for a variety of foods over the region $0.05 < a_w < 0.45$. It has also been used to estimate the monolayer value, which is equivalent to the amount of water held adsorbed on specific sites. For many foods, the monolayer value corresponds to an a_w of 0.2–0.4. A monolayer does not mean coverage of all dry matter with a closely packed, single layer of water molecules. Rather, the monolayer value should be regarded as the maximum amount of water that can be strongly bound to the dry matter. Recently, Caurie (2011) identified three types of bound water at room temperature and suggested that a food is more stable the smaller the ratio of its type III to type II bound water molecules.

The Guggenheim-Anderson-de Boer (GAB) model has been widely used by European food researchers since the late 1970s, and has now gained worldwide acceptance. It is a three-parameter model with physically meaningful coefficients, which usually fits data very well up to 0.9 a_w. The model is

$$\frac{m}{m_o} = \frac{C_g K a_w}{(1 - K a_w)(1 + C_g K a_w - K a_w)} \tag{11.27}$$

where

m is the moisture content (dry weight basis) at water activity a_w

m_o is the moisture content corresponding to saturation of all primary adsorption sites by one water molecule (equivalent to the BET monolayer)

C_g is the dimensionless GAB parameter related to the heat of sorption of the monolayer region and often referred to as the Guggenheim constant

K is the dimensionless GAB parameter related to the heat of sorption of the multilayer region

Parameters C and K can be represented by Arrhenius-type equations:

$$C = \frac{C_0 \exp(H_m - H_q)}{RT} \tag{11.28}$$

where

H_m is the total heat of sorption of the monolayer

H_q is the total heat of sorption of the multilayer covering the monolayer

and

$$K = \frac{K_0 \exp(H_1 - H_q)}{RT} \tag{11.29}$$

where

H_l is the heat of condensation of water vapor at the given temperature

C_0 and K_0 are adjusted constants for the temperature effect

This model can be considered as an extension of the BET model, taking into account the modified properties of the sorbed water in the multilayer region; when $K = 1$, the GAB model reverts to the BET model. The real advantage of the GAB model is that it offers an objective method for fitting sorption isotherm data for a majority of foods up to 0.9 a_w. To fit data, the GAB model can be transformed into a quadratic equation to obtain coefficients α, β and γ, from which the

GAB constants (m_o, C_g and K) can be calculated by direct nonlinear regression (Samaniego-Esguerra et al., 1991):

$$\frac{a_w}{m} = \alpha a_w^2 + \beta a_w + \gamma \tag{11.30}$$

where

$\alpha = (K/m_o)(1/C_g - 1)$
$\beta = (1 - 2/C_g)/m_o$
$\gamma = 1/(m_o C_g K)$

and the solution is

$$K = \frac{\sqrt{\beta^2 - 4\alpha\gamma} - \beta}{2\gamma}$$

$$C_g = \frac{\beta}{\gamma K} + 2$$

$$m_o = \frac{1}{\gamma K C_g}$$

The final choice of model will depend on a compromise between the desired closeness of fit and convenience with regard to the number of parameters involved and their calculation.

11.4.1.3 Water Activity and Food Stability

Water may influence chemical reactivity in different ways. It may act as a reactant (e.g., in the case of sucrose hydrolysis) or as a solvent, where it may exert a dilution effect on the substrates, thus decreasing the reaction rate. Water may also change the mobility of the reactants by affecting the viscosity of the food systems and form hydrogen bonds or complexes with the reacting species. Thus, a very important practical aspect of a_w is to control undesirable chemical, enzymic and microbial reactions that reduce the shelf life of foods. It is a well-known generality that rates of changes in food properties can be minimized or accelerated over widely different values of a_w, as the so-called food stability map shown in Figure 11.4 demonstrates. Small changes in a_w can result in large changes in reaction rates.

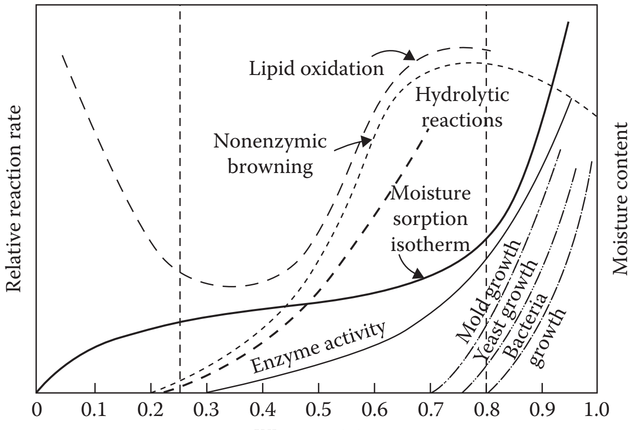

FIGURE 11.4 Relative rates of reactions and microbial growth as a function of water activity. (From Rockland, L.B. and Beuchat, L.R. (Eds), *Water Activity: Theory and Applications to Food*, Marcel Dekker, New York, 1987.)

11.4.1.3.1 Lipids

The influence of a_w on lipid oxidation has been studied extensively, mainly with the use of model systems. The general effect of a_w on lipid oxidation is shown in Figure 11.4. At very low a_w levels, foods containing unsaturated fats and exposed to atmospheric O_2 are highly susceptible to the development of oxidative rancidity. This high oxidative activity occurs at a_w levels below the monolayer level, and as a_w increases, both the rate and the extent of autoxidation decrease until an a_w in the range of 0.3–0.5 is reached. Above this point, the rate of oxidation increases until a steady-state is reached, normally at a_w levels in excess of 0.75. At $a_w s$ below the monolayer value, the oxidation rate decreases with increasing a_w. The rate reaches a minimum around the monolayer value and increases with further increases in a_w. Water may influence lipid oxidation by influencing the concentrations of initiating radicals present, the degree of contact and mobility of reactants and the relative importance of radical transfer versus recombination reactions.

11.4.1.3.2 Browning

Water may accelerate browning by imparting mobility to the substrates, or it may decrease the browning rate by diluting the reactive species. In the low a_w range, the mobility factor predominates, whereas the dilution factor predominates in the high a_w range. As a consequence, browning rate generally increases with increasing a_w at low moisture content, reaches a maximum at a_ws of 0.7–0.8, and decreases with further increase in a_w (see Figure 11.4).

11.4.1.3.3 Vitamins

The rate of degradation of vitamins A, B_1, B_2 and C increases as a_w increases over the range 0.24–0.65. Generally, the rate of ascorbic acid degradation increases exponentially with increase in a_w. The photodegradation of riboflavin has been shown to increase with increasing a_w.

11.4.1.3.4 Enzymes

Near or below the monolayer a_w value, enzyme activities are generally minimized or cease. Above the monolayer value, enzyme activity increases with increasing a_w or increased substrate mobility, as illustrated in Figure 11.4. Substrates of high molecular weight (MW) such as protein and starch are less mobile than low MW substrates such as glucose, and generally the latter have a lower a_w threshold for enzyme activity. At subfreezing temperatures, the reaction rate generally decreases with decreasing temperature and a_w, owing partly to the lower temperature, partly to the increase in viscosity of the partially frozen system, and partly to enzyme denaturation.

11.4.1.3.5 Pigments

Carotenoids are subject to changes due to heating and both enzymic and nonenzymic oxidation, all of which are influenced by water. Water appears to have a protective effect on oxidative degradation, apparently by reducing the free radical content. Values of a_w above the monolayer (up to a_w of 0.41) give almost complete protection against oxidative degradation.

Water activity has a definite influence on the rate of chlorophyll degradation, with the rate decreasing with a decrease in a_w. The color of anthocyanins increases in intensity as a_w is lowered.

11.4.1.3.6 Texture

In the case of sugars, changes in a_w may either inhibit or promote a physical change in the nature of the sugar, which, in turn, affects the texture. A low a_w maintains the sugar in the form of a glassy, amorphous, free-flowing powder, whereas an increase in a_w promotes crystallization resulting in a sticky, caking powder, which has a much lower moisture content than the amorphous sugar.

The sensory crispness of starch-based dried foods decreases with increasing a_w and become unacceptable when $a_w > 0.35$–0.50 for crisp snack foods such as chips, saltine crackers and pop corn, $a_w > 0.44$ for puffed rice cakes and $a_w > 0.28$–0.55 for breakfast cereals.

11.4.1.3.7 Microbial

Every microorganism has a limiting a_w value below which it will not grow, form spores or produce toxic metabolites. Table 11.8 lists the range of a_ws that permit the growth of various common microorganisms, together with common foods categorized according to their a_w. Certain relationships have been shown to exist between a_w, temperature and nutrition (Jay et al., 2007). First, at any temperature, the ability of microorganisms to grow is reduced as a_w is lowered. Second, the range of a_w over which growth occurs is greatest at the optimum temperature for growth; third, the presence of nutrients increases the range of a_w over which the organisms can survive. Therefore, the values given in Table 11.8 should be taken only as a guide.

Water activity can influence each of the four main growth cycle phases by its effect on the germination time, the length of the lag phase, the growth rate phase, the size of the stationary population and the subsequent death rate. Generally, reducing the a_w of a given food increases the lag period and decreases the growth rate during the logarithmic phase, the maximum of which becomes lower.

TABLE 11.8
Water Activity and Growth of Microorganisms in Food at Different Water Activities (a_w)

Range	Microorganisms Generally Inhibited by Lowest a_w of the Range	Foods Generally within This Range of a_w
1.00–0.95	*Pseudomonas*, *Escherichia*, *Proteus*, *Shigella*, *Klebsiella*, *Bacillus*, *Clostrium perfringens*, some yeasts	Highly perishable (fresh) foods and canned fruits, vegetables, meat, fish and milk; cooked sausages and breads; foods containing up to approximately 40% (w/w) sucrose or 7% sodium chloride
0.95–0.91	*Salmonella, Vibrio parahaemolyticus*, *C. botulinum, Serratia, Lactobacillus Pediococcus*, some molds, yeasts	Some cheeses (Cheddar, Swiss, Muenster, Provolone), cured meats (ham), some fruit juice concentrates; foods containing 55% (w/w) sucrose or 12% sodium chloride
0.91–0.87	Many yeasts (*Candida*, *Torulopsis*, *Hansenula*), *Micrococcus*	Fermented sausages (salami), sponge cakes, dry cheeses, margarine; foods containing up to 65% (w/w) sucrose (saturated) or 15% sodium chloride
0.87–0.80	Most molds (mycotoxigenic penicillia), *Staphylococcus aureus*, most *Saccharomyces* (*bailii*) spp., *Debaryomyces*	Most fruit juice concentrates, sweetened condensed milk, chocolate, syrup, maple and fruit syrups; flour, rice, pulses of 15%–17% moisture content; fruit cake, country-style ham, fondants, high-ratio cakes
0.80–0.75	Most halophilic bacteria, mycotoxigenic aspergilli	Jam, marmalade, marzipan, glacéd fruits, some marsh mellows
0.75–0.65	Xerophilic molds (*Aspergillus chevalieri*, *A. candidus*, *Wallemia sebi*), *Saccharomyces bisporus*	Rolled oats of 10% moisture content, grained nougats, fudge, marshmallows, jelly, molasses, raw cane sugar, some dried fruits, nuts
0.65–0.60	Osmophilic yeasts (*Saccharomyces rouxii*), few molds (*Aspergillus echinulatus*, *Monascus bisporus*)	Dried fruits containing 15–20% moisture content, some toffees and caramels; honey
0.60–0.50	No microbial proliferation	Pasta of 12% moisture content; spices of 10% moisture content
0.50–0.40	No microbial proliferation	Whole egg powder of 5% moisture content
0.40–0.30	No microbial proliferation	Cookies, crackers, bread crusts, and so forth of 3%–5% moisture content
0.30–0.20	No microbial proliferation	Whole milk powder of 2%–3% moisture content, dried vegetables of 5% moisture content; corn flakes of 5% moisture content

Source: Adapted from Beuchat, L., *Cereal Foods World*, 26, 345, 1981.

Sporulation may occur at slightly below the minimum a_w for growth. In contrast, germination of spores of some microorganisms may occur at a_w values below that required for growth. The minimum a_w for growth of microorganisms is, without exception, less than or equal to the minimum a_w for toxin production. Optimal conditions of temperature, pH, O_2 tension and nutrient availability are necessary to permit sporulation, germination and toxin production at reduced a_w.

Whether a microorganism survives or dies in a low a_w environment is influenced by intrinsic factors that are also responsible for its growth at a higher a_w. These factors include water-binding properties, nutritive potential, pH, E_h and the presence of antimicrobial compounds. The influences exerted by these factors interact with a_w both singularly and in combination. Microbial growth and survival are not entirely ascribed to reduced a_w, but also to the nature of the solute. However, the exact nature of the role that water plays in the mechanism of cell survival is not clearly understood.

Key extrinsic factors relative to a_w that influence microbial deterioration in foods include temperature, O_2 and chemical treatments. These factors can all combine in a complex way to either encourage or discourage microbial growth.

11.4.2 Oxidation-Reduction Potential

The oxidation-reduction potential (also referred to as the redox potential and abbreviated E_h or ORP) of a substrate may be defined as the ease with which the substrate loses or gains electrons. The more highly oxidized a substance, the more positive will be its electrical potential. It is a physicochemical parameter that determines the oxidizing or reducing properties of the food and depends on the composition of the food, pH, temperature, and for a large part, the concentration of dissolved O_2 (DO). Among the substances in foods that help to maintain reducing conditions are the sulfhydryl groups on proteins, and ascorbic acid and reducing sugars in fruits and vegetables. Deteriorative chemical reactions can alter the E_h value of foods during storage.

E_h plays an important role in the cellular physiology of microorganisms such as growth capacity, enzyme expression and thermal resistance. Aerobic microorganisms require positive E_h values (oxidized) for growth while anaerobes require negative E_h values (Jay et al., 2007). Alwazeer et al. (2003) demonstrated that reducing the E_h of orange juice by gas (N_2 and H_2) immediately after heat treatment maximized microbial destruction during pasteurization, prevented the development of microorganisms and stabilized color and ascorbic acid during storage at 15°C.

The relationship between E_h and DO levels in milk is not well-understood. Several modifications that occur in milk during its processing and storage are driven by different oxidation-reduction reactions. Electrolysis treatments have been applied to milk to produce milk powder with better flavor quality. E_h and DO levels in enriched milk are mainly responsible for the oxidation of unsaturated fatty acids and the loss of viability of probiotic strains such as bifidobacteria. Decreasing the E_h in milk could allow an improvement in the quality of these products. Recent studies on electroreduction of milk by membrane electrolysis have shown that this electrochemical process decreased the E_h of milk without changing the organoleptic and nutritive values (Schreyer et al., 2008).

11.5 EXTRINSIC FACTORS CONTROLLING THE RATES OF DETERIORATIVE REACTIONS

11.5.1 Temperature

Temperature is a key factor in determining the rate of deteriorative reactions, and in certain situations, the packaging material can affect the temperature of the food. This is particularly so with packaging materials which have insulating properties, and these types of packages are typically used for chilled and frozen foods. For packages that are stored in refrigerated display cabinets, most of the cooling takes place by conduction and convection. Simultaneously, there is a heat input by radiation from the fluorescent lamps used for lighting. Under these conditions, aluminum foil offers real advantages because of its high reflectivity (low emissivity) and high conductivity. However, such advantages are seldom used in the packaging of frozen and chilled foods. Recently, Davies et al. (2012) reported the potential of modern, low emissivity food packaging materials to improve the energy efficiency of open display refrigeration cabinets by up to 30% as a result of operating up to 10°C higher with no loss in food quality.

11.5.1.1 Linear Model

Early studies on the thermal processing of foods obtained a straight line when the thermal death times (now D values or the time for a 90% reduction in numbers) of microorganisms were plotted against temperature on a linear scale. The equation of such a curve is

$$\log\left(\frac{D_1}{D_2}\right) = \frac{(T_1 - T_2)}{z} \tag{11.31}$$

where z is the temperature change required to change the D value by a factor of 10.

For many microorganisms of interest in food canning, $z = 10°C$, whereas for degradation of quality factors during thermal processing, $z = 32°C$. Reactions that have small z values are highly temperature dependent, whereas reactions with large z values are less influenced by temperature. This model has been found to be satisfactory for thermal processes and is still in use today. In its more general form it can be written as shown below because $k \propto D$:

$$k = k_\mathrm{r} 10^{(T - T_\mathrm{r})/z} \tag{11.32}$$

A similar expression relating the rate of reactions and temperature has also been used for many years, especially in relation to shelf life plots (see Chapter 12):

$$k = k_o e^{b(T - T_o)} \tag{11.33}$$

where

k_o is the rate at temperature T_o (°C)
k is the rate at temperature T (°C)
b is a constant characteristic of the reaction
$e = 2.7183$

11.5.1.2 Arrhenius Relationship

The most common and generally valid relationship for the effect of temperature on the rate of deterioration is that of Arrhenius. The relationship is correctly expressed in the differential form:

$$\frac{d(\ln k)}{dT} = \frac{E_\mathrm{A}}{RT^2} \tag{11.34}$$

For practical reasons the integrated form is used:

$$k = k_o e^{-E_\mathrm{A}/RT} \tag{11.35}$$

where

k is the rate constant for deteriorative reaction
k_o is a constant, independent of temperature (also known as the Arrhenius, pre-exponential, collision or frequency factor)
E_A is the activation energy ($\mathrm{J\ mol^{-1}}$)
R is the ideal gas constant ($8.314\,\mathrm{J\ K^{-1}\ mol^{-1}} = 1.987\ \mathrm{cal\ K^{-1}\ mol^{-1}}$)
T is the absolute temperature (K)

TABLE 11.9
Typical Activation Energies for Reactions Important in Food Deterioration

Reaction	Activation Energy (E_A) (kJ mol^{-1})
Diffusion-controlled reaction	8–40
Lipid oxidation	40–105
Flavor degradation in dry vegetables	40–105
Enzymic reactions	40–130
Hydrolysis	60–110
Vitamin degradation	85–130
Color degradation in dry vegetables	65–150
Nonenzymic browning	105–210
Microbial growth	85–250
Protein denaturation	350–700

The integrated relationship contains the inherent assumption that the activation energy and the pre-exponential factor do not change with temperature. This assumption is generally, but not universally, true. Therefore, predictions based on this model sometimes fail when applied over a temperature range of greater than about 40°C. Furthermore, when the reaction mechanism changes with temperature, the activation energy may vary substantially. The value of E_A is a measure of the temperature sensitivity of the reaction; that is, how much faster the reaction will proceed if the temperature is raised. Typical activation energies for reactions important in food deterioration are listed in Table 11.9.

The activation energy is generally derived from the slope of the plot of ln k versus $1/T$ and depends on factors such as a_w, moisture content, solids concentration and pH.

11.5.1.3 Temperature Quotient

Another term used to describe the response of biological systems to temperature change is the Q value, a quotient indicating how much more rapidly the reaction proceeds at temperature T_2 than at a lower temperature T_1. If Q reflects the change in rate for a 10°C rise in temperature, it is then called Q_{10}. Mathematically,

$$Q_{10} = \frac{k_{T+10}}{k_T} \tag{11.36}$$

When the Fahrenheit temperature scale is used instead of the Celsius scale, the symbol q_{10} is used. The relationship between Q_{10} and q_{10} is

$$Q_{10} = (q_{10})^{1.8} \tag{11.37}$$

It can be shown that the rate of a deteriorative reaction at two temperatures is related to the shelf life at those two temperatures:

$$k_T \theta_{\text{s}_T} = k_{T+10} \theta_{\text{s}_{T+10}} \tag{11.38}$$

where
θ_{s_T} is the shelf life at temperature T°C
$\theta_{\text{s}_{T+10}}$ is the shelf life at temperature $(T + 10)$°C

Therefore,

$$Q_{10} = \frac{\theta_{s_T}}{\theta_{s_{T+10}}} \tag{11.39}$$

For any temperature difference Δ which is not 10°C:

$$Q_{10}^{\Delta/10} = \frac{\theta_{s_{T1}}}{\theta_{s_{T2}}} \tag{11.40}$$

It can be shown when the Arrhenius model is used that

$$\ln Q_{10} = \frac{10E_\mathrm{A}}{RT(T+10)} \approx \frac{10E_\mathrm{A}}{RT^2} \tag{11.41}$$

or

$$Q_{10} \approx \exp\frac{10E_\mathrm{A}}{RT^2} \tag{11.42}$$

and when the linear model is used:

$$\ln Q_{10} = 10b \tag{11.43}$$

or

$$Q_{10} = \mathrm{e}^{10b} \tag{11.44}$$

Note that Q_{10} is not constant but depends on both the E_A and the temperature, whereas E_A is assumed to be independent of temperature.

It can also be shown that

$$\frac{E_\mathrm{A}}{RT^2} = \frac{\ln 10}{z} = \frac{2.3}{z} \tag{11.45}$$

By combining Equation 11.41 and Equation 11.45, it can be shown that

$$z = \frac{10}{\ln Q_{10}} \tag{11.46}$$

Example 11.4

The pseudo zero-order rate constant for the degradation of ascorbic acid in dried vegetables packaged in a PET-LDPE laminate pouch is 0.0745 mg 100 g^{-1} week^{-1} when stored at 30°C, and 0.0255 mg 100 g^{-1} week^{-1} when stored at 20°C. What is the Q_{10} and activation energy for the reaction?

From Equation 11.36,

$$Q_{10} = \frac{k_{T+10}}{k_\mathrm{r}} = \frac{0.0745}{0.0255} = 2.92$$

From Equation 11.41,

$$\ln 2.92 = \frac{10E_\mathrm{A}}{8.314 \times 293 \times 303}$$

$$\therefore E_\mathrm{A} = 79.1\ \mathrm{kJ\,mol^{-1}K^{-1}}$$

11.5.1.4 Bělerádek Function

Because it is not a simple chemical reaction, the temperature dependence of microbial growth cannot be described by the Arrhenius relationship. If an Arrhenius plot of microbial growth is made, it is frequently nonlinear (van Boekel, 2009). Therefore, empirical models are used. A function which has been employed to predict the rate of microbial growth in a range of chilled flesh foods (particularly fresh fish) was first suggested by Bělerádek in the form:

$$k = a(T - \alpha)^d \tag{11.47}$$

where

k is the reciprocal of the time required to reach a specified amount of a metabolite or the specific growth rate constant of a bacterial population
T is the absolute temperature
a, α and d are constants fitted to the particular system under study

In some applications, the constant α is referred to as the "biological zero," a hypothetical temperature at which the growth rate is zero or the reaction time infinite. The exponent d has been found to be two for bacterial growth.

A particular case of the Bělerádek function was developed to describe the growth of bacteria at a fixed pH and a_w; the relationship is usually expressed in the form:

$$\sqrt{k} = b_1(T - T_{\min}) \tag{11.48}$$

or

$$\mu_{\max} = [b_1(T - T_{\min})]^2 \tag{11.49}$$

where

$\mu_{\max}$ is the maximum specific growth rate constant (time^{-1})
$T_{\min}$ is the temperature at which growth ceases
b is a regression coefficient

Equation 11.49 (also referred to as the Ratkowsky square root model) has been widely accepted in predictive microbiology and was later expanded to account for the maximum temperature at which the growth rate peaks:

$$\mu_{\max} = \left\{b_2(T - T_{\min})(1 - \exp[c_2(T - T_{\max})])\right\}^2 \tag{11.50}$$

where

$T_{\min}$ and $T_{\max}$ are minimum and maximum temperatures for growth
b_2 and c_2 are constants

11.5.2 GAS ATMOSPHERE

Atmospheric O_2 generally has a detrimental effect on the nutritive quality of foods, and it is therefore desirable to maintain many types of foods at a low O_2 tension, or at least prevent a continuous supply of O_2 into the package. Lipid oxidation causes the formation of hydroperoxides, peroxides and epoxides, which, in turn, will oxidize or otherwise react with carotenoids, tocopherols and ascorbic acid to cause loss of vitamin activity. The decomposition of hydroperoxides to reactive carbonyl compounds could lead to losses of other vitamins, particularly thiamine, some forms of B_6 and pantothenic acid (Gregory, 2007). The destruction of other oxidizable vitamins such as folic acid, B_{12}, biotin and vitamin D is also likely.

Changes in the gas atmosphere of packaged foods depend largely on the nature of the package. Correctly sealed metal and glass containers effectively prevent the interchange of gases between the food and the atmosphere. With plastic packaging, however, the diffusion of gases depends not only on the effectiveness of the closure but also on the permeability of the packaging material, which is a function of the physicochemical structure of the barrier. The gas permeabilities of the common thermoplastic packaging materials were given in Table 4.3.

The gas atmosphere inside food packages is often modified prior to closing by pulling a vacuum and removing most of the gases present, or by flushing the headspace area inside the package with an inert gas such as N_2 or CO_2. These procedures are generally referred to as MAP and are becoming increasing important, especially with the packaging of fresh fruits and vegetables, flesh foods and bakery products. Details of the actual procedures used and their effect on product shelf lives are discussed later in Chapter 16.

11.5.3 LIGHT

Many of the deteriorative changes in the quality of foods are initiated or accelerated by light (Andersen and Skibsted, 2010). Light is essentially an electromagnetic vibration in the range between 400 and 700 nm. Each color is represented by a specific wavelength: violet is in the area of 400 nm, blue and green are in the middle of the visible spectrum, and red is in the area of 700 nm. The wavelength of UV light ranges between 200 and 400 nm. The catalytic effects of light are most pronounced in the lower wavelengths of the visible spectrum and in the UV spectrum. The intensity of light and the length of exposure are significant factors in the production of discoloration and flavor defects in packaged foods.

The total amount of light absorbed by a packaged food can be calculated using the following formula (Fellows, 2009):

$$I_a = I_i T_p \frac{1 - R_f}{(1 - R_f) R_p} \tag{11.51}$$

where

I_a is the intensity of light absorbed by the food
I_i is the intensity of incident light
T_p is the fractional transmission by the packaging material
R_p is the fraction reflected by the packaging material
R_f is the fraction reflected by the food

The fraction of the incident light transmitted by any given material can be considered to follow the Beer–Lambert law:

$$I_t = I_i e^{-\alpha x} \tag{11.52}$$

where

I_t is the intensity of light transmitted by the packaging material
α is the characteristic absorbance of the packaging material
x is the thickness of the packaging material

The absorbance α varies not only with the nature of the packaging material but also with the wavelength. Thus, the amount of light transmitted through a given package will be dependent on the incident light and the properties of the packaging material. Some materials (e.g., LDPE) transmit both visible and UV light to a similar extent, whereas others (e.g., PVC) transmit visible light but absorb UV light. Not all of the light that strikes the surface of a food is absorbed and available to induce chemical reactions in the food. The surface absorption spectrum determines which wavelengths are absorbed and how efficiently they are absorbed. The remaining light is reflected by the surface, and the spectral distribution of the reflected light determines the color of the food as perceived by the human eye (Andersen and Skibsted, 2010).

Modification of plastic materials may be achieved by incorporation of dyes or application of coatings, which absorb light at specific wavelengths. A new coating containing nanoparticles of TiO_2 that is applied to the outside of plastic packaging protects products from both UVA (320–400 nm) and UVB (290–320 nm) radiation. Although it provides over 50% more total integrated UV absorbance than commonly used organic UV absorbers on an equal weight basis, it does impart a translucent appearance to the plastic. Glasses are frequently modified by inclusion of color-producing agents or by application of coatings. In this way, a wide range of light transmission characteristics can be achieved in packages made of the same basic material.

The catalytic effect of light on the free radical reactions involved in fat oxidation is well established; such oxidation is effective not only in lowering the nutritional value of the fat, but also in producing toxic compounds from the fats and oils and destroying fat-soluble vitamins, in particular vitamins A and E.

There have been many studies demonstrating the effect of packaging materials with different light screening properties on the rate of deteriorative reactions in foods. One of the most commonly studied foods has been fluid milk, and the extent of off-flavor development is related to the exposure interval, strength of light and surface area of milk exposed. Many researchers have shown that exposure to visible light between 365 and 500 nm causes a significant increase in light-induced oxidation in milk. All wavelengths below 620 nm must be blocked to prevent “sunlight” flavor in milk.

Smet et al. (2009) reported that for light-induced oxidation in milk, riboflavin was the key factor since it is an excellent photosensitizer, resulting in the production of reactive oxygen species that can catalyze oxidation reactions. The presence of light was strongly detrimental to the oxidative stability of stored milk, observed by degradation of riboflavin. During the first days of illuminated storage, hydrophilic antioxidants present in the milk serum were consumed, followed by degradation of α-tocopherol. When all these antioxidants were depleted, lipid and protein oxidation products were formed.

In summary, light plays an important role in the deterioration of nutrients. Suitable packaging can offer direct protection by absorption or reflection of all or part of the incident light, depending on the light transmission characteristics of the packaging materials. Several plastic packaging materials, while transmitting similar amounts of light in the visible range, give varying degrees of protection against damaging UV wavelengths. These materials are often characterized by a cut-off wavelength below which transmission of light becomes negligible.

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12 Shelf Life of Foods

12.1 DEFINITIONS

The term *food quality* has a variety of meanings to professionals in the food industry, but the ultimate arbiters of food quality must be consumers. This notion is embodied in the frequently cited definition of food quality as "the combination of attributes or characteristics of a product that have significance in determining the degree of acceptability of the product to a user." Another definition of food quality is "the acceptance of the perceived characteristics of a product by consumers who are regular users of the product category or those who comprise the market segment." The phrase "perceived characteristics" includes the perception of the food's safety, convenience, cost, value and so on.

The quality of most foods and beverages decreases with storage or holding time. Exceptions include distilled spirits (particularly whiskeys and brandies), which develop desirable flavor components during storage in wooden barrels, some wines, which undergo increases in flavor complexity during storage in glass bottles, and many cheese varieties, where enzymic degradation of proteins and carbohydrates, together with hydrolysis of fat and secondary chemical reactions, leads to desirable flavors and textures in aged cheeses.

For the majority of foods and beverages in which quality decreases with time, it follows that there will be a finite length of time before the product becomes unacceptable. This time from production to unacceptability is referred to as *shelf life*. Although the Wizard of Id (and maybe many consumers) thought that shelf life related to the time until the shelf displaying the food rotted out (see Figure 12.1), shelf life includes the time on the retailer's shelf as well as the consumer's shelf, plus time in warehouses and the distribution chain. Although the shelf lives of foods vary, they are generally determined routinely for each particular product by the manufacturer or processor who attempts to provide the longest practicable shelf life consistent with costs and the pattern of handling and use by distributors, retailers and consumers. Supermarkets will generally not accept product into their distribution centers unless at least 75% of the shelf life remains.

Quality loss during storage may be regarded as a form of processing at relatively low temperatures that goes on for rather a long time. It is, therefore, not surprising that many of the concepts developed in connection with food processing find application in shelf life studies. Such studies are an essential part of food product and package development, which should be carried out in parallel.

Inadequate shelf life will often lead to consumer dissatisfaction and complaints. At best, such dissatisfaction will eventually affect the acceptance and sales of brand-name products, and, at worst, it can lead to illness or even malnutrition. Therefore, food processors pay considerable attention to determining the shelf lives of their products.

Despite its importance, there is no simple, generally accepted definition of shelf life in the food technology literature. The Institute of Food Technologists (IFT) in the United States defined shelf life (Shelf life of foods, 1974) as "the period between the manufacture and the retail purchase of a food product, during which time the product is in a state of satisfactory quality in terms of nutritional value, taste, texture and appearance." This definition overlooks the fact that the consumer may store the product at home for some time before consuming it yet will still want the product to be of acceptable quality.

The Institute of Food Science and Technology (IFST) in the United Kingdom defined shelf life as "the period of time during which the food product will remain safe; be certain to retain desired sensory, chemical, physical, microbiological and functional characteristics; and comply with any label declaration of nutritional data when stored under the recommended conditions" (*Shelf Life of Foods: Guidelines for Its Determination and Prediction*, 1993).

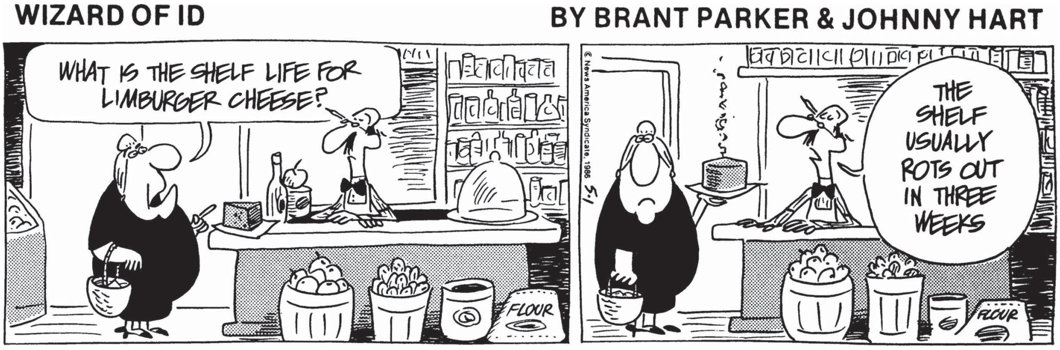

FIGURE 12.1 Shelf life according to the Wizard of Id. (Used with permission of John L. Hart FLP, Creators Syndicate, Inc., Los Angeles, CA.)

ASTM E2454 "Standard Guide for Sensory Evaluation Methods to Determine the Sensory Shelf Life of Consumer Products" defines sensory shelf life (SSL) as "the time period during which the products' sensory characteristics and performance are as intended by the manufacturer." The product is consumable or usable during this period and provides the end user with the intended sensory characteristics, performance and benefits. In this standard, shelf life is described as "the time period that a product may be stored before reaching its end point" and defines the endpoint as "the point at which a product no longer meets predetermined criteria as defined by test data (e.g., discrimination, descriptive or affective, or a combination thereof)."

Another definition is that "shelf life is the duration of that period between the packing of a product and the end of consumer quality as determined by the percentage of consumers who are displeased by the product" (Labuza and Schmidl, 1988). This definition accounts for the variation in consumer perception of quality (i.e., not all consumers will find a product unacceptable at the same time) and has an economic element in that, because it is not possible to please all consumers all of the time, a baseline of consumer dissatisfaction must be established (Labuza and Szybist, 1999).

Until recently, the European Union (EU) had no definition of shelf life or legislation on how shelf life should be determined. The consolidated EU Directive on food labeling (2000/13/EEC) requires prepackaged foods to bear a date of "minimum durability" or, in the case of foods that from the microbiological point of view are highly perishable, the "use by" date. The date of minimum durability is defined as the "date until which a foodstuff retains its specific properties when properly stored" and any special storage conditions (e.g., temperature not to exceed 7°C) must be specified. This concept (essentially equivalent to the "best before" date defined in the following) allows the processor to set the quality standard of the food, because the product would still be acceptable to many consumers after the "best before" date has passed. More recently, shelf life was defined for the first time in EU legislation in Commission Regulation (EC) No. 2073/2005 thus: "Shelf-life means either the period corresponding to the period preceding the 'use by' or the minimum durability date, as defined respectively in Articles 9 and 10 of Directive 2000/13/EC."

According to Cheftel (2005), the date of minimum durability must be indicated by the words "Best before" followed by the date (or a reference to where the date is given on the labeling). Depending on how long the food can keep, the date can be expressed by the day and the month, the month and year, or the year alone. A list of foods and beverages exempted from date marking is given in Article 9(5) of Directive 2000/13/EC. Foods that are highly perishable microbiologically (and therefore likely to be dangerous for health after a short period of time) must indicate the words "Use by" followed by the date (day and month) or a reference to where the date is given on the labeling. Any distribution after this date is forbidden. The "use by" date must be followed by a description of the storage conditions that should be observed.

In many countries a “best before” date is required to appear on the label. However, if the food is highly perishable from a microbiological point of view and, therefore, likely, after a short period, to constitute an immediate danger to human health, then the “best before” date must be replaced by a “use by” date. It is illegal to sell food after the “use by” date; food consumed after the “best before” date will still be edible but its quality will have deteriorated to a level below what the manufacturer considers desirable. Recently, the use of the hybrid term “best by” has become popular. A major U.S. brewer now labels bottles of beer with the “born on” date, that is, the date of bottling, leaving consumers to decide when the beer is no longer acceptable.

Given the variety of definitions, it is not surprising that there is no uniform or universally accepted open dating system for packaged foods. In some countries, mandatory open dating of all perishable (and sometimes semi-perishable) foods is required, while in other countries such requirements are voluntary. Arguments can be advanced both for and against the open dating of foods. However, there is an increasing quantity of open-dated food on sale throughout the world, and this trend is likely to continue.

12.2 SHELF LIFE DETERMINATION

12.2.1 Introduction

There are at least three situations when a shelf life determination might be required:

1. To determine the shelf life of existing products
2. To study the effect of specific factors or combinations of factors such as storage temperature, packaging materials, processing parameters or food additives on product shelf life
3. To determine the shelf life of prototype or newly developed products

Several established approaches are available for estimating the shelf life of foods:

1. *Literature study*: The shelf life of an analogous product is obtained from the published literature or in-house company files. Examples can be found in recent books on the shelf life of foods (e.g., Robertson, 2010; Kilcast and Subramaniam, 2011). The problem is that these data are very limited and generally apply to commodity-type foods.
2. *Turnover time*: The average length of time which a product spends on the retail shelf is found by monitoring sales from retail outlets, and from this the required shelf life is estimated. This does not give the “true” shelf life of the product but rather the “required” shelf life, where it is implicitly assumed that the product is still acceptable for some time after the average period on the retail shelf.
3. *Endpoint study*: Random samples of the product are purchased from retail outlets and then tested in the laboratory to determine their quality. From this, a reasonable estimation of shelf life can be obtained because the product has been exposed to actual environmental stresses encountered during warehousing and retailing.
4. *ASLT*: Laboratory studies are undertaken during which environmental conditions are accelerated by a known factor so that the product deteriorates at a faster than normal rate. This method requires that the effect of environmental conditions on product shelf life can be quantified. This approach is discussed later in this chapter.

Shelf life can be determined from two sides: the product side or the consumer side (van Boekel, 2009). Determining shelf life from the product side implies that the deterioration of the product is investigated as a function of time and may involve measuring the number of microorganisms or the decrease in desired components such as nutrients or texture, or the increase in undesired components such as brown pigments, off-flavors or moisture. Several models are available to assist in the determination and are discussed later in this chapter. Alternatively, determining shelf life from the consumer side implies asking consumers to accept or reject food that has been stored for various lengths of time without normally specifying the reason. In the branch of statistics known as survival analysis, consumer dissatisfaction can be related to the survival function, defined as "the probability of a consumer accepting a product beyond a certain storage time." Models permitting the application of survival analysis to the sensory shelf life of foods have been published and are discussed later in this chapter.

12.2.2 Critical Descriptors and Indices of Failure

When a food is stored, changes occur that can be defined by one or more descriptors. The critical descriptor is the one that limits shelf life (Hough, 2010). In designing suitable packaging for foods, it is important first to define the critical descriptor(s) or indices of failure (IoFs) of the food, that is, the quality attributes that will indicate that the food is no longer acceptable to the consumer. In shelf life testing, there can be one or more critical descriptors that constitute sample failure. An IoF could be development of rancid flavors in cereals due to oxidation, loss of red color (bloom) in chilled beef due to depletion of O_2, reduction of carbonation in bottled soda due to permeation by CO_2 through the bottle wall, caking of instant coffee due to moisture ingress, development of microbial taint in chilled poultry, loss of crispness in a snack food due to moisture uptake or moisture loss in green vegetables resulting in wilting.

When the shelf life is determined from the product side, sensory evaluation of the food is likely to be used either alone or in combination with instrumental or chemical analyses to determine the quality of the product. Many sensory test methodologies are available and can be classified into either analytical tests or hedonic tests as shown in Figure 12.2. Analytical tests are used to measure the sensory characteristics of foods and answer questions such as "Is there a difference?" "What is the nature of the difference?" and "How big is (are) the difference(s)?" Hedonic or affective tests are used to measure consumer response to the sensory characteristics of foods and answer questions such as "Which food is preferred?" and "How much is it liked?" (Kilcast, 2011). ASTM E2454 describes three types of SSL endpoints: (1) the product's overall sensory profile has changed;

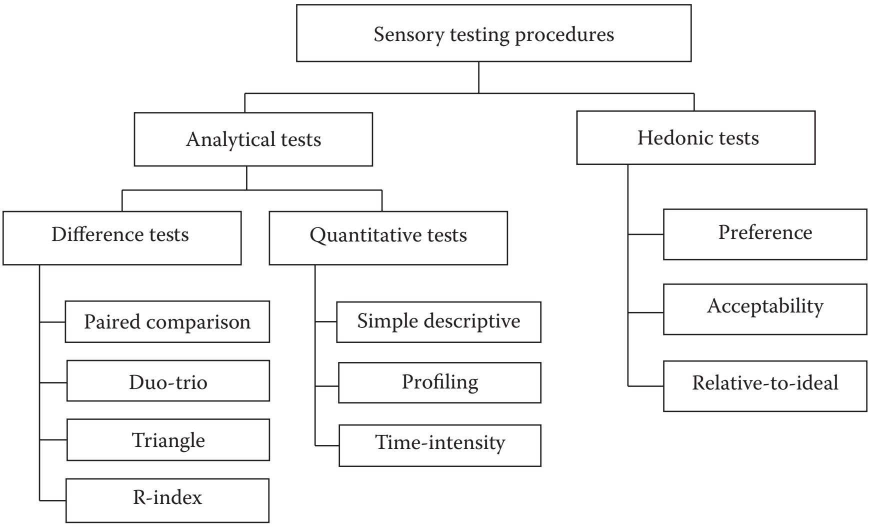

FIGURE 12.2 Main classes of sensory testing procedures. (From Kilcast, D., Sensory evaluation methods for food shelf life assessment, in: *Food and Beverage Stability and Shelf Life*, Kilcast, D. and Subramaniam, P. (Eds), Woodhead Publishing, Cambridge, England, pp. 350–380, 2011.)

(2) a product attribute(s) that is known or suspected to be key to the consumers' perception of the product has changed and (3) the acceptability of the product is too low.

12.2.3 CUTOFF POINT

Once the critical descriptor or IoF for a particular food has been defined, the next step is to specify the cutoff point (COP) or the endpoint of the particular degradation, for example, how much moisture or O_2 can react with the food, or how much the flavor can deteriorate, before the food becomes unacceptable. The COP indicates the limit on an analytical sensory scale or instrumental measurement beyond which (normally) acceptance by the consumer is significantly decreased (Hough, 2010). A sensory COP could be an increase or decrease by a specified amount in the mean panel score. The determination of a sensory COP is a function of the criteria selected, the test method used and sampling risk.

Three test methods are most commonly used: (1) discrimination, (2) descriptive and (3) affective. Descriptive methods are used to measure quantitative and/or qualitative characteristics of products and require specially trained panelists. Affective methods are used to evaluate preference, acceptance and/or opinions of products and do not require trained panelists. Further details about these tests can be found in standard texts on sensory evaluation (e.g., Meilgaard et al., 2007; Lawless and Heymann, 2010).

The selection of a particular sensory evaluation procedure for evaluating products undergoing shelf life testing is dependent on the purpose of the test. Acceptability assessments by untrained panelists are essential to an open dating program, while discrimination testing with expert panels might be used to determine the effect of a new packaging material on product stability. However, an expert panel is not necessarily representative of consumers, much less different consumer segments. Even if that assumption can be made, a cutoff level of acceptability has to be decided. The time at which a large (but predetermined) percentage of panelists judge the food to be at or beyond that level is the end of shelf life, but just what that percentage is depends on the company and is a business rather than a technical decision.

Although a consumer panel would seemingly be the most appropriate tool to determine the shelf life and quality of a food product, to repeatedly assemble consumer panels for multiple measurements would be both impractical and expensive. Although a sensory panel is more appropriate for repeated assessments, its results would be more analytical and not necessarily representative of consumer responses. By correlating data from a consumer panel with those obtained from a trained panel, these analytical measures can be used to determine the shelf life or quality of a food product, greatly benefiting sensory quality control programs.

Not surprisingly, many food scientists and technologists in industry attempt to replace human judgment or sensory panels with instrumental or chemical analyses because the latter are neither prone to fatigue nor subject to the physiological and psychological fluctuations that characterize human performance. However, because human judgment is the ultimate arbiter of food acceptability, it is essential that the results obtained from any instrumental or chemical analysis correlate closely with the sensory judgments for which they are to substitute. Correlation of values of individual chemical parameters with sensory data is often not straightforward because overall organoleptic quality is a composite of a number of changing factors (Kilcast, 2011). The relative contribution of each factor to the overall quality may vary at different levels of quality or at different storage conditions. Other problems with sensory evaluation include the high cost of using large testing panels and the ethics of asking panelists to taste spoiled or potentially hazardous samples.

Alternatively, a COP could be microbial deterioration of the sample to an extent that renders it unsuitable or unsafe for human consumption. Other COPs could relate to changes in odor, color, texture, flavor and so on, which render the sample unacceptable to the consumer. Thus, the COP can be defined as the condition when the product exhibits either physical, chemical, microbiological or sensory characteristics that are unacceptable to the consumer, and the time required for the food to exhibit such conditions is the shelf life of the food. One challenge with shelf life testing is to develop experimental designs that minimize the number of samples required (thus minimizing the cost of the testing), while still providing reliable and statistically valid answers.

12.2.4 INFLUENCE OF PACKAGING MATERIAL

The final step is to ascertain which (if any) of the critical descriptors or IoFs might be influenced by the packaging material, as packaging cannot prevent all deteriorative reactions or undesirable changes in foods. If, for example, the IoF of a snack food was loss of crispness, then the packaging material could influence this by the extent to which it permitted the ingress of moisture. Different plastic films, for example, have different WVTRs and, thus, the shelf life obtained varies depending on the particular plastic polymer(s) selected for a given pack size.

Similar considerations apply to foods for which the IoF is oxidation, as different packaging materials have different OTRs. However, it is not just the packaging material itself that can influence shelf life; the method of filling the product into the package is also important. For example, with roasted and ground coffee, vacuum filling into metal cans will remove 95% or more of the O_2 from the can compared with inert gas flush packing in plastic foil laminate pouches, which will remove or displace 80%–90% of the O_2 in the package. The residual O_2 in the package at the time of filling will have a major influence on shelf life regardless of the O_2 barrier properties of the package itself.

If the food is sensitive to light, then the packaging material can have a significant influence, depending on how much light and at what wavelengths it is transmitted, as discussed in Section 11.5.3.

12.3 DETERMINING SHELF LIFE FROM THE PRODUCT SIDE

The shelf life of a food is controlled by three factors:

1. The product characteristics including formulation and processing parameters (intrinsic factors)
2. The properties of the package
3. The environment to which the product is exposed during distribution and storage (extrinsic factors)

Intrinsic factors include pH, a_w, enzymes, microorganisms and concentration of reactive compounds. Many of these factors can be controlled by selection of raw materials and ingredients, as well as the choice of processing parameters.

Extrinsic factors include temperature, RH, light, total pressure and partial pressure of different gases, as well as mechanical stresses including consumer handling. Many of these factors can affect the rates of deteriorative reactions that occur during the shelf life of a product.

The properties of the package can have a significant effect on many of the extrinsic factors and, thus, indirectly on the rates of the deteriorative reactions. Thus, the shelf life of a food can be altered by changing its composition and formulation, processing parameters, packaging system or environment to which it is exposed.

12.3.1 PRODUCT CHARACTERISTICS

12.3.1.1 Perishability

Based on the nature of the changes that can occur during storage, foods may be divided into three categories—perishable, semi perishable and nonperishable or shelf stable, which translate into very short shelf life foods, short to medium shelf life foods and medium to long shelf life foods.

Perishable foods are those that must be held at chill or freezer temperatures (i.e., 0°C to 7°C or −12°C to −18°C, respectively) if they are to be kept for more than short periods. Examples of such foods include milk, fresh flesh foods such as meat, poultry and fish, minimally processed foods and many fresh fruits and vegetables.

Semi perishable foods are those that contain natural inhibitors (e.g., some cheeses, root vegetables and eggs) or those that have received some type of mild preservation treatment (e.g., pasteurization of milk, smoking of hams and pickling of vegetables) that produces greater tolerance to environmental conditions and abuse during distribution and handling.

Shelf stable foods are considered *nonperishable* at room temperatures. Many unprocessed foods fall into this category, and are unaffected by microorganisms because of their low moisture content (e.g., cereal grains and nuts, and some confectionery products). Processed food products can be shelf stable if they are preserved by heat sterilization (e.g., canned foods), contain preservatives (e.g., soft drinks), are formulated as dry mixes (e.g., cake mixes) or processed to reduce their water content (e.g., raisins or crackers). However, shelf stable foods only retain this status if the integrity of the packages that contain them remains intact. Even then, their shelf life is finite due to deteriorative chemical reactions that proceed at room temperature independently of the nature of the package, and the permeation through the package of gases, odors and water vapor.

12.3.1.2 Bulk Density

The free space volume of a package (V) is directly related to the bulk density (ρ_b) and the true density (ρ_p) of the food as follows:

$$V = V_t - V_p = \frac{W}{\rho_b} - \frac{W}{\rho_p} \tag{12.1}$$

where

V_t is the total volume of the package
V_p is the volume of the product
W is the weight of the product

Thus, for packages of similar shape, equal weights of foods of different bulk densities will have different free space volumes, and, therefore, package areas and package behavior will differ. This has important implications when changes are made in package size for the same food, or alterations are made to the process, which result in changes to the food bulk density.

While the true density of a food depends largely on its composition and cannot be changed significantly, the bulk density of food powders can be affected by processing and packaging. Some food powders (e.g., milk and coffee) are instantized by treating individual particles so that they form free-flowing agglomerates or aggregates in which there are relatively few points of contact; the surface of each particle is, thus, more easily wetted when the powder is rehydrated. Instantization results in a reduction of bulk density—for example, for skim milk powder, from 0.64 to 0.55 g mL^{-1}. A wide range of bulk densities is encountered in foods, from around 0.056 g mL^{-1} for potato chips to 0.96 for granulated salt.

The free space volume has an important influence on the rate of oxidation of foods: if a food is packaged in air, then a large free space volume is undesirable because it constitutes a large O_2 reservoir. Conversely, if the product is packaged in an inert gas, then a large free space volume acts as a huge "sink" to minimize the effects of O_2 transferring into the package. It follows that a large package surface area and a low food bulk density result in greater O_2 transmission.

12.3.1.3 Concentration Effects

In Chapter 11, the major types of deteriorative reactions that are likely to be encountered in packaged foods were described, with the factors affecting the rates of these reactions quantified with the aid of simple chemical kinetic expressions. Thus, the progress of a deteriorative reaction can be monitored by following the change in concentration of some key component.

However, in many foods such as those containing whole tissue components, or where the reacting species are partially bound as in membranes, structural proteins or carbohydrates, the concentration varies from one point to another, even at zero time. Furthermore, because most of these compounds will have little opportunity to move, the concentration differences will get greater as the reactions proceed out from isolated initial foci. This has been described as the "brush-fire" effect and is especially important in chain reactions such as oxidation.

In addition, there may be several different stages of the deteriorative reaction proceeding at once, and the different stages may have different dependence on concentration and temperature, giving disguised kinetics. Such a situation is frequently the case for chain reactions and microbial growth, which have both a lag and a log phase with very different rate constants.

The point to be taken from this is that for many foods, it may be difficult to obtain kinetic data of use for predictive purposes. In such situations, use of sensory panels to determine the acceptability of the food is the recommended procedure (provided, of course, that there are no microbial risks).

12.3.2 PACKAGE PROPERTIES

Foods can be classified according to the degree of protection required, and a very generalized scheme is shown in Table 12.1. The advantage of this sort of analysis is that attention can be focused on the key requirements of the package such as maximum moisture gain or O_2 uptake. This then enables calculations to be made to determine whether or not a particular packaging material would provide the necessary barrier required to give the desired product shelf life. In the case of metal cans and glass containers, these can be regarded as essentially impermeable to the passage of gases, odors and water vapor, while paper-based packaging materials can be regarded as permeable. This then leaves plastics-based packaging materials that provide varying degrees of protection, depending largely on the nature of the polymers used in their manufacture.

In Chapter 4, the permeability of thermoplastic polymers was discussed. The way in which this information can be utilized to select the most appropriate polymer for a particular product is discussed in the following.

The expression for the steady-state permeation of a gas or vapor through a thermoplastic material was derived earlier (see Equation 4.13) and can be written as

$$\frac{\delta w}{\delta t} = \frac{P}{X} A(p_1 - p_2) \tag{12.2}$$

where

P/X is the permeance (the permeability constant P divided by the thickness of the film X)
A is the surface area of the package
p_1 and p_2 are the partial pressures of water vapor outside and inside the package
$\delta w/\delta t$ is the rate of gas or vapor transport across the film, where the latter term corresponds to Q/t in the integrated form of the expression

12.3.2.1 Water Vapor Transfer

The prediction of moisture transfer either to or from a packaged food requires analysis of the preceding equation given certain boundary conditions. The simplest analysis requires the assumptions that P/X is constant, that the external environment is at constant temperature and humidity, and that p_2, the vapor pressure of the water in the food, follows some simple function of the moisture content.

External conditions will not remain constant during storage, distribution and retailing of a packaged food. Therefore, P/X will not be constant. However, using WVTRs determined at 38°C and

TABLE 12.1
Degree of Protection Required by Various Foods and Beverages (Assuming 1 Year Shelf Life at 25°C)

Food/Beverage	Maximum Amount of O_2 Gain (ppm)	Other Gas Protection Needed	Maximum Water Gain or Loss	Requires High Oil Resistance	Requires Good Barrier to Volatile Organics
Canned milk and flesh foods	1–5	No	3% Loss	Yes	No
Baby foods	1–5	No	3% Loss	Yes	Yes
Beers and wine	1–5	<20% CO_2 (or SO_2) loss	3% Loss	No	Yes
Instant coffee	1–5	No	2% Gain	Yes	Yes
Canned soups, vegetables and sauces	1–5	No	3% Loss	No	No
Canned fruits	5–15	No	3% Loss	No	Yes
Nuts, snacks	5–15	No	5% Gain	Yes	No
Dried foods	5–15	No	1% Gain	No	No
Fruit juices and drinks	10–40	No	3% Loss	No	Yes
Carbonated soft drinks	10–40	<20% CO_2 loss	3% Loss	No	Yes
Oils and shortenings	50–200	No	10% Gain	Yes	No
Salad dressings	50–200	No	10% Gain	Yes	Yes
Jams, jellies, syrups, pickles, olives, vinegars	50–200	No	10% Gain	Yes	No
Liquors	50–200	No	3% Loss	No	Yes
Condiments	50–200	No	1% Gain	No	Yes
Peanut butter	50–200	No	10% Gain	Yes	No

Source: Adapted from Salame, M., The use of low permeation thermoplastics in food and beverage packaging, in: *Permeability of Plastic Films and Coatings*, Hopfenberg, H.B. (Ed.), Plenum, New York, p. 275, 1974.

90% RH gives a "worst-case" analysis, but if the food is being sold in markets in temperate climates, use of WVTRs determined at 25°C and75% RH is more appropriate. As noted in Chapter 4, WVTRs can be converted to permeances by dividing by Δp.

A further assumption is that the moisture gradient inside the package is negligible; that is, the package should be the major resistance to water vapor transport. This is the case whenever P/X is less than about $10\,\mathrm{g\ m^{-2}\ day^{-1}\ (cm\ Hg)^{-1}}$, which is the case for most films but not paperboard under high humidity conditions.

The critical point about Equation 12.2 is that the internal vapor pressure is not constant but varies with the moisture content of the food at any time. Thus, the rate of gain or loss of moisture is not constant but falls as Δp gets smaller. Therefore, some function of p_2, (the internal vapor pressure) as a function of the moisture content, must be inserted into the equation to be able to make proper predictions. If a constant rate is assumed, then the food will be overprotected.

In low and intermediate moisture foods, the internal vapor pressure is determined solely by the moisture sorption isotherm of the food (Bell and Labuza, 2000). As discussed in Section 11.4.1.2, several functions can be applied to describe a sorption isotherm, although the preferred one is the

GAB model. If a linear model is used, the result can be integrated directly, but if the GAB model is used, then it must be numerically evaluated.

In the simplest case when the isotherm is treated as a linear function

$$m = ba_{\mathrm{w}} + c \tag{12.3}$$

where

m is the moisture content in g H_2O g^{-1} solids
a_{w} is the water activity
b is the slope of the isotherm
c is the constant

The moisture content can be substituted for water gain using the relationship

$$m = \frac{W \text{ (weight of water transported)}}{W_{\mathrm{s}} \text{ (weight of dry solids enclosed)}} \tag{12.4}$$

$$\therefore W = mW_{\mathrm{s}} \tag{12.5}$$

and

$$\delta W = \delta m W_{\mathrm{s}} \tag{12.6}$$

By substitution

$$\frac{\delta W}{\delta t} = \frac{\delta m W_{\mathrm{s}}}{\delta t} = \frac{P}{X} A\left[\frac{p_0 m_{\mathrm{e}}}{b} - \frac{p_0 m}{b}\right] \tag{12.7}$$

which on rearranging, gives

$$\frac{\delta m}{m_{\mathrm{e}} - m} = \frac{P}{X}\frac{A}{W_{\mathrm{s}}}\frac{p_0}{b}\delta t \tag{12.8}$$

and on integrating

$$\ln\frac{m_{\mathrm{e}} - m_{\mathrm{i}}}{m_{\mathrm{e}} - m} = \left[\frac{P}{X}\frac{A}{W_{\mathrm{s}}}\frac{p_0}{b}\right]t \tag{12.9}$$

where

m_{e} is the equilibrium moisture content of the food if exposed to external package RH
m_{i} is the initial moisture content of the food
m is the moisture content of the food at time t
p_0 is the vapor pressure of pure water at the storage temperature (*not* the actual vapor pressure outside the package)

A plot of the log of the unaccomplished moisture change—the term on the left-hand side of Equation 12.9—versus time is a straight line with a slope equivalent to the bracketed term on the right-hand side of the equation.

The end of product shelf life is reached when $m = m_{\mathrm{c}}$, the critical moisture content, at which time $t = \theta_{\mathrm{s}}$, the shelf life. Thus, Equation 12.9 can be rewritten as

$$\ln\frac{m_{\mathrm{e}} - m_{\mathrm{i}}}{m_{\mathrm{e}} - m_{\mathrm{c}}} = \frac{P}{X}\frac{A}{W_{\mathrm{s}}}\frac{p_0}{b}\theta_{\mathrm{s}} \tag{12.10}$$

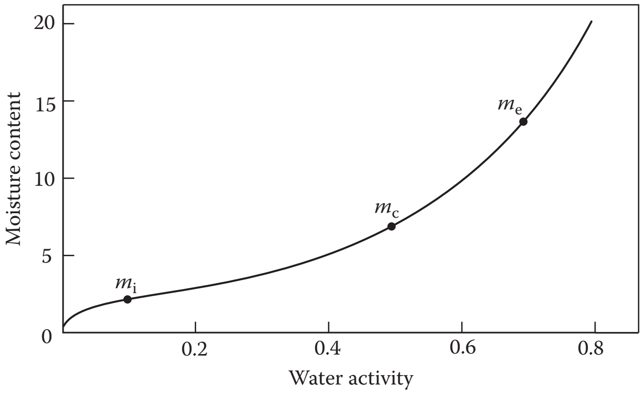

FIGURE 12.3 Typical moisture sorption isotherm for a snack bar, where m_i is the initial moisture content; m_c is the critical moisture content of product; and m_e is the equilibrium moisture content.

The relationship between the initial, critical and equilibrium moisture contents is illustrated in Figure 12.3.

Equation 12.10 and the corresponding one for moisture loss

$$\ln\frac{m_i - m_e}{m - m_e} = \frac{P}{X}\frac{A}{W_s}\frac{p_0}{b}\theta_s \tag{12.11}$$

have been extensively tested for foods and found to give excellent predictions of actual weight gain or loss. These equations are also useful when calculating the effect of changes in the external conditions (e.g., temperature and humidity), the surface area:volume ratio of the package and variations in the initial moisture content of the product.

Example 12.1

A breakfast cereal has an initial moisture content m_i of 2.5%. The COP is the critical moisture content m_c of 8% due to loss of crispness (Robertson, 2011a). The equilibrium moisture content m_e at 25°C is 14.8% and the pseudo-equilibrium moisture content m_e' obtained by extension of the linear portion of the isotherm is 11%; the slope of the line (b) is 0.147 g H_2O/g solids/unit a_w (see Figure 12.4).

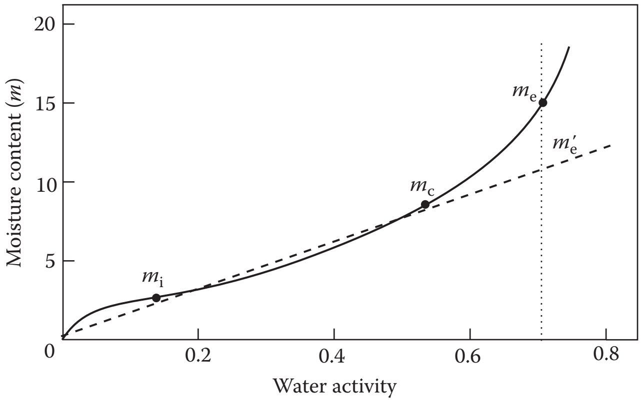

FIGURE 12.4 Schematic of a typical moisture sorption isotherm for breakfast cereal with a superimposed straight line of slope b. Initial (m_i), critical (m_c) and equilibrium (m_e) moisture contents are indicated together with the pseudo-equilibrium (m_e') moisture content used for package shelf life calculations.

Calculate the shelf life of the cereal if it is packaged in a bag of 50 µm LDPE or 50 µm OPP. The weight of dry cereal in the package is 400 g and the dimensions of the bags are 20 cm × 30 cm. The packed product is to be stored at 25°C and 75% RH.

$$\text{Surface area of the bags is } 20 \times 30 = 600\ \text{cm}^2 = 0.06\ \text{m}^2$$

$$\text{Vapour pressure of pure water at } 25°\text{C} = 2.3756\ \text{cm Hg}$$

Data from a plastic film supplier indicated that WVTRs determined at 25°C/75% RH were

$$50\ \mu\text{m LDPE} = 8.0\ \text{g m}^{-2}\,\text{day}^{-1}$$

$$50\ \mu\text{m OPP} = 1.35\ \text{g m}^{-2}\,\text{day}^{-1}$$

These WVTRs must be converted into water vapor permeances *P*/*X* by dividing by the driving force for water vapor transfer. The saturated water vapor pressure at 25°C is (from Table 4.10) 2.376. Thus, the driving force at 25°C/75% RH is

$$2.376 \times 0.75 = 1.782\ \text{cm Hg}$$

For LDPE film,

$$\frac{P}{X} = \frac{8.0\,\text{g}}{\text{m}^2\,\text{day}} \times \frac{1}{1.782\,(\text{cmHg})}$$
$$= 4.489\,\text{g}\,\text{H}_2\text{O}\,\text{m}^{-2}\,\text{day}^{-1}\,(\text{cmHg})^{-1}$$

For OPP film,

$$\frac{P}{X} = \frac{1.35\,\text{g}}{\text{m}^2\,\text{day}} \times \frac{1}{1.782\,(\text{cmHg})}$$
$$= 0.758\,\text{g}\,\text{H}_2\text{O}\,\text{m}^{-2}\,\text{day}^{-1}\,(\text{cmHg})^{-1}$$

Substituting into Equation 12.10 for cereal packed in LDPE film,

$$\ln\frac{11-2.5}{11-8} = 4.489 \cdot \frac{0.06}{400} \cdot \frac{2.3756}{0.147} \cdot \theta_s \tag{12.12}$$

Solving for shelf life θ_s,

$$\theta_s = \frac{[\ln 2.833]}{1.088 \times 10^{-2}}$$
$$= \frac{1.0413}{1.088 \times 10^{-2}}$$
$$= 96\,\text{days}$$

If the cereal were packed in OPP film instead,

$$\theta_s = \frac{[\ln 2.833]}{1.837 \times 10^{-3}}$$
$$= 567\,\text{days}$$

The shelf life is inversely related to the water vapor permeances of the film; since *P*/*X* for LDPE is 5.9 times that for OPP, the shelf life in the latter film is 5.9 times that in the former. If the required shelf life were, say, 300 days, then Equation 12.10 could be recalculated using $t_s = 300$ and solved for P/X. From this, the corresponding WVTR could be calculated and the film supplier requested to supply a film that met this specification at 25°C and 75% RH.

As noted earlier, the shelf lives calculated earlier will be longer than what would be achieved in practice because the pseudo-equilibrium moisture content m_e' used in the calculations is less than the actual equilibrium moisture content, which is the real driving force for water vapor transport. Because of the simplifying assumptions made in the earlier calculations, the calculated shelf lives should be verified by actual shelf life testing.

12.3.2.2 Gas and Odor Transfer

The gas of major importance in packaged foods is O_2 because it plays a crucial role in many reactions that affect the shelf life of foods (e.g., microbial growth, color changes in fresh and cured meats, oxidation of lipids and consequent rancidity and senescence of fruits and vegetables).

The transfer of gases and odors through packaging materials can be analyzed in an analogous manner to that described for water vapor transfer, provided that values are known for the permeance of the packaging material to the appropriate gas, and the partial pressure of the gas inside and outside the package. Regrettably, the latter data are scarce for all but the common gases.

Packaging can control two variables with respect to O_2, and these can have different effects on the rates of oxidation reactions in foods:

1. *Total amount of O_2 present*: This influences the extent of the reaction, and in impermeable packages (e.g., hermetically sealed metal and glass containers), where the total amount of O_2 available to react with the food is finite, the extent of the reaction cannot exceed the amount corresponding to the complete exhaustion of the O_2 present inside the package at the time of sealing. This may or may not be sufficient to result in an unacceptable product quality after a certain period of time dependent on the rate of the oxidation reaction. Of course, such a rate will be temperature dependent. With permeable packages (e.g., plastic packages), where ingress of O_2 will occur during storage, two factors are important: there may be sufficient O_2 inside the package to cause product unacceptability when it has all reacted with the food, or there may be sufficient transfer of O_2 through the package over time to result in product unacceptability through oxidation.
2. *Concentration of O_2 in the food:* In many cases, relationships between the O_2 partial pressure in the space surrounding the food and the rates of oxidation reactions can be established. If the food itself is very resistant to diffusion of O_2 (e.g., very dense products such as butter), then it will likely be very difficult to establish a relationship between the O_2 partial pressure in the space surrounding the food and the concentration of O_2 in the food.

The principal difference between predominantly water-vapor-sensitive and O_2-sensitive foods is that the latter are generally more sensitive by 2–4 orders of magnitude. Thus, the amount of O_2 present in the air-filled headspace of O_2-sensitive foods must not be neglected when predicting their shelf life. This amount is actually 32 times higher per unit volume of air than per unit volume of O_2-saturated water. A further complicating factor with O_2-sensitive foods is that, in these foods, a concentration gradient occurs much more frequently than in moisture-sensitive foods. In the latter, it is practically limited to hard-boiled candies and freezer burn in frozen foods.

Example 12.2

Suppose that the feasibility of packaging fine wine in an oriented PET bottle with O_2 and SO_2 permeabilities of 0.03 and 0.3 *barrer*, respectively (all permeabilities calculated in air at 25°C and 50% RH on one side and 100% RH on the other) is to be investigated. If each bottle has a surface area of 720 cm^2, a thickness of 0.046 cm and holds 1 L of wine, calculate the shelf life of the wine in the bottle, assuming that the bottles are perfectly sealed with gas-impermeable, screwcap closures. The COP for the wine is when 5 ppm O_2 and half of the free SO_2 (25 ppm) has permeated through the bottle wall.

(a) Oxygen Ingress:

Because the atmosphere has an O_2 concentration of 21%, the O_2 vapor pressure outside the bottle will be $0.21 \times 76 = 16.0$ cm Hg. Assume that the O_2 vapor pressure inside the bottle is zero.

The maximum quantity of O_2 able to be absorbed by the wine and still retain acceptable quality is 5 ppm = 5 mg L^{-1} = 5×10^{-3} g L^{-1}, and because the bottle holds 1 L, 5×10^{-3} g of O_2 can be absorbed.

Using a value for the density of oxygen of 1.43×10^{-3} g mL^{-1}, the maximum quantity of oxygen (Q) permissible = $(5 \times 10^{-3})/(1.43 \times 10^{-3}) = 3.5$ mL.

Equation 4.13 can then be used:

$$\frac{Q}{t} = \frac{P}{X} A(p_1 - p_2) \tag{12.13}$$

which, on rearrangement and letting $t = \theta_s$ (the shelf life), is

$$\theta_s = \frac{QX}{PA\Delta p} \tag{12.14}$$

$$\theta_s = \frac{3.5 \times 0.046}{0.03 \times 10^{-10} \times 720 \times 16} = 4.654 \times 10^6\,\text{s} = 54\,\text{days}$$

(b) Sulfur Dioxide Egress:

Assume that the initial concentration of SO_2 in the wine is 100 ppm and that 50% of this is in the free form. The vapor pressure of 50 ppm SO_2 in the wine has been estimated to be 1.73×10^{-3} cm Hg.

If the units for ρ are g mL^{-1} and for V_w g, then the units for Q (the quantity of SO_2 permeating through the bottle wall) will be g SO_2 g^{-1} of wine. The initial level of free SO_2 is 50 ppm or 50 mg L^{-1}; this corresponds to 50 mg kg^{-1} of wine (assuming that the wine has the same density as water) or 5×10^{-5} g g^{-1}. In this example, the shelf life of the wine can be considered to be over when half of the free SO_2 has permeated through the bottle (i.e., when 2.5×10^{-5} g g^{-1} has been lost). Using a value for the density of SO_2 of 2.93×10^{-3} g mL^{-1}, the maximum quantity of SO_2 that can be lost is $(2.5 \times 10^{-5})/(2.93 \times 10^{-3}) = 8.5 \times 10^{-3}$ mL g^{-1} = 8.5 mL for a 1 L bottle.

Substituting into Equation 12.13 and solving gives

$$\theta_s = \frac{8.5 \times 0.046}{0.03 \times 10^{-10} \times 720 \times 1.73 \times 10^{-3}} = 1.05 \times 10^{10}\,\text{s} = 333\,\text{years}$$

(c) Conclusion:

Ingress of O_2 from the atmosphere into the wine is likely to be the major mode of failure for wine packaged in a PET bottle. The calculated shelf life of 54 days is probably too short, and, therefore, the bottle would have to be laminated or coated with a barrier material. Permeation of SO_2 through the bottle walls is not going to be a limiting factor in the shelf life of wine in PET bottles.

Example 12.3

This example involves oxidation of biscuits containing 25% fat (Robertson, 2011b). Sensory testing has revealed that they become unacceptable to 50% of consumers due to rancidity when the peroxide value (PV) reaches 15.6 milliequivalents (meq) of O_2 per kg (Calligaris et al., 2007). Assume that the surface area of the package is 440 cm^2 (0.044 m^2) and each pack contains 250 g of biscuits.

Calculate the shelf life of the biscuits if they were packaged in (a) a laminate film consisting of two 25 μm layers of coextruded OPP with an overall OTR of 650 mL m^{-2} day^{-1}, and (b) a laminate film consisting of 15 μm biaxially oriented nylon-6 (BON-6) and 80 μm LDPE with an overall OTR of 2 mL m^{-2} day^{-1}, both OTR measurements being performed at 23°C and 0% RH. Assume that there is zero O_2 inside the packs immediately after sealing and that all the O_2 that enters the packs reacts with the fat in the biscuits.

Fat content of biscuits is 25%. Therefore, weight of fat in each pack is

$$25\% \times 250\,\mathrm{g} = 62.5\,\mathrm{g}$$

The maximum level of peroxide value (PV) for rejection by 50% of consumers is 15.6 meq O_2 per kg biscuits. Therefore, the maximum quantity of O_2 that can enter each pack is

$$\frac{(15.6 \times 62.5)}{1000} = 0.975 \text{ meq } O_2$$

The value expressed in millimoles of O_2 per kg is equal to half that expressed in milliequivalents of O_2 per kg. Thus, since 1 meq O_2 = 0.5 mmol,

$$0.975\,\text{meq}\,O_2 = 0.4875\,\text{mmol} = 4.875 \times 10^{-4}\,\text{mol}$$

The Ideal Gas Law can be used to convert this quantity of O_2 to mL at 23°C:

$$V = \frac{nRT}{P} = (4.875 \times 10^{-4}) \times 82.06 \times \frac{296}{1} = 11.8 \text{ mL}$$

where

R = 82.06 mL atm mol^{-1} K^{-1}

P is the atmospheric pressure = 1 atm

The OTR of laminate film (a) = 650 mL m^{-2} day^{-1}, which for a pack of surface area 0.044 m^2 means that 650 × 0.044 = 28.6 mL O_2 will permeate through per day.

Therefore, the predicted shelf life for the biscuits packed in laminate film (a) is 11.8/28.6 = 0.412 days = 9.9 h at 23°C.

The predicted shelf life for the biscuits packed in laminate film (b) with an OTR of 2 mL m^{-2} day^{-1} is 11.8/(0.044 × 2) = 134 days at 23°C.

Because various simplifying assumptions were made in the preceding calculations, the calculated shelf lives would need to be verified by actual shelf life testing.

12.3.2.3 Light Transmission

Light is known to have a damaging effect on several foods such as milk and other dairy products, and their sensitivity is attributed to the presence of light-sensitive vitamins like vitamins A and B_2, and the action of vitamin B_2 as a photosensitizer, which is able to induce a cascade of oxidative reactions leading to significant losses in other vitamins (e.g., vitamin D) and changes in sensory quality. Saffert et al. (2009) stored UHT low-fat milk under light with an intensity of 700 lx in PET bottles with varying light transmittance. PET bottle variant 1 allowed almost complete light transmittance from 700 to around 310 nm. In the critical wavelength range below 500 nm, the pigmented PET bottle variant 2 showed a light transmittance of around 25%, variant 3 of 12%–15% and variant 4 of 5%–10%. Changes in the vitamin A, B_2 and D_3 concentrations were monitored over 12 weeks at 23°C.

Milk packed in pigmented PET bottles with the lowest light transmittance were stored in the dark under the same experimental conditions and served as the control sample. In clear PET bottles, a reduction of 93% in the initial content was observed for vitamin A and 66% for vitamin D_3, while the vitamin B_2 content was completely degraded. In all pigmented PET bottles, the vitamin retention was only slightly higher; the losses ranged between 70% and 90% for vitamin A, between 63% and 95% for vitamin B_2 and between 35% and 65% for vitamin D_3 depending on the pigmentation level. In the control stored in the dark, a 16% loss was observed for vitamin A, while the level of vitamins B_2 and D_3 remained essentially stable. It was concluded that light-induced sensory changes in UHT milk under commercially relevant storage conditions can only be excluded in packages that provide an almost total barrier to light.

12.3.2.4 Package Dimensions

The dimensions of the package for a given weight of food can have a significant influence on shelf life. Although a spherical shape will minimize the surface area of the package (and thus the quantity of moisture or O_2 that will permeate the package wall), it is not a practical shape for commercial use, and in practice most packages tend to be rectangular or cylindrical. Table 12.2 gives the surface areas for a range of different shapes with the same volume (~450 mL). Compared with the surface area of a sphere, the surface area of a cylinder is 16% greater; a cube 24% greater; a tetrahedron 49% greater; a rectangular shape 58% greater and a thin rectangular shape 246% greater. Extremely thin packages have a much greater surface area:volume ratio and thus require a plastic with better barrier properties to get the same shelf life than if the same quantity of product were packaged in a thicker format.

Because the surface area:volume ratio decreases as a package size gets smaller by a factor equivalent to the characteristic thickness of the package, the shelf life using the same film will decrease directly by this thickness. In other words, when different quantities of the same product are packaged in different-sized packages using the same plastic material, the smallest package will have the shortest shelf life as it inevitably has a greater surface area per unit volume. Many food companies still seem unaware of this fact as they continue to launch smaller packages without changing the packaging material and then wonder why the shelf life is shorter for the smaller package. To ensure adequate shelf life for a food in multiple-sized packages, shelf life tests should be based on the smallest package.

12.3.2.5 Package/Product Interactions

With certain products packaged with certain materials, the end of shelf life arises when an unacceptable degree of interaction between the package and the product has occurred. The COP in these cases is normally the legal limit for a contaminant in a food, but it can be based on a sensory criterion such as flavor or color. Several examples will be given to illustrate the nature of this phenomenon.

The first example is that of a tomato product processed under typical conditions and packaged in a three-piece can with a plain tinplate body and enameled ECCS ends. Over a storage period of 24 months

TABLE 12.2
Surface Areas of Different Package Shapes, All with a Volume of ~450 mL

Shape	Dimensions cm	Surface Area cm²	Surface Area m²	Increase %	Surface Area: Volume Ratio
Sphere	Diameter 9.52	285	0.0285	0	0.63
Cylinder	Diameter 7.3 Height 10.8	331	0.0331	16	0.73
Cube	Sides 7.67	353	0.0353	24	0.78
Tetrahedron	Sides 15.65	424	0.0424	49	0.94
Rectangular pack	Height 3 Length 15 Width 10	450	0.0450	58	1.0
Thin rectangular pack	Height 1 Length 20 Width 22.5	985	0.0985	246	2.18

at ambient temperature, several deteriorative reactions occur. The concentration of tin ions in the product increases rapidly during the first 3 months from ~20 to about 160 ppm, reaching 280 ppm after 24 months. Iron also dissolves, increasing slowly from 8 ppm initially to 10 ppm after 18 months to reach 14 ppm after 24 months. The flavor score declines due to the increasing quantities of dissolved tin and iron; the color value shows a decrease due to an increase in brown pigments, but remains acceptable.

While high concentrations of tin in food may cause stomach upsets in some individuals, this is unlikely to be the case where tin concentrations remain below the legal limit of 200 mg kg^{-1} (100 mg kg^{-1} in canned beverages and 50 mg kg^{-1} in canned baby foods).

There are two factors that limit the shelf life for this tomato product. One is the deterioration in flavor resulting from the dissolution of tin and iron from the package into the product, giving an acceptable shelf life of 24–30 months. The other is the legal limit for tin in canned foods of 200 mg kg^{-1}, which is reached within 4 months. If a longer shelf life was required, it would be necessary to use a full enamel-lined can. Alternatively, the product could be stored at chill temperatures to reduce the rate of the degradative reactions.

Grassino et al. (2009) reported maximum values of tin in cans of tomato purée up to 301 mg kg^{-1} after 180 days at so-called elevated storage temperatures (36°C), which in countries near the equator is the ambient temperature. Based on the legal limit for tin, the shelf life of these canned foods would be less than 5 months.

The second example concerns foods sold in glass jars with metal lids. To ensure tight closure and fairly easy opening, the lids contain a gasket of PVC with 40%–45% plasticizer, usually epoxidized soy bean oil (ESBO) that can migrate into the food in amounts sometimes exceeding the tolerable daily intake (TDI). Fankhauser-Noti et al. (2005) reported that the migration of ESBO into food products with some free oil far exceeded the specific migration limit (SML) of 60 mg kg^{-1}. When the gasket was tightened against the rim of the jar, 60–250 mg (average 165 mg) was in contact with food and on average 70 mg ESBO was in food contact. After exposure to olive oil for 4 weeks at ambient temperature, all the ESBO was transferred; 70 mg ESBO in a 250 g jar resulted in a concentration of 280 mg kg^{-1} food; in a 100 g jar it was 700 mg kg^{-1} food. In oily foods such as garlic, chilli or olives in oil, these predicted concentrations are approached, and, therefore, the end of shelf life for these products is when the legal limit for ESBO in the food is exceeded. ESBO migration into food containing free oil in contact with the gasket has been reported with a mean of 166 mg kg^{-1} in 86 samples and a maximum of 580 mg kg^{-1} (Fankhauser-Noti et al., 2005).

A third example involves an orange juice packaged aseptically in LDPE–alufoil–paper laminate cartons and glass containers. After 2.5 months storage at 25°C, an experienced taste panel detected a significant ($p \leq 0.05$) difference between the orange juices in cartons and glass containers. Analysis of the *d*-limonene (one of the major components of the essential oils in citrus juices) content showed that it had decreased from 70 to 40 ppm in the cartons within 35 days. The limonene had been absorbed (scalped) by the LDPE surface in contact with the orange juice. As well, ascorbic acid degradation and consequent browning was accelerated due to contact with the LDPE film.

Thus, the shelf life of aseptically packaged citrus juices in cartons is limited (largely as a result of package/product interaction) to about 9 months, the end of shelf life being determined by flavor changes to the juices as a result of "scalping" of the flavor components by the package.

12.3.3 Distribution Environment

12.3.3.1 Climatic

The deterioration in product quality of packaged foods is often closely related to the transfer of mass and heat through the package. Packaged foods may lose or gain moisture; they will also reflect the temperature of their environment, because very few food packages are good insulators. Thus, the climatic conditions (i.e., temperature and humidity) of the distribution environment (warehouses; trucks and rail cars; supermarkets; consumer pantries) have an important influence on the rate of deterioration of packaged foods.

12.3.3.1.1 Mass Transfer

With mass transfer, the exchange of vapors and gases with the surrounding atmosphere is of primary concern. Water vapor and O_2 are generally of most importance, although the exchange of volatile aromas from the product, or to the product from the surroundings, can be important. As well as O_2, transmission of N_2 and CO_2 may have to be taken into account in packages where the concentration of these gases inside the package has been modified from ambient to inhibit or slow down deteriorative reactions in the food.

Generally, the difference in partial pressure of the vapor or gas across the package barrier will control the rate and extent of permeation, although transfer can also occur due to the presence of pinholes in the material, imperfect seals and closures, or cracks that result from flexing of the packaging material during filling and subsequent handling. In contrast to the common gases, the partial pressure of water vapor in the atmosphere varies continuously, although the variation is generally much less in controlled climate stores.

To summarize, mass transfer depends on the partial pressure difference across the package barrier of gases and water vapor, and on the nature of the barrier itself. These factors were discussed in Section 12.3.2.

12.3.3.1.2 Heat Transfer

One of the major determinants of food shelf life is the temperature to which the food is exposed during the time from production to consumption. Without exception, foods are exposed to fluctuating temperature environments during this time, and to accurately estimate shelf life, the nature and extent of these temperature fluctuations need to be known. There is little point in carefully controlling the processing conditions inside the factory and then releasing the product into the distribution and retail system without knowledge of the conditions that it will experience in that system. Such knowledge is essential in the case of products containing a “best before” or “use by” date.

The detailed climatic statistics of global maximum and mean temperatures, which are available in many countries, are of great assistance. Despite meteorological and secular trends, the daily (and even the annual) cycle of temperatures can be normalized to a standard cycle with a standard frequency distribution derived from the mean and range at many places. This is because of the sinusoidal trend of diurnal (Earth’s rotation) and seasonal (Earth’s revolution) solar radiation intensity.

The storage climates inside buildings such as warehouses and supermarkets are only broadly related to the external climate as reported by weather stations; climatic variations in temperature and humidity can differ as much between different building constructions as between seasons on one site. Unfortunately, there is no publicly available data on daily temperature and humidity variations in warehouses and supermarkets.

If the major deteriorative reaction causing the end of shelf life is known, simple expressions can be derived to predict the extent of deterioration as a function of available time–temperature storage conditions. The basic types of deteriorative reactions that foods undergo were discussed in Chapter 11, together with the rates of these reactions and the factors controlling these rates. These reactions and their rates will now be analyzed in relation to food shelf life.

Fundamental to such an analysis is that the particular food under consideration follows the laws of additivity and commutativity. *Additivity* implies that the total extent of the degradation reaction in the food produced by a succession of exposures at various temperatures is the simple sum of the separate amounts of degradation, regardless of the number or spacing of each time–temperature combination. *Commutativity* means that the total extent of the degradation reaction in the food is independent of the order of presentation of the various time–temperature experiences.

12.3.3.1.2.1 Shelf Life Plots A useful approach to quantifying the effect of temperature on food quality (especially when little data are available to get rate constants, or when only the time to reach a certain level of quality change has been determined) is to construct shelf life plots. As discussed

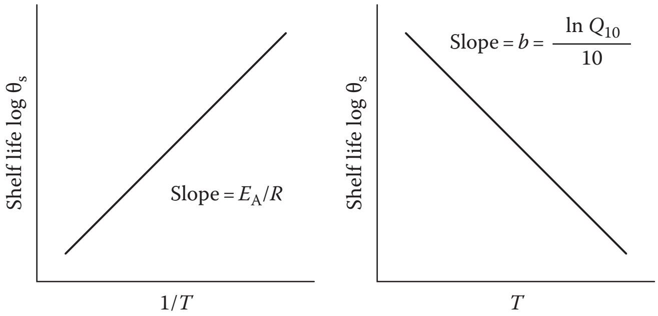

FIGURE 12.5 (a) Arrhenius plot of log shelf life (θ_s) versus reciprocal of the absolute temperature (K) showing a slope of E_A/R, and (b) linear plot of log shelf life versus temperature (°C) showing a slope of $-b$.

in Section 11.5.1, several models are in use to represent the relationship between the rate of a reaction (or the reciprocal of rate, which can be time for a specified loss in quality or shelf life) and temperature. The two most common models are the Arrhenius and linear, and these are shown in Figure 12.5.

The equations for these two plots are

$$\theta_s = \theta_0 \exp \frac{E_A}{R}\left[\frac{1}{T_s} - \frac{1}{T_0}\right] \tag{12.15}$$

and

$$\theta_s = \theta_0 e^{-b(T_s - T_0)} \tag{12.16}$$

where

θ_s is the shelf life at temperature T_s
θ_0 is the shelf life at temperature T_0

If only a small temperature range is used (less than ±20°C), there is little error in using the simpler linear plot rather than the Arrhenius plot.

Most deteriorative reactions in foods can be classified as either zero or first order, and the way in which these two reaction orders can be used to predict the extent of deterioration as a function of temperature is now outlined.

12.3.3.1.2.2 Zero-Order Reaction Prediction Equation 11.10 was derived for the change in a quality factor A when all extrinsic factors are held constant:

$$A_e = A_0 - k_z\theta_s \tag{12.17}$$

and

$$A_0 - A_e = k_z\theta_s \tag{12.18}$$

where

A_e is the value of A at the end of shelf life
A_0 is the value of A initially
k_z is the zero-order rate constant (time^{-1})
θ_s is the shelf life in days, months, years and so on

For variable time–temperature storage conditions, Equation 12.17 can be modified as follows:

$$A_e = A_0 - \Sigma(k_i\theta_i) \tag{12.19}$$

where $\Sigma k_i\theta_i$ is the sum of the product of the rate constant, k_i, at each temperature, T_i, multiplied by the time interval, θ_i, at the average temperature, T_i, for the given time period, $\Delta\theta$.

To apply this method, the time–temperature history is broken up into suitable time periods and the average temperature in that time period determined. The rate constant for that period is then calculated from the shelf life plot using a zero-order reaction. The rate constant is multiplied by the time interval, θ_i, and the sum of the increments of $k_i\theta_i$ gives the total amount lost at any time.

Alternatively, instead of calculating actual rate constants, the time for the product to become unacceptable (i.e., for A to become A_e) can be measured, and Equation 12.19 modified to give

f_c = fraction of shelf life consumed = change in A divided by total possible change in A

$$= \frac{A_0 - A}{A_0 - A_e} \tag{12.20}$$

$$= \frac{\Sigma(k_i\theta_i)}{\Sigma(k_i\theta_s)} \tag{12.21}$$

$$= \Sigma\left[\frac{\theta_i}{\theta_s}\right]T_i \tag{12.22}$$

A similar approach to that described earlier is employed. The temperature history is divided into suitable time periods and the average temperature, T_i, at each time period evaluated. The time held at that temperature, θ_i, is then divided by the shelf life, θ_s, for that particular temperature, and the fractional values summed up to give the fraction of shelf life consumed. Astute readers will recognize the similarity between this method and the graphical method used to determine the lethality of a thermal process. This is not surprising because both are concerned with summing the effects of various temperatures on the rates of reactions (in thermal processes such as canning, it is the rate of microbial destruction that is the focus).

The shelf life can also be expressed in terms of the fraction of shelf life remaining, f_r:

$$f_r = 1 - f_c \tag{12.23}$$

Thus, for any temperature T_s

$$f_r\theta_s = (1 - f_c)\theta_s = \text{shelf life left at temperature } T_s \tag{12.24}$$

In other words, the shelf life left at any temperature is the fraction of shelf life remaining times the shelf life at that temperature.

This method was initially developed by the U.S. Department of Agriculture in California during the1950s for the determination of the shelf life of frozen foods and is referred to as the *time–temperature–tolerance* (TTT) approach (Van Arsdel, 1969). In these and related studies, the period of time (designated as the *high quality life* [HQL]) for 70%–80% of a trained taste panel to correctly identify the control samples (held at −29°C) from samples stored at various subzero temperatures using the triangle or duo-trio test was determined. The change in quality at this stage has been designated the *just noticeable difference* (JND) or *first noticeable difference* (FND). The HQL has no real commercial significance and is quite different from the *practical storage life* (PSL), which is of interest to food processors and consumers. The ratio between PSL and HQL is often referred to as the *acceptability factor* and can range from 2:1 up to 6:1.

The TTT work on frozen foods demonstrated that the HQL varied exponentially with temperature. However, it has been subsequently shown that when overall quality is measured (rather than just one single quality factor), a semilogarithmic plot results in curved rather than straight lines. It was suggested that a semilogarithmic plot was convenient for products with very long shelf lives, but for other products, a plot utilizing two linear scales was more convenient.

TTT relationships are not strict mathematical functions but empirical data subject to large variability, particularly because of variations in product, processing methods and packaging (the PPP factors). Therefore, any shelf life prediction made will be specific for a particular product (e.g., specific breed of animal slaughtered at a certain age or weight) that is processed, packaged and stored under specific conditions. Failure to specify PPP factors leads to the vast plethora of seemingly contradictory shelf lives for frozen foods reported in the literature. For example, the frozen shelf life of cod stored at −18°C has been reported by various authors to be anywhere from 15 to 45 weeks, and it has been calculated that, on the basis of data in the literature, the 95% confidence interval for the HQL of frozen lean meat ranges from 8 months to 3 years. Thus, predictions cannot be made with any precision on the quality or quality change in a frozen food from knowledge of its time–temperature history and TTT literature data only. Therefore, in determining the shelf life of frozen foods, the PPP factors must be taken into account in addition to the TTT relationships.

Example 12.4

A frozen food (ground beef packaged in LDPE film) has a PSL at various temperatures as follows:

Temperature (°C)	PSL (Days)
−8	120
−12	180
−15	230
−18	300
−20	350
−23	420
−25	480

Calculate the total loss of PSL along the freezer chain from processor to consumer given the time and temperature history shown in the following.

Links in the Freezer Chain	Average Temperature (°C)	Storage Time (Days)	PSL (Days)	PSL Loss (% per Day)	Loss (%)
Processor	−23	40	420	0.238	9.5
Transport	−20	2	350	0.286	0.6
Cold store	−25	190	480	0.208	39.9
Transport	−18	1	300	0.333	0.3
Wholesale	−23	30	420	0.238	7.2
Transport	−15	1	230	0.435	0.2
Display cabinet					
Center	−20	20	350	0.286	5.8
Upper layer	−12	6	180	0.556	3.4
Transport	−8	1/6	120	0.833	0.1
Consumer	−18	50	300	0.333	16.5
Total loss of PSL			340		83.6%

By dividing the PSL into 100, the product life loss per day as a percentage at that temperature is determined (e.g., at −23°C, 100/420 = 0.238% loss per day). When the storage time in column 3 is multiplied by product life loss per day in column 5, the product life loss expressed as a percentage of the PSL can be calculated.

The total loss of PSL for the ground beef at the end of the freezer chain (340 days) is 84%. Thus, 16% of its PSL is left; that is, the product could be kept by the consumer at −18°C for another 16 × 300/100 = 49 days before it exceeds its PSL.

More recently, the TTT approach has also been applied to nonfrozen foods, for example, to determine the PSL of sweet whey powder as a result of temperature abuse (Dattatreya et al., 2007).

12.3.3.1.2.3 First-Order Reaction Prediction The equivalent expression to Equation 12.16 for a first-order reaction was derived as Equation 11.15 for the case where all extrinsic factors are held constant:

$$A_e = A_0\exp(-k\theta_s) \tag{12.25}$$

From this, an expression can be developed to predict the amount of shelf life used up as a function of variable temperature storage for a first-order reaction in the following form:

$$A = A_0\exp\,(-\Sigma k_i\theta_i) \tag{12.26}$$

where

A is the amount of some quality factor remaining at the end of the time–temperature distribution

$\Sigma k_i\theta_i$ has the same meaning as in Equation 12.18

If the shelf life is based simply on some time to reach unacceptability as defined by a COP, then Equation 12.25 can be modified to give an analogous expression to that derived for the TTT method. Note that because of the exponential loss of quality, A_e will never be zero. Thus,

$$\ln\frac{A}{A_0} = -\sum k_i\theta_i \tag{12.27}$$

and

$$k_i = \frac{\ln A_e/A_0}{\theta_s} \tag{12.28}$$

where

$\ln A/A_0$ is the fraction of shelf life consumed at time θ

$\ln A_e/A_0$ is the fraction of shelf life consumed at time θ_s

The fraction of shelf life remaining, f_r is

$$f_r = 1 - \frac{\ln A_0/A}{\ln A_0/A_e} = 1 - \Sigma\left[\frac{\theta_i}{\theta_s}\right]_{T_i} \tag{12.29}$$

12.3.3.1.3 Simultaneous Mass and Heat Transfer

In the majority of distribution environments, many packaged foods undergo changes in both moisture content and temperature during storage as a result of variable temperature and humidity conditions in the environment. This has the effect of complicating the calculations for prediction of the shelf life of packaged foods. An additional challenge is that data on the humidity distribution of environments where foods are stored are scarce and not as easily predicted as the external temperature distribution. Therefore, prediction of the actual shelf life loss of packaged foods will only be approximate. More complete data about the humidity distribution of food storage environments are required so that shelf life predictions can be further refined.

12.3.3.2 Physical

After processing and manufacture, the food leaves the factory and usually moves into the company's warehouse. It is then transported by rail or truck to a distribution center. From here, the food may be taken to the retail outlet by truck or rail or maybe to a port to be transported by sea or air to another distribution warehouse. Further transport by rail or truck then follows to the retail outlet.

Regardless of the distribution pattern, transportation damage may be incurred by the food. The extent of such damage will be a function of not only the packaging (primary, secondary and tertiary), but also the nature of the distribution environment and the method of transportation.

Most secondary packages are stacked on pallets that may or may not be shrink or stretch wrapped. Pallets are usually stacked two high in rail cars and one or two high in trucks; in warehouses, pallets may be stacked four high. Thus, the forces acting on the top tier of a four pallet stack will be quite different from those acting on the bottom tier of the same stack. The longer the time that the product spends in the distribution chain (this is usually directly related to the shelf life of the product), the more significant are the effects arising from pallet stacking height.

Ultimately, knowledge of the distribution environment (both climatic and physical) is essential before meaningful shelf life tests can be designed. Taking a product from the production line and conducting a shelf life test on it while ignoring possible distribution environment hazards will almost certainly lead to an overestimation of shelf life.

12.4 PREDICTING MICROBIAL SHELF LIFE

Microbial spoilage of foods is an economically significant problem for food manufacturers, retailers and consumers. Depending on the food, process and storage conditions, the microbiological shelf life can be determined by the growth of either spoilage or pathogenic microorganisms. In the case of spoilage microorganisms, the traditional method for determining microbiological shelf life involved storing the food at different temperatures and determining spoilage by sensory evaluation or microbial count. Where the microbiological shelf life is determined by the growth of pathogenic microorganisms, the traditional approach has been challenge testing of the food with the organism of concern, followed by storage at different temperatures and microbial analysis at intervals. For processes such as heat treatments, where the elimination of particular microorganisms is required (e.g., canning), the use of inoculated packs is common.

The primary step in the microbial shelf life determination of food is to identify the specific spoilage organisms (SSOs), defined as the fraction of the total microflora that are responsible for spoilage under the particular range of environmental conditions.

The end of shelf life is when a certain level of deterioration is reached because of the SSOs, the microbial metabolic product(s) or both (Jay et al., 2007). After determining the SSOs and the range of environmental conditions over which a particular SSO is responsible for spoilage, the next step is to decide the population level of the SSO at which unacceptable spoilage occurs and, thus, shelf life ends.

The limit of microbial growth determining shelf life differs with food type, packaging and storage conditions (Lee, 2010). SSO counts of 10^6–10^8 organisms g^{-1} or cm^{-2} are commonly used as a convenient upper limit of quality. When dealing with pathogenic bacteria such as *Bacillus cereus* and *Staphylococcus aureus*, a limit of 10^5 organisms g^{-1} has been used for risk management of the food supply system for prepared foods. The time to reach the limit based on pathogen growth should be clearly understood as the minimum requirement for shelf life control. There should always be a safety margin that results in a shorter actual shelf life, this time greatly depending on the initial contamination level. Hygienic control of food preparation and processing is required so that the end of shelf life is determined by the growth of spoilage organisms rather than of pathogens.

The four key parameters log N_o, θ_{lag}, μ_{max} and log N_c that describe the progress of microbial growth with time under certain defined conditions were presented in Section 11.3.3.1. The parameter log N_o is determined by the initial contamination level of the food, which is dictated by raw materials and food manufacturing conditions, whereas log N_c represents the critical or maximum cell density attainable under given conditions. Lag time (θ_{lag}) and maximum specific growth rate (μ_{max}), depending on environmental conditions, directly affect the time to reach a certain critical level of microbial density corresponding to acceptable quality. Therefore, in dealing with the effect of packaging conditions on microbial shelf life, these two parameters are most often employed (Lee, 2010). The time (θ_s) to reach a critical limit cell density of N_c is the shelf life and can be calculated using

$$\theta_s = \theta_{lag} + \frac{1}{\mu_{max}} \ln \frac{N_c}{N_o} \tag{12.30}$$

Example 12.5

The use of MAP to extend the shelf life of chilled, perishable foods is well established commercially. Recently, very high O_2 concentrations have been applied (mainly for fresh produce packaging) to inhibit microbial growth without the creation of anoxic conditions. Lee (2010) used Equation 12.30 to calculate the time for *Pseudomonas fluorescens* to increase $10^{3.5}$-fold based on the microbial growth parameters reported by Geysen et al. (2006). The dependence of microbial shelf life on superatmospheric O_2 and moderate CO_2 concentrations for fresh-cut lettuce is presented in Figure 12.6. The maximum extended shelf life at 100% O_2 and 20% CO_2 (hypothetical concentrations corresponding to respective partial pressures of 1.0 and 0.2 atm for O_2 and CO_2) was about six times that in a normal atmosphere (20% O_2 and 0% CO_2). Use of higher levels of CO_2 for fresh fruits and vegetables is limited because of the physiological tolerance limit of the commodity (mostly below 20%). Given the microbial inhibitory effect of superatmospheric O_2, its use eliminates the risk of O_2 depletion inside the fresh produce package because of respiration activity, particularly under temperature abuse conditions.

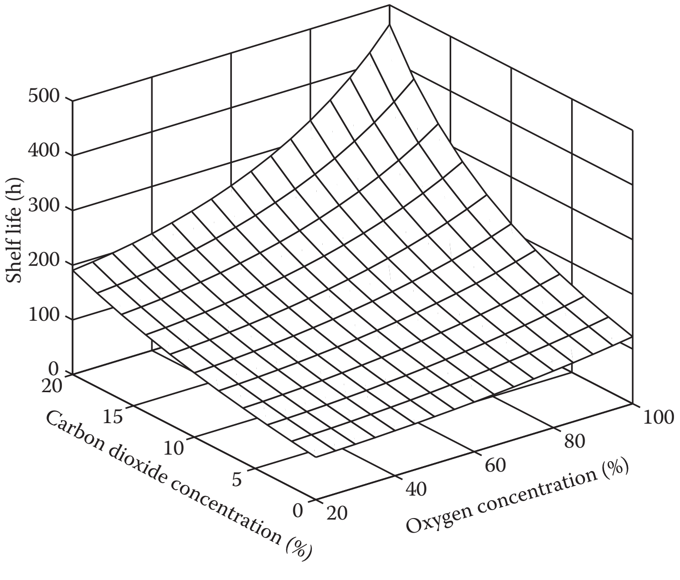

FIGURE 12.6 Estimated shelf life under MA conditions of superatmospheric O_2 and moderate CO_2 concentrations when packaging fresh-cut lettuce at 7°C based on growth of *Pseudomonas fluorescens*. (From Lee, D.S., Packaging and the microbial shelf life of food, in: *Food Packaging and Shelf Life*, Robertson, G.L. (Ed.), CRC Press, Boca Raton, FL, pp. 55–79, 2010.)

Chotyakul et al. (in press) used Monte Carlo procedures to evaluate the uncertainty of food safety and quality estimations caused by the variability in model parameters. Their shelf life predictions were based on the growth of *Lactobacillus sakei* in meat using an equation similar to Equation 12.30 with three variables: temperature, a_w and gas atmosphere. The predicted shelf life when parameter variability was not considered was 7.0 h for a temperature-only model (Case 1, $T = 4°C$), 184.6 h for a temperature and a_w model (Case 2, $T = 4°C$, $a_w = 0.98$), 6.4 h for a temperature and CO_2 model (Case 3, $T = 4°C$, $CO_2 = 2650$ ppm) and 241.6 h for a temperature, a_w and CO_2 model (Case 4.1, $T = 4°C$, $a_w = 0.98$, $CO_2 = 2650$ ppm). The shelf life values estimated considering parameter variability were 7.4 ± 3.5, 190.4 ± 34.8, 7.5 ± 2.0 and 266.1 ± 65.8 h, respectively.

Examining the frequency distribution of the predicted shelf life, as well as imposing a 95% confidence that meat would not spoil before its expiration date, lead to a recommended shelf life of 4, 141, 6 and 176 h for Cases 1–4.1, respectively. If the standard deviation (SD) of all model parameters in Case 4.1 could be lowered by 10%, 50% and 90%, the recommended shelf life time would increase from 176 to 189, 198 and 202 h, respectively. The analysis of the impact of lowering the individual SD of the model parameters showed an even lower impact. This suggested that lowering the uncertainty of microbial shelf life predictions is very difficult when multiple factors are considered in the microbial model used for this estimation.

Predictive microbiology combines mathematical modeling with experimental data on combinations of factors that influence the growth of food spoilage and/or food-borne pathogenic microorganisms. Predictive microbiology is based on the premise that the responses of microorganisms to environmental factors are reproducible, and that it is possible, taking into account past observations, to predict the responses of microorganisms in particular environments. The huge amount of data generated over the past 30 years to predict the behavior of microorganisms under different environmental conditions have allowed for the development of mathematical models, which have enabled prediction of the behavior of microorganisms under certain conditions.

The development and commercialization of predictive models have now become relatively widespread. The use of such models can reduce the need for shelf life trials, challenge tests, product reformulations and process modifications, thus saving both time and money. Although there are both mechanistic and empirical predictive models, the latter predominate. Empirical predictive models can be subdivided into probabilistic and kinetic models. The ultimate test for predictive models is whether they can be used to predict reliable outcomes in real situations.

To model food safety aspects, the predictive microbiology capability provided by the ComBase Modeling Toolbox is very useful. With this toolbox, it is possible to judge more easily the effect of production and storage regimes and changing product formulations on the possible growth of pathogens or spoilage organisms. The ComBase Modeling Toolbox consists of a set of free online applications for predicting the growth or inactivation of microorganisms (see www.combase.cc). The ComBase Initiative is a collaboration between the Food Standards Agency and the Institute of Food Research from the United Kingdom, the USDA Agricultural Research Service and its Eastern Regional Research Center and the Australian Food Safety Centre of Excellence. Its purpose is to make data and predictive tools on microbial responses to food environments freely available via web-based software.

The ComBase Database (accessible via the ComBase Browser) consists of thousands of microbial growth and survival curves that have been collated in research establishments and from publications. They form the basis for numerous microbial models presented in ComBase Predictor that can be used in assessing the microbial risk in foods and ultimately shelf life. The user identifies relevant criteria including a type or species of organism, a type or class of food, pH, temperature, a_w (or NaCl concentration) and specific food conditions. The latest version of ComBase Predictor can simultaneously produce predictions for up to four microorganisms, thereby facilitating comparisons among several scenarios (Amézqita et al., 2011).

Other software packages include the Pathogen Modeling Program (see www.ars.usda.gov/Services/docs.htm?docid=6796), which is a stand-alone software package of 38 microbial models for 11 bacterial pathogens that can be used to predict the growth and inactivation of food-borne pathogens under various environmental conditions. The Seafood Spoilage & Safety Predictor® software (see http://sssp.dtuaqua.dk/) predicts the shelf life and growth of bacteria in different fresh and lightly preserved seafood. Some of the predictive models in SSSP are equally useful for other types of food.

Despite their increasing sophistication and widespread availability, models should not be relied on completely. Rather, models are best employed as tools to assist decision making. Models do not completely negate the need for microbial testing, and do not replace the judgment of trained and experienced food microbiologists.

12.5 ACCELERATED SHELF LIFE TESTING

12.5.1 Basic Principles

The basic assumption underlying accelerated shelf life testing (ASLT) is that the principles of chemical kinetics can be applied to quantify the effects which extrinsic factors such as temperature, humidity, gas atmosphere and light have on the rate of deteriorative reactions (Corradini and Peleg, 2006). These basic principles and the way in which they can be applied to foods have been described in Chapter 11. By subjecting the food to controlled environments in which one or more of the extrinsic factors is maintained at a higher than normal level, the rates of deterioration will be accelerated, resulting in a shorter than normal time to product failure (Saguy and Peleg, 2009). Because the effects of extrinsic factors on deterioration can be quantified, the magnitude of the acceleration can be calculated and the "true" shelf life of the product under normal conditions calculated (Mizrahi, 2011). Thus, a shelf life test that would normally take a year can be completed in about a 1–2 months if the storage temperature is raised from 20°C to 40°C.

The need for ASLT of food products is simple—because many foods have shelf lives of at least 1 year, evaluating the effect on shelf life of a change in product formulation (e.g., a new antioxidant or thickener), the process (e.g., a different time/temperature sterilization regime) or the packaging (e.g., a new polymeric film) would require shelf life trials lasting at least as long as the required shelf life of the product. Companies cannot afford to wait for such long periods before knowing whether or not the new product/process/packaging will provide an adequate shelf life, because other decisions (e.g., to construct a new factory, order new equipment or arrange contracts for the supply of new packaging material) have lead times of months or years. Some way of speeding up the time required to determine the shelf life of a product is necessary, and ASLT has been developed for that reason. Such procedures have long been used in the pharmaceutical industry where shelf life and efficacy of drugs are closely related. However, the use of ASLT in the food industry is not as widespread as it might be, due in part to the lack of basic data on the effect of extrinsic factors on the rates of deteriorative reactions, in part to ignorance of the methodology required, and in part to skepticism of the advantages to be gained from using ASLT procedures.

As discussed in Chapter 11, quality loss for most foods follows either a zero- or first-order reaction. Figure 12.5 showed the logarithm of shelf life versus temperature and the inverse of absolute temperature. If only a small range of temperature is considered, then the former shelf life plot generally fits the data for food products.

For a given extent of deterioration and reaction order, the rate constant is inversely proportional to the time to reach some degree of quality loss. Thus, by taking the ratio of the shelf life between any two temperatures 10°C apart, the Q_{10} of the reaction can be found. This can be expressed by the extension of Equation 11.36, assuming a linear shelf life plot:

$$Q_{10} = \frac{k_{T+10}}{k_T} = \frac{\theta_{s_T}}{\theta_{s_{T+10}}} \tag{12.31}$$

where

θ_{s_T} is the shelf life at temperature T°C

$\theta_{s_{T+10}}$ is the shelf life at temperature $(T+10)$°C

TABLE 12.3
Effect of Q_{10} on Shelf Life

Temperature (°C)	Shelf Life (Weeks) $Q_{10} = 2$	$Q_{10} = 2.5$	$Q_{10} = 3$	$Q_{10} = 5$
50	2[a]	2[a]	2[a]	2[a]
40	4	5	6	10
30	8	12.5	18	50
20	16	31.3	54	4.8 years

Source: Labuza, T.P. and Kamman, J.F., Reaction kinetics and accelerated tests simulation as a function of temperature, in: *Computer-Aided Techniques in Food Technology*, Saguy, I. (Ed.), Marcel Dekker, New York, pp. 71–115, 1983.

[a] Arbitrarily set at 2 weeks at 50°C. Shelf lives at lower temperatures are calculated on this arbitrary assumption.

The effect of Q_{10} on shelf life is shown in Table 12.3, which illustrates the importance of accurate estimates of Q_{10} when making shelf life estimations. For example, if a product has a shelf life of 2 weeks at 50°C and a Q_{10} of 2, then it will have a shelf life of 16 weeks at 20°C. However, if Q_{10} were 2.5 rather than 2, the shelf life at 20°C would be almost twice as long (31 weeks). Thus, a small error in Q_{10} can lead to huge differences in the estimated shelf life of the product. Typical Q_{10} values for foods are 1.1–4 for canned products, 1.5–10 for dehydrated products and 3–40 for frozen products.

A further use for Q_{10} values is illustrated in Figure 12.7, which depicts a shelf life plot for a product that has at least 18 months shelf life at 23°C. To determine the probable shelf life of the product at 40°C, lines are drawn from the point corresponding to 18 months at 23°C to intersect

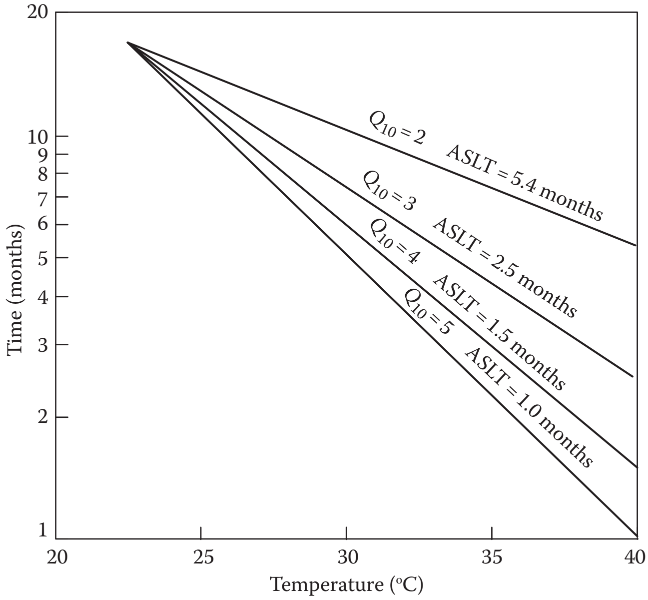

FIGURE 12.7 Hypothetical shelf life plot for various Q_{10}'s passing through a shelf life of 18 months at 23°C. Accelerated shelf life times (ASLT) are those required at 40°C for various Q_{10}'s. (From Labuza, T.P. and Kamman, J.F., Reaction kinetics and accelerated tests simulation as a function of temperature, in: *Computer-Aided Techniques in Food Technology*, Saguy, I. (Ed.), Marcel Dekker, New York, pp. 71–115, 1983.)

TABLE 12.4
Effect of E_A of the Key Deteriorative Reaction on the Time to Complete an ASLT for a Low Moisture Food Product with a Targeted Shelf Life of 2 Years at Ambient Storage

E_A (kJ mol^{-1})	Testing Time at 40°C	Testing Time at 45°C
45	224 days	171 days
85	78 days	47 days
125	28 days	13 days

Source: Taoukis, P.S. and Giannakourou, M.C., Temperature and food stability: Analysis and control, in: *Understanding and Measuring the Shelf-Life of Food*, Steele, R. (Ed.), CRC Press, Boca Raton, FL, pp. 42–68, 2004.

a vertical line drawn at 40°C; the slope of each of the straight lines so drawn is dictated by the Q_{10} value. Thus, if the Q_{10} of the product were 5, then its shelf life at 40°C would be 1 month, increasing to 5.4 months if the Q_{10} was 2. Such a plot is helpful in deciding how long an ASLT is likely to run.

Instead of Q_{10} values, the E_A can be used to determine the duration of an ASLT. An example of the effect of E_A on the time to complete an ASLT is given in Table 12.4.

12.5.2 ASLT Procedures

The following procedure should be adopted in designing a shelf life test for a food product (Taoukis et al., 1997):

1. Determine the microbiological safety and quality parameters for the product.
2. Select the key critical descriptor(s) or IoFs that will cause quality loss and, thus, consumer unacceptability in the food, and decide what tests (sensory and/or instrumental) should be performed on the product during the trial.
3. Select the package to be used. Often, a range of packaging materials will be tested so that the most cost-effective material can be selected.
4. Select the extrinsic factors that are to be accelerated. Typical storage temperatures used for ASLT procedures are shown in the following, and it is usually necessary to select at least two.

Product	Test Temperatures (°C)	Control (°C)
Frozen	−7, −11, −15	<−40
Chilled	5, 10, 15, 20	0
Dry and IMF	25, 30, 35, 40, 45	−18
Canned	25, 30, 35, 40	4

5. Using a plot similar to that shown in Figure 12.7, determine how long the product must be held at each test temperature. If no Q_{10} values are known, then an open-ended ASLT will have to be conducted using a minimum of three test temperatures.
6. Determine the frequency of the tests. A good rule of thumb is that the time interval between tests at any temperature below the highest temperature should be no longer than

$$f_2 = f_1 Q_{10}^{\Delta T/10} \tag{12.32}$$

where

f_1 is the time between tests (e.g., days, weeks) at the highest test temperature T_1
f_2 is the time between tests at any lower temperature T_2
ΔT is the difference in degrees Celsius between T_1 and T_2

Thus, if a product is held at 40°C and tested once a month, then at 30°C with a Q_{10} of 3, the product should be tested at least every

$$f_2 = 1 \times 3^{(10/10)} = 3 \text{ months}$$

More frequent testing is desirable, especially if the Q_{10} is not accurately known, because at least six data points are needed to minimize statistical errors, otherwise the confidence in θ_s is significantly diminished.

7. Calculate the number of samples that must be stored at each test condition, including those samples that will be held as controls.
8. Begin the ASLTs, plotting the data as they come to hand so that, if necessary, the frequency of sampling can be increased or decreased as appropriate.
9. From each test storage condition, estimate k or θ_s and construct appropriate shelf life plots from which to estimate the potential shelf life of the product under normal storage conditions. Provided that the shelf life plots indicate that the product shelf life is at least as long as that desired by the company, then the product has a chance of performing satisfactorily in the marketplace.

12.5.3 EXAMPLES OF ASLT PROCEDURES

12.5.3.1 Dehydrated Products

In dehydrated vegetables, lipid and hydrolytic oxidation, together with nonenzymic browning and (in the case of green vegetables) chlorophyll degradation, are the major modes of deterioration. In dehydrated fruit, the major mode of deterioration is nonenzymic browning. Samaniego et al. (1991) used temperatures of 30°C and 40°C to accelerate deterioration in sliced green beans and onion flakes and found that, for example, at 40°C, the shelf life of onions was 11 times shorter, and at 30°C, 3.5 times shorter than at 20°C when the a_w was 0.56.

12.5.3.2 Frozen Foods

Plots of HQL or PSL versus time were discussed in Section 12.3.3.1.2.2; such curves suggest that accelerated tests could be used for predicting the shelf life of frozen foods with a considerable degree of accuracy. The shape of TTT curves for a wide range of products has been determined, and for any specific set of conditions (e.g., a particular product, process or package), a more detailed TTT curve could be determined. Then, accelerated tests could be carried out at temperatures as warm as −10 or even −8°C. As a result, the shelf life of a frozen food that would normally be stored at −18°C could be predicted in a few weeks or months at these higher temperatures.

Although mold growth has been recorded down to −17°C, no evidence of microbiological growth on meat products has been found at or below −8°C, and therefore −8°C is generally recommended as the warmest temperature for ASLT of meat. Due cognizance must be taken of those frozen products such as frozen bacon, which exhibit so-called reverse stability where the keeping quality is poorer at −25°C than at −5°C.

In ASLT of frozen foods, the formation of ice has to be considered. As ice forms, the concentration of the unfrozen aqueous phase increases and influences reaction rates because they depend on both temperature and concentration. Below about −7°C, the relative change in concentration of the unfrozen aqueous phase is small, but storage at temperatures above −7°C should be avoided. In the temperature range between 0°C and −7°C, the overall observed rate of reaction may increase, stay relatively constant or decrease depending on the specific system. Consequently, there is no generally applicable method to estimate low temperature shelf life from measurements made above −7°C (Reid, 2003).

12.5.3.3 Canned Foods

It is generally assumed that if good manufacturing practices are followed, microbial deterioration of canned foods will not be a problem. If there is thermophilic spoilage when canned foods are stored at elevated temperatures, then this is more than likely due to inadequate cooling of the cans following thermal processing. Microbial spoilage at ambient temperatures is generally the result of "leaker" spoilage, so-called because the microorganisms are drawn into the can during cooling; chlorination of cooling water according to good manufacturing practice will avoid this problem. Thus, deteriorative reactions in canned foods will normally be limited to organoleptic changes such as loss of color, development of undesirable flavors and nutrient degradation.

Labuza (1982) quotes a producer of canned meat products as stating that the major mode of deterioration is H_2 production resulting from internal corrosion of the can. Samples were stored at 37.8°C to accelerate this deterioration; the shelf life at 37.8°C was 40% of the shelf life at 4.4°C, corresponding to a Q_{10} of 1.3.

12.5.3.4 Oxygen-Sensitive Products

In all the classical ASLT methods, temperature is the dominant acceleration factor used, and its effect on the rate of lipid oxidation is best analyzed in terms of the overall activation energy E_A for lipid oxidation. An inherent assumption in these tests is that E_A is the same in both the presence and absence of antioxidants, although indications are that it is in fact considerably lower in the latter case.

Although high O_2 pressures can be used to accelerate reactions involving oxidation, it is not used very often since oxidation reactions typically become independent of the O_2 concentration above a certain level which varies with temperature and other conditions. However, Cardelli and Labuza (2001) reported that increasing O_2 concentrations from 0.5 to 21.3 kPa accelerated the deterioration of roast and ground coffee 20-fold. If both temperature and O_2 concentration are accelerated, then the decreased solubility of O_2 at higher temperatures must be factored into any calculations of shelf life.

12.5.3.5 Oxygen-Absorbing Package

Gomes et al. (2009) investigated the ability of a laminate plastic–alufoil pouch containing a novel iron-based O_2 absorber (Figure 12.8) to maintain and/or extend the shelf life of a hot-filled cheese-spread MRE (meal-ready-to-eat) item. ASLT of filled pouches with and without the O_2 absorber were conducted for 3 months at 51.7°C and 6 months at 37.8°C, with pouches stored for 12 months

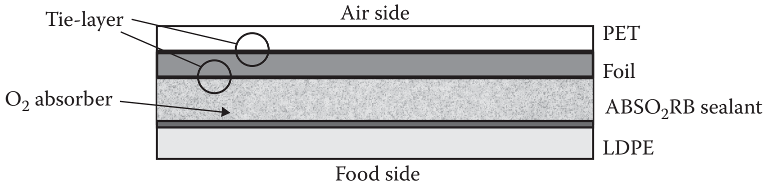

FIGURE 12.8 Schematic of the laminate structure of the oxygen-absorbing packaging material. (From Gomes, C. et al., *J. Food Sci.*, 74, E167, 2009.)

at 26.7°C serving as controls; RH was kept constant at 65%–75%. Sampling intervals consisted of 1, 2, 3, 4 and 6 weeks at 51.7°C; 1, 3 and 6 months at 37.8°C and 1, 6 and 12 months at 26.7°C.

Results showed that the proposed O_2-absorbing laminate was efficient in reducing headspace O_2 concentration from 20.4% to 6.82% within 24 h and to <0.5% in 11 days, with a significant reduction in rancidity of the cheese spread. In addition, the laminate helped delay loss of ascorbic acid. Samples also met the U.S. military shelf life requirement of 6 months at 37.8°C. They concluded that pouches containing an O_2 scavenger in the laminate can help retain nutrition and extend shelf life of high-fat, liquid-like products.

12.5.3.6 Long-Duration Spaceflight

The Advanced Food Technology (AFT) Project of the National Aeronautics and Space Administration (NASA) Human Research Program (HRP) is currently working to design a stable, palatable and nutritious food supply to support long-duration spaceflight. A large part of this food supply is expected to be positioned, unrefrigerated, at relevant destination sites prior to crew arrival. Therefore, AFT anticipates that the food products used on these missions must maintain acceptable quality for a minimum of 3–5 years at ambient conditions.

To determine the suitability of retort processed foods to support long-duration spaceflight, a series of 36 month ASLTs were performed on 13 representative retort pouch products (Catauro and Perchonok, 2012). Combined sensory evaluations, assessment of physical properties and nutritional analyses were employed to determine shelf life endpoints for these foods, which were either observed during the analysis or extrapolated via mathematical projections based on Q_{10} values. Data obtained through analysis of these 13 products were later used to estimate the shelf life values of all retort-processed spaceflight foods.

In general, the major determinants of end of shelf life appeared to be the development of off-flavor and off-color. These changes were assumed to be the result of Maillard and oxidation reactions, which can be initiated or accelerated as a result of the retort process and product formulation. Meat products and other vegetable entrées were projected to maintain their quality the longest (between 2 and 8 years) without refrigeration, followed by fruit and dessert products (1.5–5 years); dairy products (2.5–3.25 years) and starches, vegetable and soup products (1–4 years). Aside from considerable losses in vitamins B and C, nutritional value of most products was maintained throughout their shelf life. Fortification of storage-labile vitamins was proposed as a countermeasure to ensure long-term nutritive value of these products. The use of nonthermal sterilization technologies was also recommended, as a means to improve initial quality of these products and extend their shelf life for use in long-duration missions. Data obtained also emphasized the importance of low temperature storage in maintaining product quality.

12.5.4 PROBLEMS IN THE USE OF ASLT CONDITIONS

The potential problems and theoretical errors that can arise in the use of ASLT conditions have been described (Labuza and Schmidl, 1985, 1988) as follows:

1. Errors in analytical or sensory evaluation. Generally, any analytical measure should be done with a variability of less than ±10% to minimize prediction errors.
2. As temperature rises, phase changes may occur (e.g., solid fat becomes liquid), which can accelerate certain reactions, with the result that at the lower temperature the actual shelf life will be longer than estimated.
3. Carbohydrates in the amorphous state may crystallize out at higher temperatures, with the result that the estimated shelf life is shorter than the actual shelf life at ambient conditions.
4. Freezing “control” samples can result in reactants being concentrated in the unfrozen liquid, creating a higher rate at the reduced temperature and, thus, confounding estimates.

5. If two reactions with different Q_{10} values cause quality loss in a food, the reaction with the higher Q_{10} may predominate at higher temperatures while at normal storage temperatures the reaction with the lower Q_{10} may predominate, thus confounding the estimation.
6. The a_w of dry foods can increase with temperature, causing an increase in reaction rate for products of low a_w in sealed packages. This results in overprediction of "true" shelf life at the lower temperature.
7. The solubility of gases (especially O_2 in fat or water) decreases by almost 25% for each 10°C rise in temperature. Thus, an oxidative reaction such as loss of vitamin C or linoleic acid can decrease in rate if O_2 availability is the limiting factor. Therefore, at the higher temperature, the rate will be less than theoretical, which in turn will result in an underprediction of "true" shelf life at the normal storage temperature.
8. If the product is not placed in a totally impermeable pouch, then storage in high temperature/low humidity cabinets will generally enhance moisture loss, and this should decrease the rate of quality loss compared to no moisture change. This will result in a shorter estimated shelf life at the lower temperature.
9. If high enough temperatures are used, proteins may become denatured, resulting in both increases or decreases in the reaction of certain amino acid side chains, leading to either under- or overprediction of "true" shelf life.

Therefore, in light of the preceding points, the use of ASLT to estimate actual shelf life can be severely limited except in the case of very simple chemical reactions. Consequently, food technologists should always confirm the ASLT results for a particular food by conducting shelf life tests under actual environmental conditions. Once a relationship between ASLT and actual shelf life has been established for a particular food, then ASLT can be used for that food when process or package variables are to be evaluated.

Another point worth stressing is that ASLT where temperature is the accelerating factor, is really only applicable for foods marketed in temperate climates. In tropical climates, the ambient temperature is typically 30°C–40°C and even higher in warehouses, trucks, and so on. These temperatures correspond to those suggested for ASLTs in Section 12.5.2 and higher temperatures than these cannot be used for ASLT because this would lead to reactions that were not representative of how the foods would deteriorate under actual tropical conditions.

12.6 DETERMINING SHELF LIFE FROM THE CONSUMER SIDE

Acceptance or rejection of foods by consumers is based on sensory evaluation involving a complex interaction of flavor, color, texture and so on. Because quality changes in foods are very complex, it is not always possible to make accurate predictions of shelf life based on a mechanistic insight (van Boekel, 2009). In such situations, it is necessary to resort to a statistical description so that the mean time to failure and its standard deviation can be accurately estimated, and the probability of future failures predicted.

Shelf life in relation to consumer acceptance or rejection is commonly defined as the time for 50% of consumers to find the food unacceptable. Other percentages such as 25% or 75% can be used, the choice being a business decision. Although a 50% rejection rate may sound risky, it should be remembered that the consumers taste the product at the end of its shelf life. Distribution times usually guarantee that the proportion of consumers who taste the product close to the end of its shelf life is small, and of this small proportion, 50% will reject it and 50% will accept it (Hough, 2010).

Shelf life models based on consumer responses are of a probabilistic nature and lead to the prediction of the probability that a certain percentage of consumers will not accept the food anymore. The failure times collected and analyzed in shelf life studies are referred to as "time to event data," "failure time data," "survival data" or more generally "life data." The statistical techniques used to handle this type of data are referred to as "survival analysis methods" in medicine and "reliability methods" in engineering.

Shelf life data possess properties that make them different from other data collected in research and development. Among the two most important features are the non-normality of these data and the common occurrence of censored observations. The phenomenon technically referred to as "censoring" is the impossibility of systematically observing the failure times for all samples. Three censoring situations are found: left, right and interval censoring (Guillet and Rodrigue, 2010). Censored observations are incomplete or partial data, but they do contain relevant information to determine shelf life and must not be discarded from the statistical analysis of the data. However, they must not be treated as if the exact failure time were observed. Specific statistical methods exist to account for censoring. If censoring is ignored in the data analysis, a biased estimate of shelf life will be obtained (Gacula et al., 2009).

A fundamental concept in shelf life studies is that samples do not all fail at the exact same time. Therefore, to compute an estimate of shelf life, the statistical distribution of the failure times needs to be determined. Stated another way, a curve that depicts the probability of the product survival as a function of time needs to be generated. Such a curve is called a *survival curve*. In simple shelf life experiments, estimating the survival curve corresponds to the ultimate goal of the statistical analysis of the data. Once estimated, survival curves can be used for prediction, for example, to determine the percentage of samples that have failed after a given length of time, or for inverse prediction, for example, to determine the time when a given proportion of the samples have failed (Guillet and Rodrigue, 2010).

The hazard rate at a given time is defined as the risk of failure at that time knowing that the product has survived until that time. The hazard function defines the relationship between time and the hazard rate at that time. In reliability testing, the hazard function is referred to as the failure rate. A statistical relationship exists between the hazard function and the survival curve, so that knowing one gives perfect knowledge of the other.

A classical representation of the risk of failure over time is commonly represented by a "bathtub" curve, which has many applications in the actuarial and engineering sciences; an example for a refrigerated food is shown in Figure 12.9. At time x_0, the finished product leaves the processing plant and begins its journey to the many distribution outlets. During the time between x_0 and x_1, early failures may occur due to faulty packaging (e.g., pinholes or poor seals) and product abuse. However, the early failures should not be taken as true failures relative to the

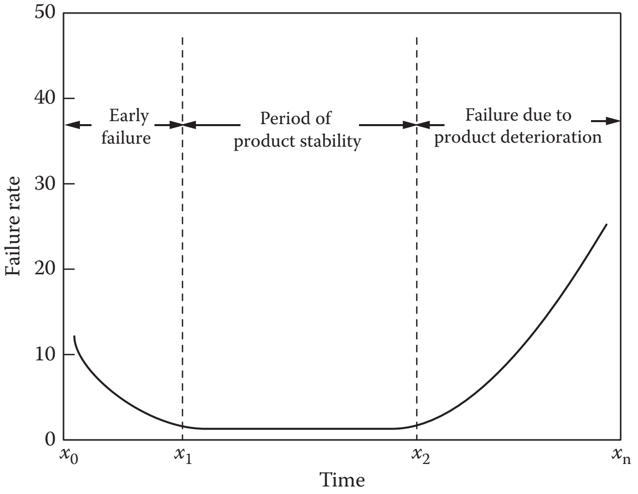

FIGURE 12.9 Bathtub curve showing failure rate as a function of time.

shelf life of the product. From x_1 to x_2, no product failures (barring random fluctuations) would be expected. From the time x_2 to the termination time x_n, the hazard (failure) rate increases, and this time represents the true failure due to deteriorative changes within the product. The length of shelf life is determined between the times x_2 and x_n, and the hazard function plays a central role in the analysis of failure data. It is important to note that the bathtub curve does *not* depict the failure rate of a single item, but describes the relative failure rate of an entire population of products over time.

Given a series of failure times observed for different samples, the goal of the data analysis is to estimate a mathematical function generalizing the distribution of the series to a specific population of products (Guillet and Rodrigue, 2010). This distribution replaces the usual normal distribution, and the way the data are used in the computations should allow for censored data. There are two classical ways of estimating such distributions. If no assumption is made on the mathematical form of the distribution of the failure times, a nonparametric technique may be used. The other, more common, approach consists of assuming a specific statistical distribution to model the failure times, and is known as the parametric modeling approach. With both approaches, survival curves can be estimated and predictions of the failure time for different survival rates can be obtained, along with uncertainty measures.

Three statistical models—lognormal, exponential and Weibull distributions—have been fitted to failure data using the method of hazard plotting that provides information about the adequacy of fit of the observed data to the proposed model, the mean or median time to failure and the probability of future failures. The Weibull distribution (defined by two parameters—shape and scale) has become the most popular model to predict the end of shelf life for foods (e.g., Cardelli and Labuza, 2001; Duyvesteyn et al., 2001). For a detailed discussion of the technique, the reader is referred to Guillet and Rodrigue (2010), Hough (2010) and Gacula et al. (2009). There is also a very useful website for self-paced learning (www.weibull.com) from which it is also possible to download software tools.

Larsen et al. (2010) investigated and compared the statistical properties of various popular estimators of shelf life, and developed a genetic algorithm for finding near-optimal staggered designs for the estimation of shelf life. For almost all of the staggered sampling parameters, the generated designs were very different from the commonly used staggered designs.

12.7 SHELF LIFE DEVICES

As mentioned at the outset of this chapter, the quality of most foods and beverages decreases over time. In other words, there is a continual loss of quality from the time they leave the food processor until they are consumed, even under ideal handling conditions. The goal of modern food distribution techniques is to minimize the extent of quality degradation so that the foods will reach the consumer's table as close to their original state as possible.

Of all the extrinsic factors that accelerate quality degradation, the one which has the greatest influence is temperature. This is well known by food technologists, and most countries have codes of practice that specify optimum storage temperatures for many foods, particularly those classed as perishable. Despite these specifications, problems of storage temperature abuse arise all too frequently. One difficulty when storage temperature abuse is suspected lies in detecting the extent of the quality degradation without sampling the food (i.e., disturbing the integrity of the package). An associated difficulty is that many of those involved in the distribution chain are not trained to make reliable judgments about the quality of the food.

Thus, food processors require a simple way of indicating whether their products have been stored at undesirable temperatures, or better still, a means of indicating how much shelf life remains. Devices that provide the first category of information are time–temperature recorders; devices for the second category are time–temperature indicators (TTIs), and these are discussed further in Chapter 15 (Section 15.4.1.2).

12.8 SOME CAUTIONARY ADVICE

Despite the hundreds of scientific publications on the shelf life of foods and the influence of various packaging materials on shelf life, caution must be emphasized in drawing conclusions from the published data. The packaging of olive oil will be used as an example. Cecchi et al. (2009) critically reviewed the literature results concerning the packaging of olive oil in glass or PET bottles (both of which are used commercially for this purpose). The influence of storage conditions (particularly light) and the initial O_2 concentration were also evaluated. Their conclusions provide a salutary message to researchers (and journal referees) in the shelf life area.

From the analysis of the cited literature, it was clear that the reliability of PET bottles as olive oil containers still needs to be demonstrated, primarily because of inconsistent results. However, the performance of glass still seems to be unsurpassed, even if PET bottles can also provide adequate shelf life. Since the initial O_2 concentration in the oil was demonstrated to play a crucial role in determining oil quality during storage, aside from the bottle material, the influence of this variable should be experimentally evaluated.

Their major criticisms of the published studies concerned the fact that important properties of the PET bottle (O_2 permeability, thickness and brand) were very seldom declared, and most experimental designs were performed using drinking water PET bottles from different commercial brands, with variable thickness and composition. In their view, the low self-consistency of literature results was also probably related to the use of different oxidation markers, and dissimilar methods to predict the shelf life by different research groups. Since olive oil is not a standardized reference material, they suggested that future experimental designs should make use of the same olive oil for all experiments or should carefully declare the initial O_2, antioxidant and pro-oxidant contents, which are widely known to influence olive oil oxidation during storage. They concluded that detailed, comprehensive and standardized experimental studies on the shelf life of olive oil packed in PET bottles should be encouraged.

A further example of the difficulties of accounting for all the variables that affect the shelf life of foods was provided by Lu and Xu (2009). They reported on the effect of the light-barrier properties of three different packaging films on the photooxidation and shelf life of commercial cookies containing 23.5% fat stored at 40°C under UV light. The end of shelf life was determined as the time to reach a critical peroxide value. However, there were large differences in the OTRs of the three films (the OTR of the best was 25 times that of the poorest) which would have had a significant influence on shelf life, in addition to the effect of the different light transmission properties of the three films that varied by a factor of 12. Therefore, it is not possible to draw any conclusions from their results.

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13 Aseptic Packaging of Foods

13.1 INTRODUCTION

Aseptic packaging is the filling of sterile containers with a commercially sterile product under aseptic conditions, and then sealing the containers so that reinfection is prevented; that is, so that they are hermetically sealed. Figure 13.1 illustrates the key aspects of aseptic packaging in diagrammatic form. The term *aseptic* implies the absence or exclusion of any unwanted organisms from the product, package or other specific areas, while the term *hermetic* (strictly *air tight*) is used to indicate suitable mechanical properties to exclude the entrance of microorganisms into a package and gas or water vapor into (or from) the package. The term *commercially sterile* is generally taken to mean the absence of microorganisms capable of reproducing in the food under nonrefrigerated conditions of storage and distribution, thus implying that the absolute absence of all microorganisms need not be achieved.

Currently, there are two specific fields of application for aseptic packaging: (1) packaging of presterilized and sterile product and (2) packaging of a nonsterile product to avoid infection by microorganisms. Examples of the first application include milk and dairy products, puddings, desserts, fruit and vegetable juices, soups, sauces and products with particulates. Examples of the second application include fresh products such as fermented dairy products like yogurt.

The three major reasons for the use of aseptic packaging are (1) to take advantage of high temperature-short time (HTST) sterilization processes, which are thermally efficient and generally give rise to products of a superior quality compared to those processed at lower temperatures for longer times, (2) to enable containers to be used that are unsuitable for in-package sterilization and (3) to extend the shelf life of products at normal temperatures by packaging them aseptically.

13.1.1 Historical Development

The first aseptic packaging of food (specifically milk in metal cans) was carried out in Denmark by Nielsen prior to 1913, and a patent for this process (termed aseptic conservation) was granted in 1921. In 1917 in the United States, Dunkley patented a method of sterilizing cans and lids with saturated steam; the cans were then filled with a presterilized product. In 1923, aseptically packaged milk from South Africa reached a trade fair in London in perfect condition. The American Can Company developed a filling machine in 1933 called the heat-cool-fill (HCF) system, which used saturated steam under pressure to sterilize the cans and ends. The sterile cans were filled with sterile product and the ends sealed on in a closed chamber, which was kept pressurized with steam or a mixture of steam and air. Three commercial plants were built and operated on this principle until 1945.

In the 1940s in the United States, W.M. Martin developed a process in which empty metal cans were sterilized by treatment with superheated steam at 210°C, before being filled with cold, sterile product. In 1950, the Dole Company bought the first commercial aseptic filling plant on the market.

At the end of the 1940s, a dairy enterprise (Alpura AG, Bern) and a machinery manufacturer (Sulzer AG, Winterthur) in Switzerland combined their knowledge to develop ultra-high temperature (UHT)-sterilized, aseptically canned milk which was subsequently marketed in Switzerland in 1953. However, this system was not economical, mainly because of the cost of the cans, and Alpura, in collaboration with Tetra Pak of Sweden, went on to develop an aseptic system based on

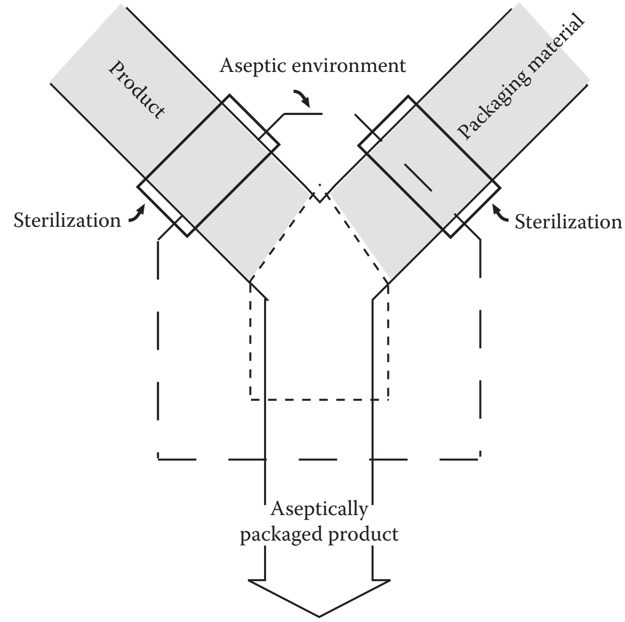

FIGURE 13.1 Diagrammatic representation of the aseptic packaging process.

paperboard cartons. The first milk with a long shelf life to be packaged in this manner was sold in Switzerland in October 1961 (Robertson, 2002).

13.1.2 PRINCIPLES OF STERILIZATION

The sterilization processes used in aseptic processing are variously described as HTST and ultra-heat treated or ultra-high temperature (UHT). The HTST process is defined as sterilization by heat for times ranging from a few seconds to 6 min. The International Dairy Federation has suggested that UHT milk should be defined as "milk which has been subjected to a continuous flow heating process at a high temperature for a short time and which afterward has been aseptically packaged. The heat treatment is to be at least 135°C for one or more seconds." More generally, the term UHT refers to in-line, continuous flow sterilization processes, which employ heat treatments within the temperature range 130°C–150°C with holding times of 2–8 s. The upper end of the temperature range tends to be used for low viscosity products such as milk, and the lower end for more viscous products.

The quality advantages that accrue from the use of HTST and UHT processes can best be understood by comparing the z value for microbial destruction with the z value for the loss of desirable quality factors in the food such as nutrients. A common z value for the former is 10°C, and for the latter, 33°C. A C_0 or cooking index has been proposed to describe the overall sensory quality deterioration which occurs during thermal processing. It is defined analogously to the F_0 value, except that the reference temperature is 100°C, rather than 121.1°C:

$$C_0 = 10^{(T-100)/z}T \tag{13.1}$$

The implications of the differences in z value are evident from a consideration of Figure 13.2. The regions which result in an F_0 value of 10 are typical of the low temperature-long time (LTLT) processes used for sterilizing foods in conventional canning processes; the C_0 values associated with such processes are in the order of 30–300. When an F_0 value of 10 is achieved at higher

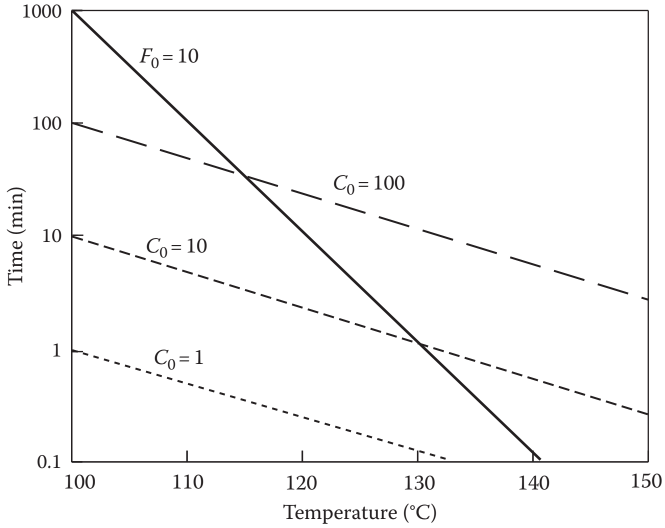

FIGURE 13.2 Comparative enzyme and bacterial spore inactivation curves.

temperatures (130°C–150°C), the corresponding C_0 values are around 1–10. Thus, while there is the same level of microbial destruction in both LTLT and HTST processes, the latter results in considerably less quality degradation and explains the preference of consumers for HTST- rather than LTLT-processed foods. Many chemical reactions such as nonenzymic browning, chlorophyll degradation and nutrient loss have z values of 33–50, and therefore the extent of the reaction at HTST conditions will be significantly less than at LTLT conditions.

One problem associated with the use of HTST processes is that of adequate enzyme inactivation. This is a particular problem with vegetable enzymes (especially peroxidases) and bacterial proteases and lipases produced by psychrotrophic bacteria, usually *Pseudomonas* spp. The heat resistance of bacterial enzymes is very high, and it has been calculated that one such enzyme is 4000 times more heat resistant than spores of *Geobacillus stearothermophilus*, the most resistant of the spores to be destroyed by a heat treatment process. Bacterial enzymes that have shown extreme heat resistance have z values in the range of 20°C–60°C. Thus, as the processing temperature is raised, an increasing percentage of the enzymes survive for the same sterilizing (F_0) performance. As a consequence, the probability of enzymic deterioration during storage of the processed product increases as the heat treatment temperature increases (Burton, 1988). This can lead to quality defects during storage of UHT milk products; for example, the proteases can led to the development of bitter flavors and age gelation (see Chapter 19 for more details).

From a commercial point of view, the aim of sterilizing food with the highest temperatures possible for the shortest possible times has lead to a number of different equipment designs and configurations. The heat exchange equipment can be classified into two groups:

1. Indirect heat exchange where the product and the heat exchange fluid are separated by the heating surface. There are three types:
    a. Tubular heat exchanger
    b. Plate heat exchanger
    c. Scraped surface heat exchanger
2. Direct heat exchange where steam is condensed in the product for heating, and vapor is removed from it by evaporation resulting in cooling. There are two means of heating:
    a. Steam injection (steam into product)
    b. Steam infusion (product into steam)

The objective in the design of the aforementioned equipment has been to improve the rate of heat transfer into and out of the food product in ways which minimize the required heating and cooling times. Generally, the direct systems give more rapid come-up and cooldown times than the indirect systems and present fewer problems with formation of scale and burn on. The indirect systems lend themselves to better heat recovery, tend to give a more stable output temperature and are not prone to contamination from condensables in the steam. In recent years, much work has been conducted on the use of microwave and dielectric heating, as well as resistive (ohmic) heating, for the sterilization of food. A few systems using such processes have become commercially available.

Regardless of the type of sterilizer used, the sterile product is cooled to an appropriate temperature, typically 20°C for low viscous food products like milk and fruit juices and 40°C for products of higher viscosity such as puddings and desserts. A presterilized container is then filled with the cooled, sterile product.

An aseptic filling system must meet a series of requirements, each of which must be satisfied individually before the whole system can be considered satisfactory. These are (Burton, 1988) as follows:

1. The container and method of closure must be suitable for aseptic filling and must not allow the passage of microorganisms into the sealed container during storage and distribution.
2. The container (or that part of it which comes into contact with the product) must be sterilized after it is formed and before being filled.
3. The container must be filled without contamination by microorganisms either from the equipment surfaces or from the atmosphere surrounding the filler.
4. If any closure is needed, it must be sterilized immediately before it is applied.
5. The closure must be applied and sealed in place while the container is still within a sterile zone to prevent the passage of contaminating microorganisms.

There are many possible ways of meeting the aforementioned requirements, and the remainder of this chapter will describe the major sterilization and packaging systems which have been developed and commercialized to meet the aforementioned requirements.

13.2 STERILIZATION OF PACKAGING MATERIAL FOOD CONTACT SURFACES

13.2.1 Required Count Reduction

The required count reduction (number of *D* values) for the sterilization of the food contact packaging material surface is determined by the type of product, its desired shelf life and likely storage temperature. For nonsterile acidic products of pH < 4.5, a minimum of four decimal reductions in bacterial spores is required. For sterile, neutral, low acid products of pH > 4.5, a six decimal reduction is required. However, if there is the possibility that *Clostridium botulinum* is able to grow in the product, then a full 12 decimal reduction process should be given.

The nonsterility rate or error rate, E_r, is the number of nonsterile or faulty packages as a proportion of the total number of packages processed over a given period. It can be calculated using the following equation:

$$E_r = A - N/R \tag{13.2}$$

where

N is the number of microorganisms on the food contact surface of the packaging material
A is the area of the food contact surface of the packaging material
R is the number of decimal reductions obtained in the sterilization process

Smaller containers with a smaller food contact surface area will have correspondingly less initial contamination and a less severe sterilization process will be needed to give a certain nonsterility rate E_r. Conversely, larger containers will require a more severe sterilization process. However, because container volume varies with the cube of the linear dimensions whereas surface area varies only with the square of the dimensions, the variation in the sterilization process according to container size is less than might be expected (Burton, 1988). Commercial requirements of less than one faulty package out of 10,000 produced are common (Moruzzi et al., 2000).

Because of the importance of the initial level of microbial contamination of the packaging material, steps should be taken to ensure that it is as low as possible. Thus, it should be produced, transported and stored under conditions which are as free from microorganisms as possible.

Three main sterilization processes for packaging material are in common use, either individually or in combination: irradiation, heat and chemical treatments. These will each be considered in turn.

13.2.2 IRRADIATION

13.2.2.1 Ionizing Radiation

Particle irradiation techniques using gamma rays from cobalt-60 or cesium-137 have been used to sterilize the interior of sealed but empty containers, especially those made of materials which cannot withstand the temperatures needed for thermal sterilization or that, because of their shape, could not be conveniently sterilized by other means. A radiation dose of 25 kGy or more is generally accepted to be sufficient to ensure sterility. The packages are sealed into microbial-proof containers prior to the irradiation treatment. It is also possible to use low-energy (80–150 keV), large area electron beams for the surface sterilization of packaging materials and containers including preforms, bottles and caps (Haji-Saeid et al., 2007).

13.2.2.2 Pulsed Light

By storing electrical energy in a capacitor and releasing it in short pulses, high peak power levels can be generated. The use of intense and short-duration pulses of broad-spectrum “white” light (200–1000 nm) to sterilize aseptic packaging material underwent considerable research and development in the 1990s. The duration of the pulses ranges from 1 μs to 0.1 s, and the flashes are typically applied at a rate of 1–20 flashes per second. Approximately 25% of the emitted light, which has an intensity of about 20,000 times that of sunlight at the Earth’s surface, is UV, 45% visible and 30% infrared. Generally, a few flashes applied in a fraction of a second provide high levels of microbial inactivation. Despite a successful field trial, this system has not yet been commercialized. Surface topography has a complex influence on the efficacy of pulsed light treatments for surface microbial reduction (Oms-Oliu et al., 2010).

13.2.2.3 UV-C Radiation

UV radiation has a wavelength of 200–315 nm; it is most effective in terms of microbial destruction between 248 and 280 nm (the so-called *UV-C range*), with an optimum effectiveness at 253.7 nm. Mercury vapor lamps emit UV-C at 253.7 nm. UV-C irradiation is generally only used commercially in combination with hydrogen peroxide. Recently, UV (Excimer) lasers operating at 248 nm and using rare (noble) gas halides such as krypton fluoride have been commercialized. Illumination of the carton interior by laser light is problematic: the beam has to be projected physically to different areas of the carton interior by moving the carton into the laser beam (Warriner et al., 2004).

13.2.2.4 Plasma

Nonthermal plasma (NTP) is electrically energized matter and is composed of highly reactive species including gas molecules, charged particles in the form of positive ions, negative ions, free radicals, electrons and quanta of electromagnetic radiation (photons) at near-room temperature (Misra et al., 2011). NTP can be used for the surface decontamination of packaging materials, and a low-pressure microwave plasma reactor has been evaluated for sterilization of PET bottles (Deilmann et al., 2008). A mixture of N_2, O_2 and H_2 gases is ignited inside a bottle; the resultant plasma consists of both UV photons and short-lived, antimicrobial free radicals. A treatment time of 5 s provided a reduction of 10^5 cfu. Commercialization of this cold sterilization process is presently under way.

13.2.3 HEAT

Heat sterilization processes can involve either steam (moist heat) or dry heat. Steam is pure gaseous water with no air or other gases present. Dry heat is hot air in the absence of water molecules. The sterilization effect depends on time and temperature, and steam is much more efficient than dry heat. Steam sterilization at 121°C for 20 min is equivalent in effectiveness to dry heat sterilization at 170°C for 60 min (Robertson, 2011).

13.2.3.1 Saturated Steam

The most reliable sterilant is steam. However, in order to reach temperatures sufficiently high to achieve sterilization in a few seconds, the steam (and thus the packaging material with which it comes into contact) must be under pressure, necessitating the use of a pressure chamber. In addition, any air that enters the pressure chamber with the packaging material must be removed to prevent it interfering with the transfer of heat from the steam to the package surface. Finally, condensation of steam during heating of the packaging material surface produces condensate which, if not removed, could remain in the container and dilute the product.

Despite these problems, saturated steam under pressure is being used to sterilize plastic containers. For example, immediately after deep drawing, molded PS cups and foil lids are subjected to steam at 165°C and 600 kPa for 1.4 s (cups) and 1.8 s (lids). In order to limit the heating effect to the internal surface of the cups, the exterior of the cups is simultaneously cooled. This process has been shown to achieve a five to six decimal reduction in *Bacillus subtilis* spores.

13.2.3.2 Superheated Steam

Superheated steam was the method used in the 1950s for the sterilization of tinplate and aluminum cans and lids in the Martin–Dole aseptic canning process. The cans were passed continuously through 220°C–226°C saturated steam at normal pressure for 36–45 s, depending on the construction material given that aluminum cans have a shorter heating time because of their higher thermal conductivity.

13.2.3.3 Hot Air

Dry heat in the form of hot air has the advantage that high temperatures can be reached at atmospheric pressure, thus simplifying the mechanical design problems for a container sterilization system. Hot air at a temperature of 315°C has been used to sterilize paperboard laminate cartons where a surface temperature of 145°C for 180 s is reached. However, such a system is apparently only suitable for acidic products having a $\mathrm{pH} < 4.5$.

13.2.3.4 Hot Air and Steam

A mixture of hot air and steam has been used to sterilize the inner surfaces of cups and lids made from PP, which is thermally stable up to 160°C. In this process, hot air is blown into the cups through a nozzle in such a way that the base and walls of the cup are uniformly heated.

13.2.3.5 Extrusion

During the extrusion of plastic granules prior to blow molding of plastic containers, temperatures of 180°C–230°C are reached for up to 3 min. However, because the temperature distribution inside the extruder is not uniform and the residence time of the plastic granules varies considerably, it is not possible to guarantee that all particles will achieve the minimum temperature and residence time necessary to result in sterility. Extrusion results in a three to four decimal reduction in microbial spores, and therefore extruded containers should only be aseptically filled with acidic products with a pH < 4.5. For products with a pH > 4.5, it is recommended that extruded containers be poststerilized with hydrogen peroxide (H_2O_2) or peracetic acid (PAA).

13.2.4 CHEMICAL TREATMENTS

13.2.4.1 Hydrogen Peroxide

The lethal effect of H_2O_2 on microorganisms (including resistant spores) has been known for many years, with the first commercial aseptic filling system being devised in 1961. It used a combination of peroxide and heat to sterilize the surface of paperboard laminate packaging material. Although there have been many studies into the death of resistant spores in suspension in peroxide solutions, the actual mechanism of death is not fully understood. It has been found to induce higher heat resistance in *Bacillus sporothermodurans* strains, indicating that sublethal stress conditions may affect heat resistance (Scheldman et al., 2006). Because even concentrated peroxide solutions at room temperature have hardly any destructive effect, a minimum temperature of 70°C, a minimum concentration of 30% and a minimum time of 6 s are necessary to achieve destruction of the most resistant spores on packaging materials within seconds.

There are many uncertainties in the use of peroxide for surface sterilization, and therefore it is difficult to predict the sterilizing effect that any specific combination of peroxide concentration and temperature is likely to have. Therefore, in most situations where peroxide is used to sterilize packaging materials prior to aseptic filling, the sterilization conditions have been determined empirically. These conditions include the peroxide solution concentration, the quantity applied to the packaging material per unit area, the intensity of the radiant or irradiant heat (see the following) and the temperature and quantity of the drying air and the time for which it is applied.

The U.S. Food and Drug Administration has ruled that the concentration of H_2O_2 present in food products packaged in material sterilized by H_2O_2 must be no greater than 500 ppb (500 parts in 10^9) at the time of filling and must fall to approximately 1 ppb within 24 h. Since peroxide cannot be measured accurately in food products because of the presence of reducing compounds that rapidly eliminate it, checks of the initial level must be made on packs filled with water.

Because peroxide solution by itself is unable to sterilize packaging material, a number of systems have evolved which increase the efficacy of the peroxide treatment by combining it with heat and/or radiant or irradiant energy. These processes are briefly described in the following.

13.2.4.1.1 Dipping Process

In one process, the packaging material is unwound from a reel and passed through a bath of 30%–33% H_2O_2 solution containing a wetting agent to ensure uniform wetting of plastic surfaces that tend to be hydrophobic. The liquid H_2O_2 solution is reduced to a thin film, either mechanically by means of a squeeze roll, or with jets of sterile air; the adhering liquid film is then dried with hot air.

13.2.4.1.2 Spraying Process

In this process, H_2O_2 is sprayed through nozzles onto prefabricated packages. The peroxide is then dried using hot air. The death rate is dependent on the volume of sprayed H_2O_2 (larger volumes require longer drying times) and the temperature of the hot air. The trend now is to completely avoid spraying liquid droplets and instead use a mixture of hot air (130°C) and vaporized peroxide instead.

13.2.4.1.3 Rinsing Process

When the prefabricated container is of an intricate shape such that the spraying process is unsuitable, it can be rinsed with peroxide or a mixture of peroxide and PAA. After spraying, the container is drained and then dried with hot air. This process has been used to sterilize glass containers, metal cans and blow molded plastic bottles.

13.2.4.1.4 Combined with UV Irradiation and Heat

When UV irradiation and H_2O_2 are used together, they act synergistically, with the UV irradiation promoting the breakdown of the peroxide into hydroxyl radicals. The overall lethal effect is greater than the sum of the individual effects of peroxide and irradiation, the optimum effect being at a relatively low peroxide concentration of between 0.5% and 5%.

It is usual to use heat as well as UV irradiation and peroxide in the sterilization of packaging materials. The advantage of such a combination is that much lower concentrations of peroxide can be used (less than 5% compared with 30%–35% for peroxide and heat together) and the problems of atmospheric contamination by peroxide and residual peroxide in the filled product are reduced. However, because too high a peroxide concentration reduces the effectiveness of sterilization, strict control of concentration is essential.

13.2.4.2 Peracetic Acid

PAA (also known as peroxyacetic acid) is a liquid sterilant, which is particularly effective against spores. It is produced by the oxidation of acetic acid by H_2O_2, and the solution containing PAA and H_2O_2 is effective against resistant bacterial spores, even at 20°C (Cords et al., 2005). Unlike H_2O_2, PAA causes corrosion of metals such as iron, copper and aluminum. In closed containers, concentrations of PAA greater than 60% can lead to explosive decomposition and therefore it is normally stored at concentrations of 40% (Muranyi et al., 2010).

PAA is used for sterilizing filling machine surfaces as well as packaging materials such as PET bottles prior to aseptic filling, with the PET bottles being rinsed with sterile water rather than hot air.

13.2.5 VERIFICATION OF STERILIZATION PROCESSES

Sterilization of the packaging material is verified by inoculation of the surface of the web, cup or lid stock with the proper concentration of the test organism and allowing this to dry. The system is usually run as for a commercial test batch, and the finished containers are filled with an appropriate growth medium, incubated and observed for growth. At least 100 containers should be tested for each time, temperature or sterilizing agent concentration.

13.3 ASEPTIC PACKAGING SYSTEMS

The aseptic packaging system must be capable of filling the sterile product in an aseptic manner, and sealing the container hermetically so that sterility is maintained throughout the handling and distribution processes. An aseptic packaging system should be capable of meeting four criteria:

1. Able to be connected to the processing system in a manner that enables aseptic transfer of product to take place
2. Able to be effectively sterilized before use
3. Able to carry out the filling, sealing and critical transfer operations in a sterile environment
4. Able to be cleaned properly after use

The type of packaging material used is influenced by the nature of the product, the cost of both the product and the package and the preferences of the consumer. Although the most widespread consumer package for aseptic foods is the paperboard laminate carton, five major categories of aseptic packaging equipment are available and their major features and characteristics are described in the following.

13.3.1 CARTON SYSTEMS

The carton material consists of layers of unbleached and/or bleached paperboard coated internally and externally with polyethylene, resulting in a carton that is impermeable to liquids and in which

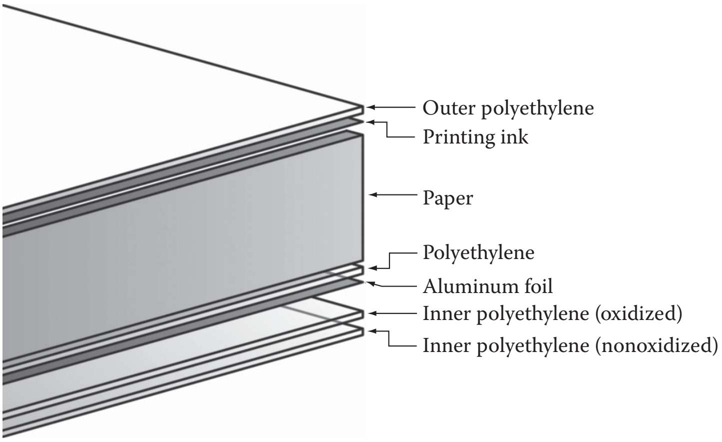

FIGURE 13.3 Typical structure of a paperboard laminate carton for aseptic filling.

the internal and external surfaces may be heat sealed. There is also a thin (6.3 μm) layer of aluminum foil which acts as an O_2 and light barrier. The structure of a typical paperboard carton is shown in Figure 13.3. The functions of the various layers are as follows:

1. The outer polyethylene (12 gsm) protects the ink layer and enables the package flaps to be sealed.
2. The bleached paperboard (186 gsm) serves as a carrier of the decor and gives the package the required mechanical rigidity.
3. The lamination layer of polyethylene (20 gsm) binds the aluminum to the paperboard.
4. The 6.3 μm thick aluminum foil (17 gsm) acts as a gas barrier and provides protection of the product from light.
5. The adhesive layer of poly(ethylene-*co*-methacrylic acid) (6 gsm) ensures good adhesion between the aluminum foil and the polyethylene.
6. The inner polyethylene layer (29 gsm) provides a heat sealable liquid barrier.

13.3.1.1 Form-Fill-Seal Cartons

The packaging material is supplied in rolls that have been printed and creased, the latter being necessary to ease the forming process. A longitudinal seal strip (LS-strip) is sealed to one edge (the reason for this is described later). The LS-strip is composed of a core layer of either PET or EVOH depending on the O_2 sensitivity of the product, coated with LDPE or LLDPE or a mixture of the two. The packaging material is sterilized using one of two procedures: a wetting system or a deep bath system.

In the wetting system, a thin H_2O_2 film (15%–35% concentration), containing a wetting agent (Tween-20 or polyoxyethylene sorbitan monolaurate at 0.2%–0.3%) to improve the formation of a liquid film, is applied on the inner packaging material surface. The material then passes through a pair of rollers to remove excess liquid and under a tubular electric heater, which heats the inside surface to about 120°C and evaporates the H_2O_2.

In the deep bath system, the packaging material is fed through a deep bath containing H_2O_2 (35% concentration) at a minimum temperature of 70°C, the residence time being 6 s. After squeezer rollers have removed much of the peroxide, both sides of the material are heated with air (directed through nozzles) at a temperature of 125°C to evaporate the peroxide.

The sterilized packaging material is fed into a machine where it is formed into a tube and closed at the longitudinal seal by induction heating. In the process, the LS-strip that was added prior to sterilization is heat sealed across the inner surface of the longitudinal seal to prevent contact between

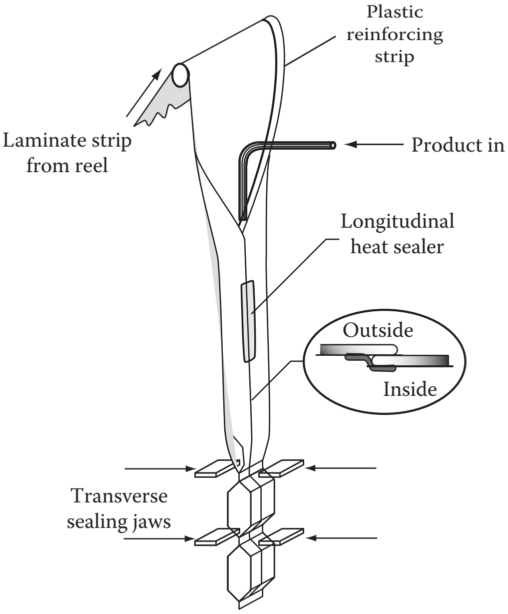

FIGURE 13.4 One method of forming cartons from a continuous web; the cross section of the longitudinal seal is enlarged to show the plastic strip which protects the internal edge of the carton.

the outside and the inside of the carton. It also provides protection of the aluminum and paperboard layers from the product, which could corrode or swell the layers if such a strip were absent.

The tube is then filled with the product and a transverse induction seal made below the level of the product, thus ensuring that the package is completely filled. Alternatively, the packages may be produced with a headspace of up to 30% of the total filling volume by injection of either sterile air or inert gases such as N_2. The sterilization, filling and sealing processes are all performed inside a chamber maintained at an over-pressure of 0.5 atm with sterile air.

One method of forming cartons from a continuous web is shown in Figure 13.4; also included in the diagram is a cross section of the longitudinal seal. The sealed packages are then pressed by molds into rectangular blocks, after which the top and bottom flaps or wings are folded down and heat sealed to the body of the package using electrically heated air.

13.3.1.2 Prefabricated Cartons

In systems of this type, prefabricated carton blanks are used, the cartons being die cut, creased and the longitudinal seam completed at the factory of origin by skiving the inner layer of board and folding it back (see Figure 13.5). The cartons are delivered to the processor in lay-flat form ready to be finally shaped in the filler and the top seam formed and sealed. Although the aforementioned operations take place under nonsterile conditions, steps are taken to avoid recontamination.

The aseptic area of the filling machine consists of several separate functional zones where operations are carried out in sequence. Sterility is maintained in each zone by a slight overpressure of sterile air. The inside surface of the carton is sterilized with a 35% solution of H_2O_2, delivered either as a fine spray or a vapor in hot air that condenses as liquid peroxide on the carton surface. The peroxide is removed by a jet of hot air at 170°C–200°C. Alternatively, the inside of the carton can be sprayed uniformly with a 1%–2% solution of H_2O_2 and then irradiated for about 10 s with high intensity UV radiation. The peroxide is then heated and removed by hot air jets. The problems of residual peroxide in the carton and peroxide contamination in the surrounding atmosphere are more easily dealt with in this latter process because the total quantity of peroxide used is 20–30 times less than in the former.

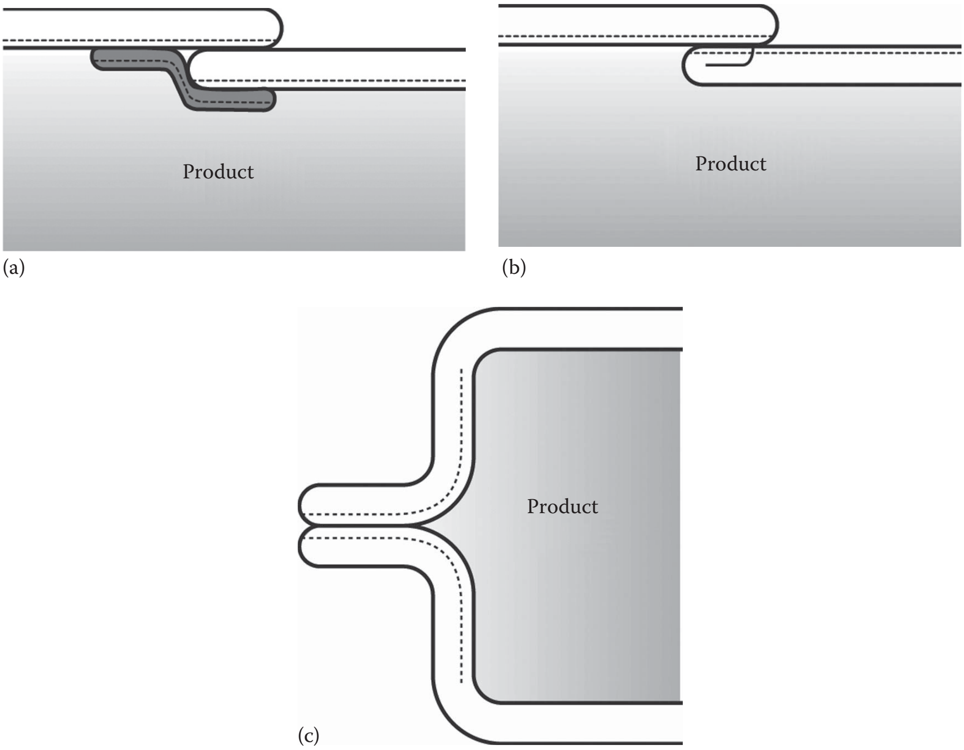

FIGURE 13.5 Three types of side seams used with aseptic paperboard laminate cartons. (a) plastic strip overlaps internal side of longitudinal seam (as used with form-fill-seal cartons); (b) inner layer of board is skived (pared down) and the reduced-caliper edge is folded back and sealed off from the product (as used with prefabricated cartons) and (c) fin seal which avoids exposure of the product to any cut edges of paperboard.

The next stage of the process is filling. A certain amount of headspace is always advisable to ensure that the package can be opened and poured without spilling. A headspace is essential when the contents require shaking (as is the case with flavored milk drinks and pulpy fruit juices). It is advantageous to fill the area between the product and the top of the package with steam or an inert gas such as N_2 for products such as fruit juices. If steam is used, then the headspace volume is reduced as a result of condensation of the steam. A headspace is also crucial when it is not possible to seal the filled package through the product such as when it contains particulate solids. A headspace ensures that sealing can occur above the product line, thus preventing solid material from getting caught up in the top seal where its presence would lead to loss of sterility.

The carton top is folded and closed after filling, and the seal made by either induction heating or ultrasonic welding. Production and date codes are added afterward by ink jet printing or by burning into the top seal. The protruding flaps or "ears" on each side are folded down and sealed to the package with hot air. The finished cartons are then discharged onto a conveyor belt, ready for the final packing process.

13.3.2 CAN SYSTEMS

This system was pioneered by W.M. Martin in the late 1940s, and, in 1950, the first commercial aseptic filling machine was commissioned by the James Dole Corporation in California for soups. The system uses superheated steam at temperatures of up to 225°C for up to 40 s to sterilize the cans and can ends. The three basic types of metal cans (tinplate, ECCS and aluminum) can be used in this system and various can sizes from 125 mL to 22 L can be handled. Product quality is the same for large and small containers, an important feature with products which are difficult to process because of heat sensitivity or poor heat transfer properties.

After the cans are filled with the cold, sterile product, they are sealed using a conventional can seamer which has been modified for aseptic operation. Superheated steam is used to maintain asepsis during the filling operation and results in a high vacuum in the can. To prevent excessive vacuum in the can which could later lead to leaker spoilage, either sterile air or N_2 is blown into the headspace of the can immediately prior to seaming; this results in a vacuum of about 27 cm Hg compared with 50–60 cm Hg without air injection.

An additional important packaging-related factor concerns the lining compound in the lid. At the seaming temperature of 220°C, it is very plastic, and for this reason the seamed can must be transported in an upright position for at least 15 s to allow the compound to settle down and hermetically seal the can. Only then may the can be rinsed to remove filling residues or transported by rolling.

Composite cans consisting of a spirally wound body made from laminations of foil, plastics and paper with metal ends are sterilized using hot air at 143°C for 3 min. This process renders the container and end sterile in respect of acid-tolerant microorganisms such as yeasts, molds and non-spore-forming bacteria, thus permitting the aseptic packaging of acidic products such as fruit juices and other beverages. The use of steam to sterilize composite cans is not practicable since swelling of the paper layers would result.

13.3.3 BOTTLE SYSTEMS

13.3.3.1 Glass

Aseptic filling into glass bottles was attempted following on from the success of aseptic filling into metal cans. The bottles were sterilized either by saturated steam under pressure or by dry heat. When the latter process was used, extended cooling with sterile air was required to minimize the risk of bottle breakage from thermal shock when bottles were filled with cool product. None of the prototypes for aseptically filling glass bottles were successfully commercialized.

However, there has been a revival of interest in aseptic packaging in glass containers and several new systems have been developed. One of these uses dry heat sterilization, while others use a H_2O_2 bath or spray followed by drying with hot air. None of these new glass bottle systems has found widespread acceptance.

13.3.3.2 Plastics

Blow molded plastic bottles have been used for many years as a cheaper alternative to glass for nonreturnable containers. HDPE and PP are the two most common thermoplastics used, sometimes with pigments added so that the contents are better protected from light. It is also possible to mold bottles from multilayered material, resulting in much improved barrier properties and thus longer shelf lives for the products packaged in them. More recently, aseptic PET systems capable of packaging a variety of products including milk, juice and water have been commercialized.

Four different types of systems are in use, as described below.

13.3.3.2.1 Nonsterile Bottles

After blowing (either immediately prior to the following steps or on a separate site), the plastic bottles are conveyed into a sterile chamber, the air pressure of which is kept at a slight overpressure with sterile air. The bottles are inverted and sprayed inside and outside with a solution of H_2O_2 or PAA. The H_2O_2 is evaporated by passing the bottles through a hot air tunnel prior to filling. Bottles sterilized with PAA are rinsed with sterile water and then filled. A chemically sterilized, heat sealable closure such as a plastic film or cap is then applied.

13.3.3.2.2 Sterile Blown Bottles

Bottles are extruded, blown with sterile air and sealed under conditions that ensure internal sterility. The sealed bottles are then introduced into a sterile chamber (maintained under a slight positive pressure) where the outside surfaces are sterilized with H_2O_2 sprays. The closed top of the bottle is cut away, the neck trimmed, the bottle filled and a foil cap or heat sealable closure (which has been sterilized outside the chamber) is applied.

13.3.3.2.3 Sterilization of Preformed Containers

Recently, a dry decontamination system that uses 5–15 mg of H_2O_2 per preform (40 times less than those involving bottle rinsing) was commercialized; no water is needed for the process. The method works by first transferring preforms by the neck on a wheel from the in-feed to the oven entrance. Nozzles, calibrated to between 120°C and 140°C, apply the H_2O_2 vapor, which condenses evenly on the internal walls of the performs; these are then heated in the oven to 100°C.

13.3.3.2.4 Single Station Blowing, Filling and Sealing

In this mechanically complex system, the separate operations of parison extrusion, blow molding, bottle filling and sealing all take place in sequence in a single mold. Sterility of the inside surface of the containers is ensured by the high temperature of the plastics material during extrusion of the parison, and the use of sterile air for blowing. The thermoplastics used for this type of container include HDPE, PP and PETG copolyester, the extrusion temperature ranging from 165°C to 235°C depending on the resin. After filling, the tube projecting from the bottle mold is vacuum formed or sealed with jaws into a cap which closes the bottle. No special arrangements to ensure sterility are required because the filling and sealing are carried out within the closed mold.

13.3.4 SACHET AND POUCH SYSTEMS

13.3.4.1 Form-Fill-Seal Systems

In this system, a vertical form-fill-seal machine operates in a sterile chamber. The packaging material is passed through 35% H_2O_2 and then drained, dried with hot air and irradiated with UV light. The film used is typically a laminate of LLDPE with a center layer of EVOH copolymer and carbon black to give the pouch the required shelf life. Pouches typically have fin seals on all four sides.

An aseptic pouch, similar in structure to the laminate carton shown in Figure 13.3, was commercialized in 1997, the difference being that the paperboard was replaced by paper of 80 gsm. Similar filling machines and procedures are used as for aseptic cartons.

Recently, a chalk-filled multilayer plastic pouch material was commercialized. It consists (from outside in) of a PP layer, a 40% w/w calcium carbonate-filled PP layer to provide stiffness and integrity, EVOH to protect against O_2, a carbon black layer to protect against light and LLDPE as a sealing and food contact layer (Figure 13.6). The material is presterilized using electron beams. Compared to other traditional aseptic packaging concepts, this system is claimed to offer lower environmental impacts in terms of energy consumption, waste generation and emissions to air and water.

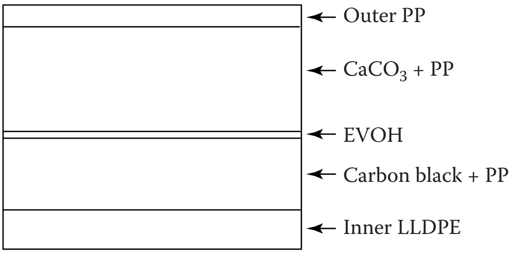

FIGURE 13.6 Structure of chalk-filled plastic material for aseptic pouch.

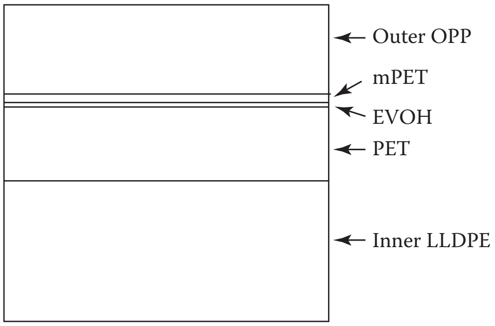

FIGURE 13.7 Structure of bag used for aseptic bag-in-box system for packaging UHT products.

13.3.4.2 Bag-in-Box System

An aseptic bag-in-box system for packaging UHT products consists of a filler that provides a sterile, enclosed product transfer path from process to package utilizing a unique steam-sterilized double-membrane technology. The inner membrane, heat sealed under completely secure conditions during the fill process, remains sealed until the pack is opened by the consumer, thus eliminating any risk of product contamination during storage and transport. Bags range in size from 1.5 to 1400 L and contain EVOH and metalized PET (mPET) as barrier layers (Figure 13.7). Bags are manufactured fully sealed with minimum air content and then sterilized using gamma radiation. During filling, the transfer area is fully sterilized before the first membrane is pierced to ensure a completely aseptic transfer of product. Sterilization is accomplished using only steam, eliminating the need for chemical sterilants, and the steam inlet is specially designed to safeguard the quality of the product. The double membrane on the bags also ensures complete tamper evidence both before and after filling. After filling, the bag is placed inside a paperboard box.

13.3.4.3 Lay-Flat Tubing

This system uses a blown film polymer in the form of lay-flat tubing so that only a transverse seal is required to form the bag. The assumption is made that the inside of the tubing is sterile because of the temperature achieved during the extrusion process. Either a single film or a coextrusion material can be used. The tubing is fed from the reel into a sterile chamber in which an overpressure of air is maintained. The sachets are sealed at the bottom, cut and moved to a filling section. They are sealed at the top after filling and leave the chamber through a water seal.

13.3.5 CUP SYSTEMS

13.3.5.1 Preformed Plastic Cups

The cups are usually made from HIPS, PP or coextruded, multilayered polymers if improved barrier properties are required. A typical example of the latter would be an outer layer of HIPS, a laminating adhesive, a barrier layer of PVdC or EVOH copolymer, a laminating adhesive and finally LDPE.

The cups are fed onto a conveyor which is inside a sterile tunnel supplied with sterile air. The cups are sprayed inside with 35% H_2O_2 solution, and after about 3 s, the solution is removed with compressed hot air at a maximum temperature of 400°C, depending on the material from which the cups are made. The inside surface of the cups reaches a temperature of about 70°C which completes surface sterilization and reduces the peroxide residue to acceptable levels.

Cups can also be sterilized by carrying them through a 35% H_2O_2 bath at 85°C–90°C before heating and passing through a water bath. The cups then enter a sterile chamber where sterilization is completed by spraying with sterile water and drying with hot air.

The lidding material (usually aluminum foil with a thin coating of a thermoplastic polymer) is typically sterilized with 35% H_2O_2 which is then removed either by radiant heat, hot sterile air or by passing the material over a heated roller. In some systems, UV radiation is used, either alone or in conjunction with peroxide.

13.3.5.2 Form-Fill-Seal Cups

The plastic material (commonly HIPS because it is easily thermoformed) in the form of a web is fed from a roll into a thermoformer to give multiple containers (still in web form). More complex coextruded multilayer materials that incorporate a barrier layer of either PVdC or EVOH copolymer can also be treated in this way. However, mechanical forming (rather than thermoforming) is used if an aluminum foil layer is incorporated into the laminate.

The advantages in thermoforming cups from a reel compared to using premade cups include a favorable price ratio, simplified handling because the constant reloading of magazines is avoided, higher output by utilizing multiple tools, smaller storage requirements for the packaging materials and maximum sterility of the cups (both inside and outside surfaces) and lids from running flat material through sterilizing baths.

Sterilization of the web is carried out prior to forming by passing it through a 35% H_2O_2 bath at room temperature, with typical residence times being in the order of 15 s. Air knives remove surplus liquid prior to the web passing through a sterile tunnel where it is prepared for thermoforming by heating it to 130°C–150°C. Alternatively, radiant heat can be used to heat the web after it has left the peroxide bath. The containers are then formed (usually by a combination of mechanical forming and compressed air) into a water-cooled mold below the web. Sterilization of the lidding material is achieved in a similar manner to the container web.

An alternative type of form-fill-seal system sterilizes the containers after they have been formed using saturated steam under pressure at 3–6 atm (135°C–165°C) for about 1.5 s; the lidding material is again sterilized in a similar manner.

Using the high temperatures reached during the extrusion process to ensure sterility is the feature of another form-fill-seal system based on coextruded multilayer films which typically contain PVdC or EVOH copolymer as a barrier layer. The outer layer of the coextrusion is peeled away within a sterile chamber, exposing a sterile inner surface which is then heated by radiation and thermoformed into the desired container shape. It is important that uniform wall thickness is maintained during the thermoforming process, otherwise the thickness of the barrier layer will vary and dramatically affect the shelf life of the product. The lidding material also has a peelable outer layer which is removed to expose a sterile material which can be heat sealed in place.

A special feature of the system is the in-mold labeling process, wherein the label is positioned in the mold and applied and heat sealed to the external surface of the container during the thermoforming process; this imparts strength to the container as well as providing an economical labeling system.

13.4 INTEGRITY TESTING OF ASEPTIC PACKAGES

Assessment of package integrity is one of the most critical issues in the aseptic packaging of foods, and it is imperative that package integrity be maintained to ensure the safety and quality of the product. In addition to the performance tests described in the following, the effects that shipping containers, palletizing, packaging materials and the form of packaging have on the integrity of the aseptic package are also important and should be evaluated before a particular aseptic packaging system is operated commercially.

Several performance tests are in use to assess the likelihood of an aseptic package maintaining its integrity during distribution and handling. Package and seal integrity have traditionally been verified using destructive methods such as biotesting, electrolytic testing, dye penetration or bubble testing. However, destructive test methods are often laborious and time consuming to perform, and clearly it is not possible to test and reject all defective packages.

There is growing interest in nondestructive (or noninvasive) package integrity testing, which allows the online testing of every package produced, while leaving both product and package intact.

Such tests need to meet three criteria: nonspecificity, high sensitivity and rapidity. Most nondestructive leak inspection systems are based on a stimulus–response technique with stimuli including pressure, a trace gas such as CO_2 or helium, and ultrasound. The package response can be package movement, pressure change, trace gas detection or sound attenuation. Recently, a cyclic voltametric method was developed to identify pinholes arising from cracks in the inner plastic layers of aseptic cartons (Hsu and Chang, 2007). An online pressure differential leak detector has also been shown to be effective in assessing the quality of seals in cartons in less than 30 s (Sivaramakrishna et al., 2007).

Other nondestructive tests involving computer-aided video inspection or automatic profiling of the packages have been developed and are being improved upon all the time. Profile scanning with aseptic packages is ineffective because, even if the package leaks and air enters, the package profile does not change immediately.

Despite considerable research in recent years, the availability of commercially viable, nondestructive package integrity testing equipment is still very limited. Continuing research is in progress and new possibilities may be commercialized in the coming years.

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14 Packaging of Microwavable Foods

14.1 INTRODUCTION

Microwaves are a common designation for electromagnetic waves at frequencies between 300 MHz and 300 GHz, sitting between the lower frequency of radio waves and the higher frequency of infrared and visible light. Microwaves have a wavelength from 1 m to 1 mm. The history of the microwave oven began in England in 1940 when two scientists working at Birmingham University (Professors Randall and Boot) devised an electronic tube (which they named a *cavity magnetron*) that generated large amounts of microwave energy very efficiently. The unique ability of the magnetron to transmit microwaves at very high power enabled radar equipment to be built that was much smaller, more powerful and more accurate than anything previously designed.

The magnetron was taken to the United States in September 1940, and Percy LeBaron Spencer at the Raytheon Manufacturing Company received a contract to manufacture copies of it for use in radar by the Allies in World War II. While he was working close to a magnetron, a peanut bar melted in his pocket and this provided the inspiration to use microwaves to heat foods. Spencer then popped some corn in front of a waveguide horn, and the concept of using microwaves for heating foods was proven. He filed a patent application in 1945 which was issued in 1950 (Spencer, 1950). In 1947, he filed another application that was issued in 1949 (Spencer, 1949), which showed a pouch specifically designed for microwave heating of an entire cob of popcorn. The first commercial microwave oven was released in 1947 for institutional and restaurant use. When Spencer's basic patent expired in 1967, the microwave oven domestic market grew rapidly, achieving a penetration rate in U.S. households of over 100% (i.e., more than one per household on average) by the early 1990s.

Consumer interest in the microwave created a growing demand for microwavable foods. Initially, many companies took advantage of the microwave "mania" by simply giving a new designation—either dual ovenable or microwavable—to an already-established product, without changing either the formulation or the packaging. Today, the microwave foods segment has passed into a new phase with the development of microwave-only products. However, although much has been accomplished, more advanced technological research and development of microwavable foods and packaging is required to fully realize the potential of the microwave oven. Milestones in the history of the microwave oven are listed in Table 14.1.

14.2 BASIC PRINCIPLES

14.2.1 Microwave Oven Operation

Microwaves are characterized by wavelength and frequency. Virtually all microwave ovens used by consumers operate at a frequency of 2450 million cycles per second (cps) or 2450 MHz, and in free space (air is a good approximation), the wavelength λ associated with this frequency ($\lambda = c/\nu$, where c = speed of light = 3×10^8 m s^{-1} and ν = frequency) is 122.4 mm. Many industrial microwave heating applications in North and South America operate at 915 MHz (wavelength is 328 mm) and at 896 MHz (wavelength is 335 mm) in the United Kingdom.

The energy delivered is in the form of sine waves, with the electrical and magnetic components orthogonal to each other and also in phase as shown in Figure 14.1. The strength of the electric

TABLE 14.1
Milestones in the History of the Microwave Oven

1945	Percy Spencer from the Raytheon Manufacturing Company files a patent for a method of treating food by application of microwave energy for sufficient time to cook the food to a predetermined degree
1947	First commercial microwave oven introduced by Raytheon for restaurant and institutional use
1955	First consumer microwave oven introduced
1967	First countertop domestic microwave oven introduced
1975	First commercial use of susceptors for pizzas
1984	First use of susceptors in microwave popcorn applications

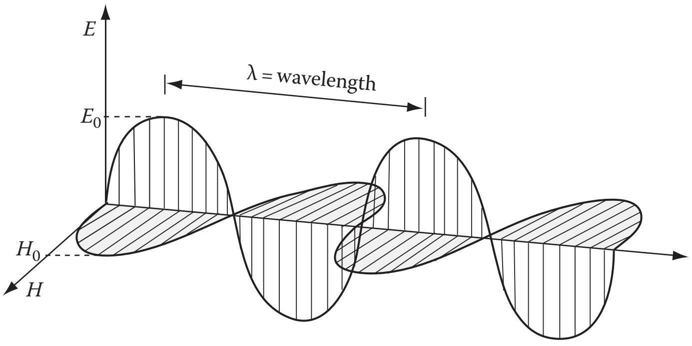

FIGURE 14.1 Diagrammatic view of a plane electromagnetic wave. E and H represent the electrical and magnetic components of the wave, respectively; E_0 and H_0 are their respective amplitudes and λ the wavelength.

field in volts per unit distance oscillates from ground state to a maximum positive voltage, decaying back to zero, then building up to a maximum voltage of opposite polarity and decaying back to zero. This full cycle occurs 2450 million times per second, and the same phenomenon is seen in the magnetic field. The relationships between the components of any electromagnetic field are given by Maxwell's equations, a set of four equations first formulated by the Scottish physicist James Clerk Maxwell around 1860. They will not be given here but can be found in standard physics textbooks.

In the microwave oven, the oven cavity is three dimensional and waves are scattered in all directions. For this reason, it is often convenient to consider the variations in electric field along the three principal directions in the oven. These are referred to as the *three orthogonal components* of the electric field.

Microwaves are generated in a magnetron which consists of a vacuum tube with a central electron-emitting cathode. The waves are transferred to a cavity or oven by means of a waveguide. Waveguides are often aluminum tubes with rectangular or circular cross-sections along which the waves are internally reflected. In an attempt to provide an even distribution of the field, a metal fan, which reflects the radiation randomly, or a turntable, which rotates the food through a variable field, or both, are incorporated into microwave ovens. The metallic walls of a microwave oven are coated with a material which almost totally reflects the microwaves, thus providing a set of boundary conditions. As a result, the walls of the oven do not rise in temperature. Because the walls are good conductors, an electric field parallel to the oven wall cannot exist at the wall.

The interface between the food and the air in the microwave oven (or between various packaging materials and the food) also imposes a boundary condition. At the air/food interface, there is a change in the way microwaves propagate (due to large differences in the dielectric properties between the food and the air), and this controls the ratio of the reflected (from the food surface) and transmitted (passing into the food) waves.

When a beam of microwaves is reflected, the incident beam and the reflected beam interact to form a standing wave pattern. The standing wave pattern is such that at certain distances from the reflecting surface, the field variations have maximum values which correspond to the added values of the incident and reflected waves at those points. At other distances between these maxima, the incident and reflected fields cancel out, resulting in a minimum value which is zero if the reflection is total. Although the incident and reflected beams are always in continuous motion, the resultant electric field pattern appears to be stationary.

The multiple reflections in three dimensions which occur in the microwave oven result in a number of possible three-dimensional standing wave patterns, where each pattern is referred to as a *mode*. In a typical microwave oven, the field can be described in terms of a mixture of about 20 or 30 modes, leading to the description of ovens as *multimode cavities*. Placing a container of food into an oven will change the reflections and therefore modify the mixture of modes in the oven.

14.2.2 Microwave Heating Mechanisms

Microwave heating depends on fundamental principles that must be considered in both product and package design. In conventional heating, foods are placed in a high temperature environment and absorb heat from the oven over time. In a microwave oven, foods are placed in an electromagnetic field at ambient (room) temperature and heat is generated by the food's own ingredients and sometimes the packaging. The temperature gradients that might be observed if the same food were heated in a conventional and a microwave oven are depicted in Figure 14.2.

The rapidly varying electric field of microwaves is responsible for most of the heating of food in a microwave oven. Although there is also an analogous set of magnetic field components, they are not normally important in determining the heating behavior because foods do not interact with magnetic fields. However, certain special types of packaging materials have been developed which do make use of magnetic interactions to generate heat and these are discussed in Section 14.4.

In developing products for microwave processing and heating, it is important to recognize that microwaves are a form of energy, not a form of heat, and are only manifested as heat on interaction with a material as a result of one or more energy-transfer mechanisms. When exposed to an alternating electric field, foods can partially store electrical energy as a capacitor, and partially convert electrical energy into heat, like a resistor (Tang and Resurreccion, 2009). There are two main mechanisms by which microwaves produce heat in foods and these are now discussed in turn.

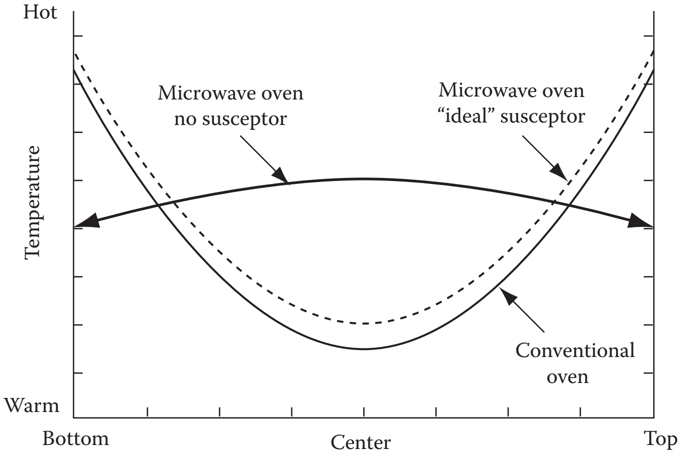

FIGURE 14.2 Temperature gradients in microwave and conventional heating of foods. (From Turpin, C., *Microw. World*, 10(6), 8, 1989.)

14.2.2.1 Dipole Polarization

Polar molecules (water is the most common polar material in foods) are charged, asymmetric molecules which are randomly oriented under normal conditions. In the presence of an electric field, the polar molecules attempt to align themselves with the rapidly changing, alternating electric field. The polarity of the field is varied at the rate of the microwave frequency. At 2450 MHz, this occurs 4.9 billion times per second, that is, about every 0.5 ns (Risman, 2009). In this field, the molecules act as miniature dipoles and follow the changing field if they are small enough to do so. However, at 2450 MHz, their inertia is such that a lag occurs, that is, a resistive action resulting in energy absorption. This dipole lag effect is the dominating microwave absorption mechanism in cold and frozen foods, in the latter case by the strong absorption in the remaining unfrozen water. It is reduced at increasing temperatures due to fewer molecules sticking together by the so-called hydrogen bonding, reducing the inertia.

Dipole polarization is the phenomenon responsible for the majority of microwave heating effects observed in moist foods.

14.2.2.2 Ionic Conductivity

Ionic conductivity occurs when ions in solution move in response to an electric field. Ions carry an electric charge and are accelerated by the electric field, changing direction as the polarity of the electric field changes; this effect is frequency dependent. The most common ions in food are those from salts such as NaCl. Energy is given up by the field to the ions, which collide with other ions, converting kinetic energy into heat. The more concentrated or dense the solution (i.e., the higher the salt concentration), the greater the number of ions and thus more kinetic energy is released. The effect becomes stronger at higher temperatures, since the ions become more “naked” due to the reduced hydrogen bonding. The physiological salt content in meat (about 0.6%) results in a good balancing effect of the microwave absorption under temperature change. The dipole and ionic absorption effects are then thus about equal.

However, because ions are generally less abundant than water molecules in most foods, ionic conductivity tends to play a less important role than dipole polarization in the heating of foods in a microwave.

Microwave heating is also dependent on the physical state of the material. In ice, the water molecules are not held together by hydrogen bonding but instead are individually locked in the crystal matrix. Their inertia is therefore very small and results in ice absorbing microwaves several hundred times less than liquid water.

For most foods, dielectric spectroscopy measurements of the loss factor and dielectric constant show that ionic conduction is generally the more important of the two mechanisms, in some instances contributing up to three to four times more to the heating of foods. For foods which have an electrical conductivity higher than that of water, the ionic conductivity mechanism will, in general, make a significant and most probably larger contribution to microwave heating than the dipole polarization mechanism. If excessive absorption is a problem (i.e., a high loss factor and short penetration depth), then the ionic strength of the food should, if possible, be reduced (Chouikhi, personal communication, 2011).

With conventional heating, moisture is first flashed off the surface of the food and water then moves toward the surface as a result of a driving force due to a dry surface and a wet interior. This movement is primarily by capillarity and is limited by the diffusion rate. With microwave heating, the interior temperature may be higher than that on the surface, causing a higher internal vapor pressure, which effectively pumps water as vapor toward the surface. The result is often a much higher rate of water movement and evaporation than in a conventional oven, and frequently the surface remains constantly wet. Because the air in the microwave oven is cool, the water vapor condenses. In addition, any evaporation will cause surface cooling.

14.2.3 DIELECTRIC PROPERTIES

Foods in general are neither good electrical insulators nor good electrical conductors, and thus fall into the category known as *lossy* dielectric materials. The dielectric properties of interest are the *relative dielectric constant* ε' and the *relative dielectric loss factor* ε'' which are the real and imaginary parts of the *relative complex dielectric constant* or *permittivity* ε (relative to free space or air):

$$\varepsilon = \varepsilon' - j\varepsilon'' = \left|\varepsilon\right| e^{-j\delta} \tag{14.1}$$

where

δ is the *dielectric loss angle* ($\tan\delta = \varepsilon''/\varepsilon'$)

Imaginary unit $j = \sqrt{-1}$ (Tang and Resurreccion, 2009)

The permittivity describes the ability of a material to absorb, transmit and reflect electromagnetic energy.

The *relative dielectric constant* ε' is the ratio of the capacity current through the food to the capacity current which would flow if the same field intensity were applied to free space (in a vacuum or air, $\varepsilon' = 1$). It is a measure of the speed of the electromagnetic wave through a food. The frequency of the waves in a microwave oven is constant (2450 MHz) regardless of the medium they are traversing. If the propagation speed changes and the frequency remains unchanged, then the wavelength will change. The larger the permittivity for a given food, the shorter the wavelength, and thus the slower the wavespeed.

The *relative dielectric loss factor* ε'' is an intrinsic property of a food and is a measure of a food's ability to dissipate electrical energy. It indicates the efficiency with which electromagnetic radiation is converted to heat. The greater the *lossiness* of a food, the greater the absorption of microwave energy and the higher the rate of temperature increase within the food. Thus, foods with a high loss factor are termed *lossy materials* and are very suitable for microwave heating. The loss factor varies irregularly with frequency, temperature and the nature of the food.

The dielectric properties of most foods, at least near 2450 MHz, parallel those of water, the principal lossy constituent of food (see Table 14.2). The dielectric properties of free water are well known and serve as the basis for absorption in most foods, as the dipole of the water molecule interacts with the microwave electric field. By comparison, ice and water of crystallization absorb very little microwave energy. Unfrozen water below 0°C can absorb microwaves. The ways in which the dielectric constant and the dielectric loss factor change with temperature are presented in Figures 14.3 and 14.4. Increased ionic conductivity in salted products such as ham leads to an increase in the dielectric loss factor with an increase in temperature, whereas for other foods, the dielectric loss factor decreases with temperature after peaking just above 0°C.

14.2.4 ENERGY CONVERSION

There are some popular misconceptions about microwave heating, and statements such as "the food heats up from the center" are not uncommon. Therefore, it is helpful to understand how microwave radiation is adsorbed by a food. For simplicity, consider microwave radiation which is incident on one surface only. As the wave passes through the food, it is attenuated (i.e., it loses energy). It is this energy which is converted to heat at the point where the energy is lost. Any temperature gradients that develop within the food are then eliminated by normal processes of conduction and/or convection.

TABLE 14.2
Dielectric Constant (ε′), Dielectric Loss Factor (ε″) and Penetration Depth (d_p) of Various Materials at 2450 MHz

	Temperature (°C)	ε′	ε″	d_p (mm)
Air		1.0	0	
Water (distilled)	20	78.7	10.3	16.8
	50	69.3	4.7	
	100	55.3	1.7	
Water + 0.5 M NaCl	23	75.8	15.6	10.9
Ice	−12	3.2	0.003	11,615
Corn oil	25	2.5	0.14	220
Lard	20	2.5	0.09	350
	60	2.6	0.15	220
Milk (3.2% fat)	25	78	23	
Yogurt	22	68	18	9.0
Lean meat	25	40	12	
Fatty meat	25	53	16	
Cooked fish	25	46	12	
Cooked ham	25	60	42	3.8
	50	53	55	2.8
Cooked beef	25	72	23	9.9
	50	68	25	8.9
Potato				
Raw	25	54	16	9.0
Mashed	30	72	24	7.0
Asparagus	21	71	16	10.3
Apples (87.5% moisture)	22	57	12	12.3
Apples (34.5% moisture)	60	19.7	6.6	13.2
Apples (30.3% moisture)	22	10.7	5.5	11.9
Apples (9.2% moisture)	22	2.2	0.1	28.9
Butter (salted)	25	4.6	0.60	69
Butter (unsalted)	25	2.9	0.45	74
Bread dough	25	22.0	9	10
Bread	25	4.6	1.2	35
Paper	25	3	0.15	148
Polyethylene	25	2.3	0.003	700
Glass	25	5.2	0.02	

The fundamental equation for microwave power absorption by a food is (Wäppling-Raaholt and Ohlsson, 2005)

$$P_v = 2\pi f \varepsilon_0 \varepsilon'' E^2 \tag{14.2}$$

where

P_v is the power absorbed in a volume of food (W m^{-3})
f is the frequency of the microwaves (Hz)
ε_0 is the permittivity in free space (8.854×10^{-12} F m^{-1})
ε'' is the relative dielectric loss factor of the food
E is the electric field strength inside the food (V m^{-1})

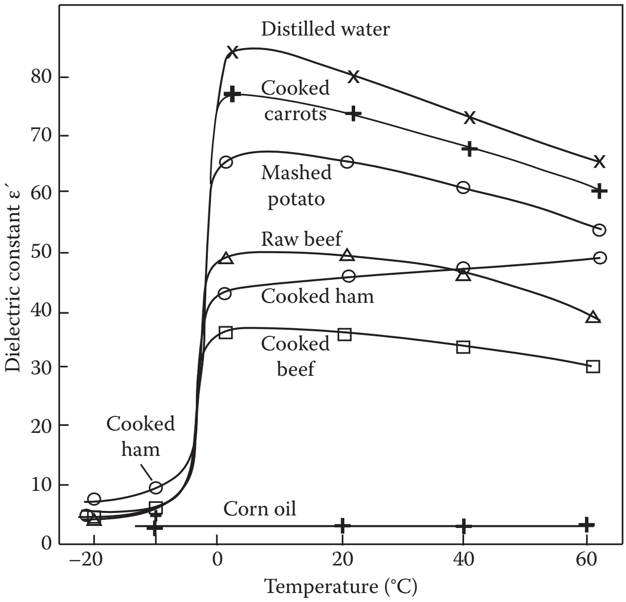

FIGURE 14.3 Relative dielectric constant ε′ of some foods at various temperatures. (From Bengtsson, N.E. and Risman, P.O., *J. Microw. Power*, 6(2), 107, 1971.)

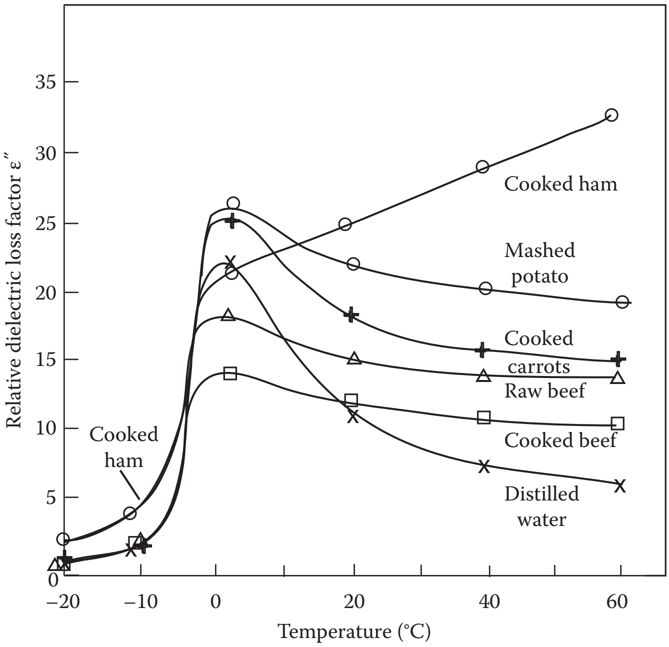

FIGURE 14.4 Relative dielectric loss factor ε″ of some foods at various temperatures. (From Bengtsson, N.E. and Risman, P.O., *J. Microw. Power*, 6(2), 107, 1971.)

From Equation 14.2, it is evident that the converted thermal energy for microwave heating is proportional to the value of the loss factor and the square of the electric field within the food. Unfortunately, the electric field strength is variable and very difficult to estimate or measure in a microwave oven. The increase in temperature (ΔT) of a food, without consideration of heat transfer, is (Tang and Resurreccion, 2009)

$$\frac{\Delta T}{\Delta\theta} = \frac{2\pi f \varepsilon_0 \varepsilon'' E^2}{\rho C_\mathrm{p}} \tag{14.3}$$

where
ΔT is the temperature rise (°C)
$\Delta\theta$ is the time increment (s)
ρ is the density of the food (kg m^{-3})
C_p is the specific heat (J kg^{-1} °C^{-1})

Two of the parameters (field strength and frequency) are properties of the energy source (i.e., fixed by the microwave oven). The dielectric loss factor, density and specific heat are properties of the foods being heated. Increasing the value of any of these factors increases the amount of energy converted. The food product developer may be able to increase the latter two factors by altering the food composition. Although changes in formulation will affect the dielectric properties, Ryynänen et al. (2004) concluded that the factors that are most significant in controlling the temperature profile of a ready meal are the geometry and placement of the food components and the design of the tray.

As mentioned earlier, there are two main mechanisms by which foods heat when exposed to a microwave field. Using ε' and ε'' to characterize heating in the oven eliminates the need to distinguish the particular heating mechanisms of the food under study, and they are therefore very useful characteristics.

14.2.5 PENETRATION OF MICROWAVES

When microwaves strike the surface of a food, they arrive with some initial level of power P_o, which is a function of the power output of the magnetron, oven cavity size and uniformity of the fields. As the waves begin penetrating the food, some of the power is absorbed and the wavelength changes, depending on the dielectric constant of the food.

For practical use in industry, the dielectric properties are converted to an attenuation factor or its inverse, the penetration depth d_p, which defines the depth into the food at which the energy has decreased to $1/e$ (about 37% because $e = 2.718282$).

The penetration depth d_p can be calculated as follows (Tang and Resurreccion, 2009):

$$d_\mathrm{p} = \frac{C_\mathrm{p}}{2\pi f \{2\varepsilon'[(1+\tan^2\delta)^{1/2} - 1]\}^{1/2}} \tag{14.4}$$

The penetration depth can give insight into the heating behavior of foods (see Table 14.2). For example, at a depth d_p into the product, 63% of the energy has been absorbed; at $2d$, only 14% of the incident power level remains; and after $3d$, just 5% is left. Thus, assuming a homogeneous food and constant penetration depth at different levels, it is apparent that the outer layer heats faster than the inner layers. As long as the food thickness is equivalent to or smaller than the penetration depth, this effect is not major, but for very thick foods, the outer surface will get much hotter than the inner one. In addition, because microwaves strike foods from all sides, there could also be a "hot spot" in the center where the waves from all sides overlap, creating a superposition of power.

The actual wavelength of microwaves in different foods can be calculated from (Tang and Resurreccion, 2009)

$$\lambda_{\mathrm{m}} = \frac{\lambda_{\mathrm{o}}}{\left\{(\varepsilon'/2)[(1+\tan^2\delta)^{1/2}+1]\right\}^{1/2}} \tag{14.5}$$

where

λ_{m} is the wavelength in a food
λ_{o} is the wavelength in free space
ε' is the relative dielectric constant of the food

That is, the wavelength is inversely proportional to the square root of the relative dielectric constant of the food ε'. Because values for ε' are much greater than 1, the wavelength of microwaves will be sharply reduced when they enter foods. For example, from Table 14.2, the wavelength can be calculated to be 13.8 mm in water, 16.6 mm in potato and 15.0 mm in ham. This compares with a value of 122 mm in air.

14.2.6 NONUNIFORM HEATING

Many of the more serious problems associated with foods heated in a microwave oven can be attributed to nonuniform heating (Lorenson et al., 1990). For example, it is not uncommon for a frozen entree to thaw, heat and begin to boil around the edges while the center remains frozen. If the heating time is chosen to ensure that the center temperature is acceptable (say 50°C), then the product around the edges is dried and charred. Alternatively, if the heating time is reduced to avoid deterioration around the edges, then the center of the product will be unacceptably cold. Because of such nonuniformity, it is impossible to achieve a result which approaches a satisfactory quality.

A number of factors contribute to the nonuniformity of microwave heating. The three principal effects are (Lorenson et al., 1990)

1. Undesirable field distribution, with the microwave energy being significantly more intense around the periphery than in the center of the oven
2. Microwave energy entering through the sidewalls of the container, causing further heating of the food nearest the walls and very little heating in the central region
3. Differences in absorption of microwave energy for frozen and thawed foods, where there is a dramatic increase in lossiness as the food thaws

Three distinct approaches are used to eliminate or minimize the effects of nonuniform heating. These are

1. *Food formulation*, where by the careful selection of ingredients and food combinations, it is possible to prepare meals that are more tolerant to variations in heating.
2. *Heating procedures*, which include the use of intermediate standing times, low power settings and stirring operations (if appropriate) to allow the temperature of the overheated regions to be reduced. However, because of the low thermal conductivity of most foods and the short times involved, there is little significant transfer of heat. Thus, only minimal improvements in product quality are obtained using this approach
3. *Packaging systems*, which interact with and modify the microwave field distributions by simultaneously increasing field intensities at the center of the food and reducing the field intensity at the edges. Such systems are discussed further in Section 14.4

14.3 EFFECT OF FOOD PRODUCT

If the dielectric properties of the food materials are known, then the penetration depth can be calculated using Equation 14.4. This offers an insight into the heating behavior of foods and packaging. Determining dielectric properties is quite a sophisticated procedure, and most product developers rely on published data. The dielectric properties of foods at microwave frequencies are, for many practical purposes, determined by their moisture, solids and salts contents. Microwave absorption will tend to be reduced, and the microwave penetration depth in food will be raised, by lowering the water content and/or mixing with material of low permittivity. Increasing the ionic content, for example, by adding salt, will increase the dielectric loss and reduce penetration depth without affecting the wavelength in the food (Wäppling-Raaholt and Ohlsson, 2009). However, sensory requirements and the trend toward lower salt content in foods severely limit the changes in dielectric or thermal properties that can be achieved using this approach.

Generally, it is found that both the dielectric constant and the loss factor are temperature dependent. The following example for water illustrates this:

$$\text{At } 1.5°\text{C}, \varepsilon' = 80.5, \quad \varepsilon'' = 25.0 \quad \text{and} \quad \tan\delta = 0.31. \text{ By calculation, } d_p = 14.2 \text{ mm.}$$

$$\text{At } 25°\text{C}, \varepsilon' = 78, \quad \varepsilon'' = 12.5 \quad \text{and} \quad \tan\delta = 0.16. \text{ By calculation, } d_p = 27.6 \text{ mm.}$$

$$\text{At } 70°\text{C}, \varepsilon' = 63.6, \quad \varepsilon'' = 3.0 \quad \text{and} \quad \tan\delta = 0.05. \text{ By calculation, } d_p = 71 \text{ mm.}$$

Compare these values with those of ice where $\varepsilon' = 3.20$, $\varepsilon''=0.003$ and $\tan\delta = 0.0009$. In this situation, $d_p = 24.2$ m! This explains why it is difficult to rapidly thaw foods in a microwave oven; little energy is absorbed by ice, even when reasonably thin, giving rise to the expression that "ice is highly transparent to microwaves."

The physical geometry of the product exerts its influence in several ways. However, because the microwaves can be assumed to follow the laws of optics with reflections and refractions at interfaces between materials of different optical/dielectric properties, many of the peculiarities in microwave heating can be explained. The more regular the shape, the more uniform the heating. Sharp edges and corners should be avoided, because these will tend to overheat. Round is better than square, and a torus (doughnut) is an ideal shape. The sphere acts as a microwave resonator, with the microwaves that enter the sphere being internally reflected because of their very limited angle of incidence and the effect of refraction.

14.4 PACKAGING

Packaging materials can react in three ways to microwaves: they can reflect the radiation, absorb the radiation or transmit the radiation (so-called *RAT characteristics*). Transparent materials do not appreciably react to the microwave field of the oven or significantly modify the power distribution in the oven and are referred to as passive packages (Bohrer and Brown, 2001). The various types of packaging materials used to package food in a microwave oven are described in the following.

14.4.1 TRANSPARENT MATERIALS

In these types of packages, the microwaves penetrate the transparent material and are absorbed by the food. All the polymers currently used for food packaging, as well as paper products and glass, are transparent to microwaves. Because paper products contain some water and mobile ions in their structure, they will heat in the microwave, but the rate is generally slow and negligible.

Closure of these packages can enhance product performance and temperature uniformity by transforming the energy used to vaporize water that may otherwise escape into general heating of the product. Localized drying of products in corners and thin layers on the edges can lead to localized heating. As the product temperature rises, adjacent packaging materials will be heated by the product, and therefore temperature resistance of the packaging material needs to be evaluated.

The types of problems encountered in microwave ovens with foods packaged with transparent packaging materials include (Bohrer and Brown, 2001)

1. Sogginess or lack of development of crisping
2. Lack of browning or color development
3. Nonuniformity of moisture loss, leading to localized toughening
4. Nonuniform temperature distribution
5. Boil-out or run-off of sauces and toppings
6. Inappropriate heating rates for proper cooking of multiple component food products

In recent years, multilayer plastic structures containing self-venting valves have been used to effectively cook foods in a microwave using steam generated by the moisture in the food. Typical structures consist of an LDPE outer layer laminated to a PET substrate with a PP inner layer to provide good heat resistance and a robust seal. As the food heats in the microwave oven, water is converted to steam and the pack gradually expands with excess steam venting through a valve on the package.

14.4.2 ABSORBENT MATERIALS

Packaging materials that absorb microwave energy and reemit that energy as heat are commonly called *susceptors* but are also referred to as *receptors*, *absorbers* or *heater elements*. They have been used commercially in various forms since 1975, with the key microwave susceptor patent being granted in 1986 to Oscar Seiferth (U.S. No. 4,641,005). Susceptors are used to achieve localized effects such as crisping (surface drying) and browning, and are an example of active packaging (see Chapter 15) because they perform functions beyond that of just containment, and enhance the performance of the package.

An ideal susceptor would heat up very rapidly to a predetermined temperature and remain at that temperature throughout the whole heating process. Unfortunately, thin film susceptors do not perform well in many applications; they either overheat locally and burn the product, or become damaged during the heating process in the microwave. Such damage is characterized by a premature reduction in their heating capability and an unevenly heated product (Zuckerman and Miltz, 1994).

To produce a thin film susceptor, particles of a metal such as aluminum are applied at a particular density (typically a thickness of 3–6 nm) to a heat-resistant surface such as 12 μm biaxially orientated PET film, which is adhesive laminated to a low loss, temperature-stable substrate such as bleached kraft paperboard (the final material is often referred to as a heater board). The four basic layers consist of the following:

1. A heating surface (often 12 μm of heat-set, biaxially orientated PET)
2. A thin metal layer (usually vacuum deposited aluminum at 50–250 Ω sq^{-1})
3. An adhesive (typically PVA)
4. A substrate (usually paper or paperboard)

Usually, the food is in direct contact with the heating surface (PET), which may have a release coating. The metallized side of the susceptor is placed away from the food to protect the metal from chemical or physical damage.

Two techniques are used to produce thin film susceptors: physical vacuum deposition (PVD) and sputter deposition. The PVD process (described in Section 5.5.1) is carried out in a vacuum chamber, and the most common way to heat the source material is by the passage of a current. The most widely used material is aluminum. Metal oxides such as tin oxide can also be used, as can stainless steel alloys, but this is rare in food packaging.

Sputter deposition is also a high vacuum process in which high energy particles (typically ions) are accelerated toward a solid coating material target, resulting in atoms and molecules being ejected from the target at high velocities. The ejected particles are then deposited onto the substrate (Perry and Lentz, 2009). Sputtering is several times more expensive than PVD and this is the principal reason it is not widely used.

Although susceptors are referred to in the literature as *conductive coatings*, it is the resistance between the metal particles at their contact points which results in the generation of heat. Very thin layers of conductive material have significant electrical resistance and generate localized resistance heating where they are exposed to a rapidly oscillating electric field. When the susceptor is placed in a magnetic field, a current flows through the metallic coating.

The most important property of a metal film is its surface resistivity, which is a measure of the ability of a thin metal coating to conduct electricity. The surface resistivity is defined as the ratio of the potential gradient parallel to the current along its surface to the current per unit width of surface, and is numerically equal to the surface resistance between two electrodes forming opposite sides of a square; the size of the square is immaterial, leading to the somewhat strange units of ohms per square.

For a thick metal, the surface resistivity is close to zero and all of the energy of the incident microwaves is reflected as shown in Figure 14.5. As the metal thickness is reduced, the surface resistivity starts to increase and some of the energy is then transmitted, some is absorbed and less is reflected. As the thickness of the metal is reduced further, the amount of energy absorbed increases rapidly until it reaches 50% of the incident energy, after which absorption gradually falls to zero while the surface resistivity increases to infinity (Turpin, 1989). Maximum power absorption occurs theoretically at a surface resistivity of $188.5\,\Omega\ \text{sq}^{-1}$ (Česnek et al., 2003).

Susceptors heat in the presence of microwave energy, and temperatures in excess of 200°C can be achieved in only a few seconds as shown in Table 14.3. PET susceptors limit temperature by mechanically breaking the originally continuous aluminum thin film into small islands, thus reducing current flow and power absorption. The driving force behind the mechanical breakup is the biaxial orientation and heat set performed during film manufacture (Perry and Lentz, 2009). Stresses in the film are relieved up to the temperature at which it is heat set. However, once this

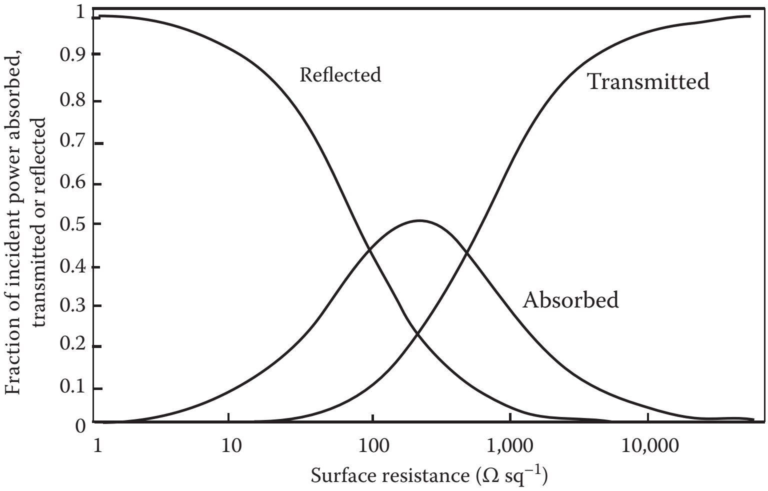

FIGURE 14.5 Fraction of microwave power absorbed, transmitted and reflected by a susceptor as a function of surface resistivity. (From Perry, M.R. and Lentz, R.R., Susceptors in microwave packaging. In: *Development of Packaging and Products for Use in Microwave Ovens*, Lorence, M.W. and Pesheck, P.S. (Eds), CRC Press, Boca Raton, FL, pp. 207–236, 2009.)

TABLE 14.3
Maximum Observed Interface Temperatures between Product and Susceptor

Product	Maximum Temperature (°C)	Heating Time (s)	Comments
Susceptor alone	316	100	No food load
Popcorn	247	150	Normal
Popcorn	280	220	Extended heating
Fish fillet	222	290	Not turned
Pizza	223	290	Not turned

temperature is exceeded, the remaining residual stresses in the film cause it to shrink and shrivel as it returns toward its shape prior to biaxial orientation. Eventually, the film and the laminating adhesive soften to a point where the PET begins to stretch and thin itself, ultimately tearing itself apart.

This breakup of the thin coating provides a maximum temperature limit, although unfortunately this upper limit is very hard to control or predict because it depends on the balance between microwave power absorption and heat removal, as well as the biaxial orientation and heat set performed on the PET. The need for a heat sink to pull heat away from the susceptor coating in order to avoid an excessive decrease in lossiness is one reason why intimate contact with the food is important to effective thin film susceptor operation (Turpin, 1989). As with other packaging components used in the microwave, there are no guarantees on heating performance for the multitude of products where the susceptor would appear to be applicable.

To improve susceptor performance, it is usual to have a deliberate pattern of metallization dependent on the nature of the food, rather than metallizing the whole surface. Patterned susceptors allow selective heating at different locations on the food. There are several methods which can be used to obtain pattern metallizations:

1. Pattern demetallization involves taking a full web of metallized substrate and coating the metal side with a clear lacquer in the pattern desired on the finished product. The coated substrate is then subjected to an acidic bath, which removes the unprotected metal, creating a susceptor pattern ready for lamination to paper or paperboard stock.
2. Hot stamp transfer combines conventional hot stamping technology with susceptor metallizing technology to create a transferable susceptor with standard hot stamping equipment. This type of pattern transfer offers the best utilization of susceptor film and more control over inventory by the converter, who can change patterns simply by changing the die.
3. Hot nip transfer is similar to hot stamp transfer, with the difference being that the final coating or adhesive coating is applied in a pattern using a cylinder similar to the demetallization process. This method allows the converter to produce a roll-to-roll transfer of susceptor directly to paper or paperboard stock.
4. Film-to-film transfer is done just like hot nip transfer, except that the susceptor is transferred to film rather than paper or paperboard.

14.4.3 SHIELDING AND FIELD MODIFICATION

Thick, conductive metal films behave quite differently from the thin, resistive metal susceptor films discussed earlier and form the basis for shielding and field modification packages and package components (Bohrer, 2009). *Shields* are metallic structures that are thick enough so as not to heat, but can reflect microwaves in the same way as the oven walls. For example, a product encased in foil would not exhibit any microwave heating, because no energy is able to penetrate the foil to reach the product. Examples of shield materials include foil, foil laminated to a substrate or aluminum sheet converted into pans and trays.

Special precautions are necessary when using shields. Although they are good conductors of heat, a large electrical potential can build up, and if the potential comes close to a grounded surface or another piece of foil with a different potential, an electric discharge (spark) can occur. This arcing phenomenon can occur between two packages, between layers of foil insulated from each other; across tears, wrinkles or gaps in a single piece of foil and between foil packages and oven walls. Arcing can be controlled using common sense and some simple precautions, but it is important to exhaustively test the package/product combination to understand the hazards involved.

Field modification packages go a step further by affecting in a controlled and predictable fashion either local energy distribution, or by transferring energy from the point of incidence to another point where this energy can be used more advantageously (Bohrer, 2009).

14.4.4 Doneness Indicators

Doneness indicators are devices which detect and visually indicate the state of readiness of foods heated in a microwave oven. They are classed as *intelligent packaging* and discussed in Section 15.4.2.2. Difficulty in determining when a product is "done" is high on the consumer complaint list for microwavable foods. Temperature sensors indicating doneness have been used on some microwavable foods; they essentially responded to steam development inside a package, but this is not always the best indicator of doneness when uneven heating occurs. A Japanese company produced a package with a tuned notch in the lid that whistled like a tea kettle once the product was done. A microchip could possibly be used to provide an audible or visual signal that acts as an indicator.

14.4.5 Testing Methods and Safety

The ASTM has published several standards for evaluating susceptors. F874 details a method for measuring and profiling surface temperatures attained by susceptors in a microwave. It is useful for measuring susceptor/food interface temperatures during microwave preparation of foods with susceptor-based packaging, heating pads, crisping sleeves and so on. It may also be used to measure the temperature of a susceptor exposed to extractives testing or in a liquid extraction cell to be used for nonvolatile extractives testing. The latter procedures are performed to establish test conditions for conducting extraction and migration studies using temperature versus time profiles approximating those for actual microwave preparation of the product.

F1308 covers a procedure for quantitating volatile compounds whose identity has been established and which are evolved when a microwave susceptor sample is tested under simulated use conditions. It may be a useful procedure to assist in minimizing the amount of volatile extractables either through susceptor design or manufacturing processes. F1349 establishes the apparatus required, the standard procedures and associated calculations involved in the determination of relatively polar nonvolatile UV-absorbing extractable components that may migrate from microwave susceptor packaging constructed of paperboard, adhesive and PET film into food simulants. F1500 covers a procedure for quantitating non-UV-absorbing nonvolatile compounds, which are extractable when the microwave susceptor is tested under simulated use conditions for a particular food product. F1519 covers a procedure for identifying volatile extractables which are released when a microwave susceptor sample is tested under simulated end-use conditions, the extractables being identified using GC/MS.

The high temperatures reached by packaging materials in microwave ovens led the U.S. FDA to announce its intention to publish an advance notice of proposed rulemaking (ANPR) in 1988. Its main concern was that the temperatures reached during microwave heating were much higher than those considered for polymers cleared for use in cooking and holding food. There was also concern about the adhesives used. The food and packaging industries responded by conducting extensive research and submitting the results to the FDA. The ANPR was published in 1989

(Risch, 2009) and the FDA issued regulations relevant to microwave susceptors in 2008 (see 21 CFR 173 and 175 to 179).

In 2000, eight workers at a microwave popcorn production plant in Jasper, Missouri, were diagnosed with the severe lung disease *bronchiolitis obliterans*. Subsequently, more than 100 VOCs (volatile organic compounds) were identified inside the Missouri plant. Rosati et al. (2007) characterized the chemicals released and found that the greatest amount (more than 80% of the total) were emitted when the bag was opened after popping. Among the chemicals emitted were diacetyl and furfural originating from the popcorn flavorings, and *p*-xylene originating from the inks or glues used on the bag at concentrations of 779, 37 and 27 μg bag^{-1}, respectively. The chemical diacetyl (a naturally occurring chemical compound that gives butter its flavor) was the subject of lawsuits and multi-million-dollar verdicts in 2004 and 2005 from factory workers testing and inhaling the fumes from hundreds of bags of microwave popcorn a day.

14.5 CONCLUSION

The development of microwavable foods to meet consumer expectations for convenience and quality is a major challenge for food product developers and packaging technologists.

Technological limitations are very real and it is impossible to change the laws of physics simply to meet market demand. To avoid failure in the market place, product and package development must be thoroughly researched. An understanding of the fundamental principles involved in the microwave heating of foods is essential to successful development. Because the package is an integral part of a microwave product, development of microwavable foods must go hand-in-hand with development of suitable packaging. A holistic approach to product and package design should lead to further significant improvements in the quality and convenience of microwavable foods.

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15 Active and Intelligent Packaging

15.1 HISTORICAL DEVELOPMENT

The first widely reported use of the term active packaging is generally attributed to the seminal review presented at an EU conference in Iceland in 1987 by Dr. Theodore Labuza from the University of Minnesota (Labuza, 1987; Labuza and Breene, 1989). Labuza had just spent a sabbatical year at 3M working with the Packaging Systems Division on a new time–temperature indicator (TTI) and, during a visit to Tokyo Pack in 1986, had seen many commercial examples of active packaging. He and Curt Larson from 3M conceived the term *active packaging* (short for interactive) for his valedictory presentation to 800 scientists at 3M at the conclusion of his sabbatical year.

Smart films were first mentioned in the literature in 1986 (Sneller, 1986), the word "smart" being used in connection with selectively permeable films used for MAP. The selective permeability was created by strip lamination of HDPE and PET films, allowing CO_2 to exit the package and preventing excess O_2 from entering. Such films are no longer available.

Smart packages were defined (Wagner, 1989) as "doing more than just offer protection. They interact with the product, and in some cases, actually respond to changes." The term smart packaging enjoyed a short renaissance in the early twenty-first century when the *Smart Packaging Journal* was published online from mid-2002 until 2005. It defined smart packaging as "the use of features of high added value that enhance the functionality of a product, notably mechanical, electronic and chemical features that improve safety and efficiency." The journal urged readers to forget about all the numerous definitions—active, diagnostic, intelligent, smart, functional and enhancement—to describe smart packaging and accept that it is all one big continuum of functionality. It was suggested that one should think of smart as meaning clever, neat or "wow." Today, smart packaging is used almost exclusively to refer to certain types of intelligent packaging; the associated term "smart label" was discussed in Section 9.6.

Various authors have attempted to identify the origins of what is now referred to as active packaging. The patent literature from more than 70 years ago abounds with ideas that could be considered active packaging. For example, a Finnish researcher described the use of iron, zinc or manganese powders to remove O_2 from the headspace of cans in a 1938 patent; a 1943 patent from a researcher in England described removing O_2 from a container containing vacuum or gas-packed food in which a metal such as iron absorbed O_2 to form an oxide. In the United States, the removal of O_2 by the catalytic conversion of H_2 to H_2O was first described in 1955 and applied to spray dried milk powder in initially tinplate cans and later laminate pouches. The package was flushed with a mixture of H_2 (7%) in N_2 and necessitated the use of a palladium catalyst.

The fungistatic effectiveness of a wrapper made of RCF impregnated with sorbic acid and used to package natural and processed cheeses was reported in 1954, together with an alternative approach whereby sorbic acid was mixed into a wax layer for natural cheese. These were probably the first antimicrobial (AM) films.

The use of enzymes and in particular glucose oxidase to remove O_2 has been studied since the initial patent in 1956, which described the impregnation of a fabric sheet with glucose oxidase and catalase (the latter to destroy the H_2O_2 formed by the former). The concept of incorporating enzymes into a packaging material was overtly described in a 1956 patent, and in 1958, the first publication on the use of packets or sachets of chemicals in packages to remove O_2 appeared. A 1968 German patent proposed a sodium carbonate powder to absorb O_2 in food packages.

In 1970, researchers in Australia and the United States published details on the use of potassium permanganate in LDPE bags as an ethylene absorbent to delay ripening in bananas, but the approach was not widely adopted commercially for many years. In 1973, researchers in India published the details of fungistatic wrappers to extend food shelf life, but these were not commercialized.

Although almost none of the aforementioned patents were commercialized, they laid the groundwork for the subsequent development in Japan in 1976 of sachets containing iron powder to absorb O_2. This is generally regarded as the first widespread commercial application of active packaging. Intelligent packaging of which TTIs represent the most well-known example has been used commercially since at least 1971 so that historically, intelligent packaging is an antecedent of active packaging.

15.2 DEFINITIONS

A variety of terms can be found in the literature to describe the growing and important areas of active and intelligent packaging, including active, interactive, smart, clever and intelligent packaging. Often the terms are used without being defined, or if they are defined, the definitions are either so broad that they include many packages which are not active or intelligent or so narrow that they exclude important examples. The meanings of words gain their legitimacy from shared use, so in the final analysis there is no "correct" meaning. However, unless there is a general consensus around the meaning of these terms, there will continue to be confusion.

Before giving a definition, it is worth recapping some basic facts. Foods are packaged using a variety of materials, and the primary function of such materials is to contain and protect the food. In many cases, there is a headspace or void inside the package and the composition of that headspace can have an important influence on the shelf life of the food. In addition, the packaging material, or a component of it such as a seal or closure, may interact with the package or permit the transfer of certain compounds into or out of the package. In addition to the food, the package might also contain a sachet or pad which might absorb or emit a specific gas in the case of a sachet or water in the case of a pad. These facts should be kept in mind when the definitions of active and intelligent packaging are considered.

15.2.1 Active Packaging

First, a summary of what active packaging can achieve: it can be used to remove an unwanted compound (e.g., C_2H_4 produced by respiring fruits, or O_2 present inside a package), add a desirable compound (e.g., CO_2 or ethanol to inhibit microbial growth), prevent microbial growth (e.g., incorporate an AM chemical into a film), change a film's permeability to gases as the temperature changes by several of orders of magnitude greater than normal polymeric films or change the physical conditions inside the package (e.g., remove water vapor by absorption or change the temperature of the food).

In this book, *active packaging* is defined as *packaging in which subsidiary constituents have been deliberately included in or on either the packaging material or the package headspace to enhance the performance of the package system*. The two key words are "deliberately" and "enhance." Implicit in this definition is that performance of the package system includes maintaining (and often improving) the sensory, safety and quality aspects of the food.

In light of the aforementioned definition, it is possible to list processes which are not active packaging although some authors have described them as such. MAP, as normally practiced (see Chapter 16), is passive not active packaging per se, unless there is some way in which the package (or a sachet added to the package) actively affects the internal gas atmosphere other than via normal permeation through plastic films. The reason for confusion over whether or not MAP is active packaging is that the creation of the MA can be either passive (the atmosphere changes over time as a result of biochemical activity by the food or its microorganisms) or active (air is removed from the pack or a gas mixture is admitted immediately prior to sealing), but active MAP is not necessarily active packaging. However, if the package contained gas scavenging or emitting sachets, then it could be classified as active packaging. The interaction between tin and food constituents inside a can is corrosion—not active packaging. The aforementioned definition also excludes the scalping of aromatic flavors by, for example, the plastic layer in contact with fruit juices on the inside of laminate paperboard cartons.

An interesting case is that of wooden barrels that are very widely used for the storage and maturation of whisky, wine and other alcoholic drinks. This packaging application both releases and adsorbs compounds to change and improve the organoleptic qualities of the stored drink. Recently, the EU released a document (EU Guidance to the Commission Regulation (EC) No 450/2009 of 29 May 2009 on active and intelligent materials and articles intended to come into contact with food, 2011) giving guidance on active and intelligent materials and articles intended to come into contact with food. It argued that active food contact materials and articles should be distinguished from materials and articles which are traditionally used to release their natural ingredients into specific types of food during the process of their manufacture, such as wooden barrels. In its view, because wooden barrels are not designed to deliberately incorporate components that would release substances into the food, they are not considered as active. This interpretation may come as a surprise to those who enjoy the characteristic flavors of oak-aged wines. Selected examples of active packaging systems are given in Table 15.1.

TABLE 15.1
Selected Examples of Active Packaging Systems

Active Packaging System	Mechanisms	Food Applications
Oxygen absorbers	Iron-based, metal/acid, metal (e.g., platinum) catalyst, ascorbate/metallic salts, enzyme-based and nylon MXD6	Bread, cakes, cooked rice, biscuits, pizza, pasta, cheese, cured meats and fish, coffee, snack foods, dried foods and beverages
Carbon dioxide absorbers/emitters	Iron oxide/calcium hydroxide, ferrous carbonate/metal halide, calcium oxide/activated charcoal and ascorbate/sodium bicarbonate	Coffee, fresh meats and fish, nuts and other snack foods and sponge cakes
Ethylene absorbers	Potassium permanganate, activated carbon and activated clays/zeolites	Fruits and vegetables
AM packaging	Organic acids, silver zeolite, spice and herb extracts, BHA/BHT antioxidants, vitamin E antioxidant, chlorine dioxide and sulfur dioxide	Cereals, meats, fish, bread, cheese, snack foods, fruits and vegetables
Ethanol emitters	Encapsulated ethanol	Pizza crusts, cakes, bread, biscuits, fish and bakery products
Moisture absorbers	Poly(vinyl acetate) blanket, activated clays and minerals and silica gel	Fish, meats, poultry, snack foods, cereals, dried foods, sandwiches, fruits and vegetables
Flavor/odor adsorbers	Cellulose triacetate, acetylated paper, citric acid, ferrous salt/ascorbate and activated carbon/clays/zeolites	Fruit juices, fried snack foods, fish, cereals, poultry, dairy products and fruits
Self-heating and self-cooling	Quicklime/water, ammonium nitrate/water and calcium chloride/ water	Ready meals and beverages
Changing gas permeability	Side chain crystallizable polymers	Fruits and vegetables

Source: Day, B.P.F., Active packaging of food, in: *Smart Packaging Technologies for Fast Moving Consumer Goods*, Kerry, J. and Butler, P. (Eds), John Wiley & Sons, Ltd, New York, pp. 1–18, 2008.

15.2.2 INTELLIGENT PACKAGING

First, a summary of what intelligent packaging can achieve: it can inform the consumer about the quality of the food by indicating when it is ripe or fresh, or whether its shelf life has expired; it can indicate the temperature of the food through the use of thermochromic inks or microwave doneness indicators (MDIs); it can indicate the temperature history of the food through the use of TTIs; and it can indicate whether a package has been tampered with. In other words, intelligent packaging senses some properties of the food it encloses or the environment in which the package is kept and is able to inform the manufacturer, retailer or consumer of the state of these properties (Kerry et al., 2006).

Intelligent is defined as "having or showing understanding; clever, quick of mind." The primary meaning intended when the word is applied to packaging is "showing understanding" although "clever" is preferred for nontechnical audiences. In this book, *intelligent packaging* is defined as *packaging that contains an external or internal indicator to provide information about the history of the package and/or the quality of the food* (Table 15.2). The key word in this definition is "indicator" and includes all the indicators (whether for gases, ripeness, temperature or tampering) including radio frequency identification (RFID) sensors but not RFID tags or labels because the latter do not indicate the history of the package or the quality of the food but merely its location. RFID tags are an example of smart labels and are, in essence, data carriers (see Section 9.6). This is in contrast to the earlier editions of this book and many publications which classified RFID tags as intelligent packaging. From now on, only RFID tags that incorporate sensors should be classed as intelligent packaging.

In light of the aforementioned definition, it is possible to list packaging which is not intelligent packaging although some authors have described it as such. As mentioned earlier, the so-called intelligent polymers do not qualify as intelligent packaging because they do not provide any information about the package or the food. Microwave susceptor packaging (see Section 14.4.2) is also not intelligent packaging for the same reasons. Devices that have been used for many years, such as the button on metal closures attached to glass containers which have been retorted, and the tamper-evident band located on the skirt of screw closures attached to glass and plastic bottles could qualify as intelligent packaging according to the aforementioned definition. However, only the newer and more sophisticated tamper-evident devices will be classified as intelligent packaging in this book. The pressure-relief valve found on packs of roasted coffee is not an intelligent package because it does not provide information; it simply relieves the pressure caused by a buildup of CO_2 inside the package. The bulging of the ends of a metal can due to internal gas formation (either as a result of microbial growth or from corrosion resulting in the production of H_2) is not intelligent packaging, although some might argue that it does qualify under the aforementioned definition.

TABLE 15.2
Definitions of Active and Intelligent Packaging

Active Packaging

Packaging in which subsidiary constituents have been deliberately included in or on either the packaging material or the package headspace to enhance the performance of the package system

Intelligent Packaging

Packaging that contains an external or internal indicator to provide information about aspects of the history of the package and/or the quality of the food

15.3 ACTIVE PACKAGING SYSTEMS

Despite intensive research and development work, numerous patents, many conferences, dozens of graduate student theses and countless publications on active packaging over the last 30 years, there are only a few commercially significant systems on the market. Of these, the O_2 absorbers contained in small sachets, which are added separately to the package headspace, are the most widely used, followed by moisture absorbers, ethanol emitters/generators, ethylene absorbers and CO_2 emitters and absorbers.

There are several ways in which active packaging systems can be classified; typically, the classification is based on what the system actually does (e.g., absorbs O_2) rather than its impact on the food (e.g., prevents oxidation). A similar classification will be adopted here. In addition, active packaging systems will be divided into two categories: those in which the active compounds are filled into sachets or pads, which are then placed inside packages, and those in which the active compounds are incorporated directly into or on the packaging materials.

15.3.1 Sachets and Pads

Sachets and pads can be a highly efficient form of active packaging, but they suffer from two major drawbacks: they cannot be used in liquid foods, and in packages made from or containing a flexible film, the film may cling to the sachet and isolate it from areas where it is needed to perform its function. To overcome the latter problem, the sachet can be glued to the inner wall of the package or the active ingredients incorporated into a label, which can be affixed to the inside wall of the package. Despite these drawbacks, sachets and pads are the most widely used forms of active packaging and the various functions which they perform are discussed in the following.

15.3.1.1 O_2 Absorbers

O_2 absorbers (also referred to as O_2 *scavengers* and abbreviated OS) use either powdered iron or ascorbic acid, the former being more common. Powdered iron is used to provide a large reaction surface area, the overall reaction proceeding as follows:

$$\mathrm{Fe} + \tfrac{3}{4}\mathrm{O_2} + 1\tfrac{1}{2}\mathrm{H_2O} \rightarrow \mathrm{Fe(OH)_3} \tag{15.1}$$

By using iron powder, it is possible to reduce the O_2 concentration in the headspace to less than 0.01%, which is much lower than the typical 0.3%–3.0% residual O_2 levels achievable by vacuum or gas flushing. Absorbers can be characterized by two main properties: absorption capacity and absorption rate constant. Although the absorption capacity of commercial sachets is well documented, few studies have been made to evaluate the absorption rate which is often the parameter of prime importance for food quality. In general, 1 g of iron can react with 0.0136 mol of O_2 (STP), which is equal to approximately 300 mL. Various sizes of O_2 sachets are available commercially, with the ability to consume 20–2000 mL of O_2 (an air volume of 100–10,000 mL). Several interrelated factors influence the choice of the type and size of absorbent required. These include

- Nature of the food (i.e., size, shape, weight)
- a_w of the food
- Amount of dissolved O_2 in the food
- Desired shelf life of the food
- Initial O_2 level in the package headspace
- O_2 permeability of the packaging material

The last factor is critically important to the overall performance of the absorbent and the food shelf life, and if a long shelf life is desired, films containing PVdC copolymer, EVOH copolymer or a metallized layer as a barrier are necessary. Such films have an O_2 permeability of <0.0004 *barrer*, and the headspace O_2 should be reduced to 100 ppm within 1–2 days and remain at that level for the duration of the storage period, provided packaging integrity is maintained.

The most widely used OS take the form of small sachets containing various iron-based powders, together with an assortment of catalysts that scavenge O_2 within the food package and irreversibly convert it to a stable oxide. Water is essential for O_2 absorbents to function (see Equation 15.1 shown earlier) and, in some sachets, the water required is added during manufacture while, in others, moisture must be absorbed from the food before O_2 can be absorbed. The iron powder is separated from the food by keeping it in a small sachet (labeled *do not eat*) that is highly permeable to O_2 and, in some cases, to water vapor. Pereira de Abreu et al. (2012) list commercially available OS.

Brandon et al. (2009) evaluated the O_2 scavenging capacity of four commercially available iron-based OS at 3°C and 10°C. None of the OS absorbed their nominal capacity in 24 h, meaning that they were not fast enough to create the anoxic conditions required to prevent metmyoglobin formation in beef steaks, particularly in those cuts, which are highly susceptible to metmyoglobin formation. Reproducibility was also a critical issue particularly at low O_2 concentrations. None of the scavengers had a coefficient of variation of less than 20% at the low O_2 concentrations, and, therefore, to obtain consistent results, it was recommended that multiple scavengers be used.

Until recently, the mechanism of iron-based O_2 scavenging was usually described in the relevant scientific/technical literature without taking into account the effect of chlorine-containing salts (primarily NaCl) which are also present. However, Polyakov and Miltz (2010) showed that the efficiency of O_2 scavenging is related to the rate of corrosion that occurs in the active component—iron powder. The chloride ions play an important role in this process, which includes electrochemical and chemical reactions resulting in the formation of a porous rust shell around each iron particle core. The rate-limiting reaction in this case is the electrochemical cathodic reaction of O_2 reduction. Adsorption of water within the rust shell results in the formation of an electrolyte (water + NaCl) in the rust pores. The O_2 diffusion to the iron–rust interface increases when the amount of adsorbed water decreases. Simultaneously, the anodic iron dissolution rate decreases since the solubility of the reacting species decreases at low amounts of water. On the other hand, high amounts of water results in a reduction in the "gas–electrolyte" interfacial area and an impairment of gas transfer within the rust shell.

Polyakov and Miltz (2010) found that an increase in the rate of O_2 absorption resulted in a decrease in the porosity, an increase in the specific surface area of the iron powder's corrosion products and a decrease in the O_2 diffusivity through the particles. The heat evolved during the exothermic reaction led to a decrease in the amount of water adsorbed on the corrosion products. Their results elucidated the effect of moisture on O_2 absorption by iron-based O_2 scavengers and can be used for the proper design of packages intended for storage of foods of intermediate and high a_w.

One disadvantage of iron-based scavengers is that they normally cannot pass the metal detectors often installed on packaging lines. Nonmetallic O_2 scavengers include those that use organic reducing agents such as ascorbic acid, ascorbate salts or catechol. They also include enzymic O_2 scavenger systems using either glucose oxidase or ethanol oxidase, which can be incorporated into sachets, adhesive labels or immobilized onto package surfaces. However, their use is not widespread.

OS were first marketed in Japan in 1977 but were not adopted by North America and Europe until the 1980s and then only slowly. The reason for the success of OS in Japan may be the ready acceptance by Japanese consumers of innovative packaging. The possible accidental ingestion of the sachet contents by the consumer has been suggested as a reason for their limited commercial success, particularly in North America and Europe. However, ingestion does not result in adverse health impacts because a sachet typically contains 7 g of iron which is approximately 160 times less than the LD_{50} for a 70 kg adult. The development of O_2-absorbing adhesive labels that can be attached to the inside of packages has helped overcome this perceived problem and aided the commercial acceptance of this technology, although their O_2-absorbing capacity is limited to 100 mL.

OS have been used for a range of foods including sliced, cooked and cured meat and poultry products, cured fish, coffee, pizzas, specialty bakery goods, dried food ingredients, cakes, breads, biscuits, croissants, fresh pastas, tea, powdered milk, dried egg, spices, herbs, confectionery and snack foods.

15.3.1.2 CO_2 Absorbers/Emitters

Sachets that absorb only CO_2 are rare. CO_2 scavengers can be composed either of a physical absorbent (zeolite or an active carbon powder) or a chemical absorbent such as $Ca(OH)_2$ or $Mg(OH)_2$, typically packaged in small pouches of paper coated with perforated PP:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 \tag{15.2}$$

Sachets that contain $Ca(OH)_2$, in addition to iron powder, absorb CO_2 as well as O_2 and find a niche application inside packages of roasted or ground coffee. Fresh roasted coffee releases considerable amounts of CO_2 (formed by the Maillard reaction during roasting) and, unless it is removed, it can cause swelling or even bursting of the package.

Charles et al. (2006) reported the absorption kinetics of two commercial O_2 and CO_2 scavengers. They identified significant “parasite” CO_2 absorption for O_2 scavengers (i.e., a carbonation reaction of the iron hydroxide that was formed following O_2 absorption) and underlined the need to take into account the important variation of the absorption rate constant among individual gas scavengers (about 20%), as well as the temperature effect, for reliable evaluation of the gas kinetics when using O_2 or CO_2 scavengers.

Other sachets are available based on either ascorbic acid and ferrous carbonate or ascorbic acid with sodium bicarbonate that absorb O_2 and generate an equivalent volume of CO_2, thus avoiding package collapse or the development of a partial vacuum, which can be a problem in flexible packages if only O_2 is removed.

CO_2 Fresh Pads (from CO_2 Technologies, Iowa) have been adapted for meat, poultry and seafood processors. The system contains citric acid and sodium bicarbonate as moisture-actuated CO_2 generating materials in the pads, located between layers of absorbent material and bound to fibers of the material. Verifrais™ (from Codimer SARL in France) consists of a tray with a perforated false bottom in which a porous sachet containing sodium bicarbonate/ascorbate is deposited. When exudate from the food (typically meat) penetrates the sachet, CO_2 is released.

15.3.1.3 Ethylene Absorbers

The plant hormone ethylene (C_2H_4) is produced during the ripening of fruits and vegetables and can have both positive and negative effects on fresh produce. Positive effects include catalyzing the ripening process, while negative effects include increasing the respiration rate (which leads to softening of fruit tissue and accelerated senescence), degrading chlorophyll and promoting a number of postharvest disorders.

Many C_2H_4-absorbing substances have been described in the patent literature but those that have been commercialized are based on potassium permanganate ($KMnO_4$), which oxidizes C_2H_4 in a series of reaction to acetaldehyde and then acetic acid, which, in turn, can be further oxidized to CO_2 and H_2O with the overall reaction as follows:

$$3C_2H_4 + 12KMnO_4 \rightarrow 12MnO_2 + 12KOH + 6CO_2 \tag{15.3}$$

Because $KMnO_4$ is toxic, it cannot be integrated into food contact packaging. Instead, about 4%–6% of $KMnO_4$ is added to an inert substrate with a large surface area such as perlite, alumina, silica gel, vermiculite, activated carbon or celite and placed inside a sachet which can be safely added to packages.

15.3.1.4 Ethanol Emitters

Ethanol (ethyl alcohol) has been used as an AM agent for centuries, with Arabs having used it over 1000 years ago to prevent mold spoilage of fruit. Ethanol exhibits AM effects even at low concentrations, and a novel and innovative method of generating ethanol vapor was developed in Japan using sachets. The sachets contain ethanol (55%) and water (10%), which are adsorbed onto SiO_2 powder (35%) and filled into a paper-EVA copolymer sachet. To mask the odor of alcohol, some sachets contain traces of vanilla or other flavors. The sachet contents absorb moisture from the food and release ethanol vapor, so the a_w of the food is an important factor in the vaporization of ethanol into, and the absorption of ethanol from, the package headspace.

Ethanol emitters are used mainly in Japan to extend the shelf life of high-moisture bakery products by up to 20 times. The main disadvantages of using ethanol vapors (apart from the cost) are the formation of off-flavors and off-odors in the food, and absorption of ethanol from the headspace by the food which can lead to ethanol concentrations of 2% in the food and result in regulatory problems. This is not a problem if the product is heated in an oven prior to consumption because the ethanol will then evaporate.

15.3.1.5 Moisture Absorbers

Liquid water can accumulate in packages as a result of temperature fluctuations in high-moisture packages, “drip” or tissue fluid from flesh foods and transpiration of horticultural produce. If this water is allowed to build up inside the package, it can lead to the growth of molds and bacteria, as well as fogging of films.

Drip-absorbent pads consist of two layers of a microporous or nonwoven plastic film, such as LDPE or PP, between which is placed a superabsorbent polymer that is capable of absorbing up to 500 times its own weight of water. Typical superabsorbent polymers include polyacrylate salts, carboxymethyl cellulose (CMC) and graft copolymers of starch, which have a very strong affinity for water.

15.3.2 ACTIVE PACKAGING MATERIALS

15.3.2.1 O_2-Absorbing Materials

The most common O_2 absorbers used in the food industry are the porous sachets containing iron powder discussed earlier. However, there is still consumer resistance to sachets in many markets, and they cannot be used in liquid foods. Furthermore, in close-fitting packages such as vacuum packs for cheese and meats where O_2 permeation is a prime cause of quality loss, sachets cannot be used. Therefore, a more attractive alternative is the incorporation of O_2-absorbing materials into the plastics components of packages.

O_2-absorbing polymers are versatile in that their layer thickness or blend composition can be varied to match the amount of O_2 to be removed. However, one major limitation to the large-scale adoption of the presently available O_2-absorbing materials is that the speed and capacity of O_2-absorbing films are considerably lower than the widely used O_2-absorbing sachets. An additional challenge is that the O_2-absorbing films must be stable in the O_2-rich environment of air and not start consuming O_2 until the food is packaged. Activation or triggering mechanisms based on exposure to light or elevated moisture have been the main approaches adopted, although the storage of O_2-absorbing PET preforms in barrier bags with a slight overpressure of N_2 to prevent absorption of O_2 until blown is also used.

The patent literature of the past 80 years contains many ideas for O_2-absorbing systems which can be incorporated into package structures, and various films with the required reactive ingredients dispersed within the polymer matrix or sandwiched between film layers have been trialed commercially. However, despite the enthusiastic write-ups in trade magazines and exciting presentations at conferences, very few have been successfully commercialized.

The first O_2-absorbing polymer useful as a blend with PET involved the cobalt-catalyzed oxidation of nylon-MXD6. When used with 200 ppm of cobalt as the stearate salt, this polyblend allowed blowing of bottles with an O_2 permeability of essentially zero for 1 year. More cost-effective ways of providing an O_2 barrier in PET bottles have limited the application of this approach. It should be noted that any O_2 absorber proposed as a middle layer in PET-based structures will not be a rapid headspace scavenger due to the reasonable O_2 barrier provided by the inner PET layer.

In one approach, a polymer-based absorber was coextruded in various packaging structures including bottles, films, coatings, sheet, adhesives, lacquers, can coatings and closure liners where it acted as both a headspace O_2 absorber and a barrier to O_2 permeation into the package. The O_2-absorbing capability was UV activated, meaning it had to be exposed to UV light before it could begin absorbing O_2. Another O_2-absorbing material was a copolymer that served as a clear layer in a bottle, jar or other rigid PET container. A converter could laminate or extrude the material as a middle layer in a multilayer structure; it removed O_2 from within the package headspace, as well as any that entered the package by permeation or leakage.

In another approach developed to remove O_2 from beverages such as beer after they are capped, a multilayer barrier liner is fitted into crown caps, plastic and metal closures. The active ingredients consist of ascorbic acid which is oxidized to dehydroascorbic acid while, in another, sodium sulfite is oxidized to sodium sulfate. Other proprietary systems are also available.

Many patent applications are based on ethylenic unsaturated hydrocarbons such as squalene, fatty acids or polybutadiene with the latter being the most promising because its transparency, mechanical properties and processing characteristics are similar to those of polyethylene. These unsaturated hydrocarbons, after being functionally terminated with a chemical group to make them compatible with the polymer, can be mixed with thermoplastics during conventional extrusion or blending processes. In some cases, transition metal catalysts such as cobalt II neodecanoate or octoate are used to accelerate the scavenging rate. As well, photoinitiators can be added to further facilitate and control the scavenging process and prevent premature oxidation of the scavenger during processing and storage. The main problem with this technology is that during the reaction between polyunsaturated molecules and O_2, by-products such as organic acids, aldehydes or ketones can be generated that can affect the sensory quality of the food. This problem can be minimized by the use of functional barriers that limit the migration of undesirable oxidation products (Galdi et al., 2008).

Galotto et al. (2009) studied the absorption kinetics of an iron-based OS (Shelfplus® from BASF) in sheet and film materials at various concentrations and RHs. Both the absorption capacity and final absorption rate increased with RH and temperature, with high RH being necessary to activate the scavenger. However, the incorporation of these substances into polymeric films can cause the loss of mechanical properties and the reduction of transparency and therefore their use is limited.

Galdi and Incarnato (2011) characterized the scavenging activity of cast monolayer PET films containing different concentrations of OS (Amosorb® from ColorMatrix Group Inc., Texas) and obtained the best results at 10% concentration where scavenging capacity was 4.68 mL O_2 g^{-1} with an exhaustion time of 170 h. The scavenger reaction is catalyzed by transition metals with cobalt salts and iron being frequently used. Amosorb is commercialized in many countries for clear bottle juice applications, and its regulatory position allows the use of this material in direct contact with food and beverages. Amosorb is supplied in air and moisture-tight sealed containers, and the formulations are added to the PET melt using conventional pellet handling systems. For noncarbonated PET bottles of 300 mL to 1 L capacity, a target shelf life of 6–12 months with an OS level of 1% ~ 5% Amosorb is recommended by the supplier. Possible applications include beer, wine, fruit juices, nectars, teas, UHT milk and tomato-based products in both mono- and multilayer containers.

Recently, Anthierens et al. (2011) proposed a model system for a very novel OS PET using an endospore-forming bacteria *Bacillus amyloliquefaciens* as the active ingredient. Spores were incorporated in PETG, an amorphous PET copolymer having a considerably lower processing temperature and higher moisture absorption compared to PET. They showed that endospores were able to survive incorporation into PETG at 210°C, and that these spores could actively consume O_2 for a minimum of 15 days, after an activation period of 1–2 days at 30°C under high humidity conditions.

15.3.2.2 Ethylene Adsorbers

In the 1980s, a number of packaging films were released commercially based on the reputed ability of certain finely dispersed minerals to adsorb C_2H_4. These minerals were typically local kinds of clay such as pumice, zeolite, cristobalite (SiO_2) or clinoptilolite (hydrated NaKCaAl silicate) that were sintered together with a small amount of metal oxide before being dispersed in a plastic film. The resulting films are translucent and have increased permeability to gases which may, by itself (regardless of any adsorption of C_2H_4), increase the shelf life of fresh fruits and vegetables. Although the minerals may have C_2H_4-adsorbing capacity, this capacity is often lacking after they have been incorporated into plastic films. There have been no peer-reviewed publications demonstrating the efficacy of these films in adsorbing C_2H_4 and extending the shelf life of fruits and vegetables, but many such bags are sold to consumers for home use.

15.3.2.3 Antioxidant Packaging

Antioxidants have been incorporated into plastic films (particularly polyolefins) to stabilize the polymer and protect it from oxidative degradation. The potential for evaporative migration of antioxidants from plastics packaging into foods has been known for many years. The challenge lies in matching the rate of diffusion with the needs of the food. In the United States, release of BHA and BHT from the inner plastic liner has been applied to breakfast cereals and snack products. There has also been interest in the use of vitamin E as a replacement for BHA and BHT as it is equally effective (Day, 2008).

15.3.2.4 Antimicrobial Packaging

The burgeoning interest in AM food packaging is driven by increasing consumer demand for minimally processed, preservative-free, "fresh" foods.

AM food packaging acts to reduce, inhibit or retard the growth of microorganisms that may be present in the packed food or packaging material itself, and can take several forms (Appendini and Hotchkiss, 2002) including

1. Addition of sachets or pads containing volatile AM agents into packages
2. Incorporation of volatile and nonvolatile AM agents directly into polymers
3. Coating or adsorbing AMs onto polymer surfaces
4. Immobilization of AMs to polymers by ionic or covalent linkages
5. Use of polymers that are inherently AM

Since food spoilage occurs primarily on the surface, incorporation of relatively large quantities of the AM agents into the bulk of the food is not justified. A major advantage arising from the use of AM packaging is that only low levels of preservative come into contact with the food, compared to the direct addition of preservatives to the food.

AM packaging materials have to extend the lag period and reduce the growth rate of microorganisms to prolong shelf life and maintain food safety. To be effective, they need to be present at the food surface above their minimum inhibitory concentration (MIC). A large number of agents with AM properties have been tested or proposed as AMs, including ethanol (discussed earlier) and other alcohols, organic acids and their salts (such as benzoates, propionates and sorbates), fungicides (such as imazalil and benomyl), enzymes (such as glucose oxidase, lactoperoxidase and lysozyme), extracts from spices and herbs, SO_2 and ClO_2, silver and bacteriocins. However, data on the MIC of these and other AM agents are not always readily obtainable from the literature.

Recently, Bastarrachea et al. (2011) reviewed how the incorporation of AM substances affected the properties of food packaging systems with an emphasis on diffusion studies of AM substances through packaging films, The review found that although the properties of packaging materials are altered by the addition of AMs such as organic acids, enzymes and bacteriocins, every packaging material is unique, and these effects cannot be generalized.

An alternative to the incorporation of AM compounds during extrusion is to apply the AM additives as a coating. This has the advantage of placing the specific AM additive in a controlled manner without subjecting it to high temperature or shearing forces. In addition, the coating can be applied at a later step, minimizing the exposure of the product to contamination. Alternatively, nonmigratory AM packaging can be made by covalently immobilizing amine-terminated bioactive molecules onto surface-functionalized polymers such as LDPE (Barish and Goddard, 2011).

In contrast to naturally AM polymers such as chitosan (see the following text), some bioactive materials have been produced by modifying the surface composition of the polymer. For example, the use of 193 nm UV irradiation to convert amide groups on the surface of PAs to amines having AM activity has been reported but not commercialized.

Controlled release packaging offers significant potential for extending the shelf life of foods by continuously replenishing active compounds at the food surface and compensating for the consumption or degradation of these compounds, so that the MIC of active compounds is maintained in the food to achieve the desired shelf life. Recently, Mastromatteo et al. (2010) reviewed the fundamental mechanisms involved in release phenomena, as well as mathematical approaches describing controlled release systems.

Despite considerable research over the last 20 years to develop and test films with AM properties to improve food safety and shelf life, few such systems are commercially available. A comprehensive review (Joerger, 2007) catalogued and analyzed the outcome of 129 published studies on AM films and noted that the methodologies for measuring AM activity varied considerably among the studies. The bacteriocin nisin was the AM most commonly incorporated into films, followed by acids and salts, chitosan, plant extracts and the enzymes lysozyme and lactoperoxidase. Results, defined as the difference in the log colony forming units (cfu) of a test organism exposed to a control film and the log cfu of the organism exposed to the AM film, ranged from 0 to 9 for many of the AMs tested. The majority of results centered around 2 log reductions, suggesting that AM films still face limitations and are perhaps best viewed as part of a hurdle strategy to provide safe foods. The legislative status of AMs is also a limiting factor in their commercialization.

Packaging systems that release volatile AMs include ClO_2, SO_2, CO_2, ethanol and plant extracts such as essential oils and AIT (allyl isothiocyanate—the active ingredient in wasabi or Japanese horseradish). The advantage of volatile AMs is that they can penetrate the food without the package being in direct contact with the food.

ClO_2 is a strong oxidizing agent and its major industrial use is the bleaching of wood pulp (see Chapter 6). It has also proven effective against bacteria, fungi and some viruses. In recent years, ClO_2 has been used as a headspace gas in packaging systems where it can extend the shelf life of perishable foods including meat, poultry, fish, dairy products, confectionery and baked goods. The use of ClO_2 combined with MAP enhances its effectiveness, reduces the amount needed and decreases the risk of off-flavors and discoloration of flesh foods. The introduction of gaseous ClO_2 within food packaging systems is often by means of a sachet, either slow or fast release. In 2001, the U.S. FDA approved the incorporation of ClO_2 precursors in food packaging films used for uncooked meats such as poultry and seafood. In Europe, ClO_2 is not regulated as a food additive, and therefore cannot be used in active food packaging. Netramai et al. (2009) reported the mass transfer characteristics of ClO_2 in a range of food packaging films; the best barriers were provided by BOPP, PET, PLA and EVA-EVOH-EVA films.

Another way of tackling the problem of microbial growth is by the use of nonvolatile AM additives. Many preservatives (sorbic acid, benzoic acid, propionic acid and its salts, or bacteriocins like nisin, natural spices, silver ions, etc.) are added to plastic films and materials and used as AM packaging. The attraction of these packages is based on the reduction in the amount of additive that is incorporated into the material to exert the AM effect. However, these nonvolatile agents require direct contact with the food so that they can exert their AM effect.

Chitosan has been extensively studied as an AM agent in food packaging due in part to its intrinsic AM properties, as well as its ability to perform a dual role as a film matrix and a carrier of AM additives such as acids and salts, essential oils, lysozyme and nisin. The AM activity exhibited by chitosan-containing films varies considerably and is possibly the consequence of the variability of different chitosan preparations and the limited availability of active chitosan molecules for interaction with microbes after film formation. Joerger et al. (2009) covalently attached chitosan to ethylene copolymer films and evaluated its AM activity. It was most effective when used in combination with other treatments such as high pressure or silver ions.

Spices and herbs are rich in compounds such as flavonoids and phenolic acids, which exhibit a wide range of biological effects, including antioxidant and AM properties. The use of natural AMs derived from herbs and essential oils has been widely studied; the concept involves using volatiles from these compounds to provide the AM action. A recent review (Kuorwel et al., 2011) examined the more common synthetic and natural AM agents incorporated into or coated onto synthetic packaging films for AM packaging applications with a focus on the widely studied herbs basil, oregano and thyme and their essential oils. Although AM agents such as essential oils and/or their principal components may exhibit AM activity against various microorganisms when incorporated into packaging materials, any change in the organoleptic properties of the packaged food must be taken into consideration and is often a limiting factor.

A *bacteriocin* is a proteinaceous compound (usually a peptide) that has bactericidal action against a limited range of organisms which are usually closely related to the producer organism. Bacteriocins are commonly found in foods owing to their production by the lactic acid bacteria used to ferment dairy, vegetable and meat products. Nisin from *Lactococcus lactis* was one of the earliest bacteriocins to be described and is the only one that has been recognized as a safe biological food preservative. It is commercially exploited, particularly in processed cheeses and cold-pack cheese spreads, as it is effective against outgrowth of, and toxin production by, *Clostridium botulinum*. Other bacteriocins used in development of AM packaging include lactocins, enterocins and pediocins, although they lack regulatory approval. The advantages of bacteriocins are that they are thermostable, apparently hypoallergenic and easily degraded by proteolytic enzymes in the human gastrointestinal tract.

Silver has a long history of use as an AM agent in food and beverage applications and has numerous advantages over other AM agents. Compared to molecular AMs, silver is broad spectrum and toxic (to varying degrees) to numerous strains of bacteria, fungi, algae and possibly some viruses (Duncan, 2011). One commercial AM film introduced in Japan was a synthetic zeolite which had a portion of its sodium ions replaced with silver ions. The Ag-zeolite was extrusion coated as a thin (3–6 μm) layer directly onto a food contact film at levels of 1%–3% w/w. It continuously released a small quantity (ca. 10 ppb) of silver ions, resulting in long-term, broad spectrum AM activity that was not harmful to tissue cells. Because amino acids can react with silver ions, they are relatively ineffective in nutrient-rich foods, but highly effective in nutrient-poor drinks such as water or tea.

Various AM papers containing silver-based zeolites are available commercially in the United States and are targeted mainly at restaurants and food service establishments; a range of plastics are also available commercially for nonpackaging applications. In the EU, silver zeolites in food contact applications should not be used to extend shelf life, and the presence of silver ions in food matrices is limited to 50 μg Ag^+ kg^{-1} food, which is not biocidal in food. In the United States, the FDA approved the use of silver as an AM in bottled water, with a concentration not exceeding 17 μg Ag^+ kg^{-1} (Llorens et al., 2012).

Silver is currently the most commonly used nanoengineered AM material in consumer goods. Silver nanoparticles (AgNP) have been found to be potent agents against numerous species of bacteria. The controlled release properties of AgNPs can be engineered to remain potent AM agents for long periods of time, making AgNP/PNCs (polymer nanocomposites) attractive materials for use in food packaging to extend shelf life. Because silver particles catalyze the destruction of ethylene gas, fruits stored in the presence of AgNPs have slower ripening times and thus extended shelf lives.

Despite all of these advances in the use of silver nanostructures for food packaging applications, comprehensive studies in various polymer systems are still lacking, and much work needs to be done to elucidate key relationships that influence the AM strength of various AgNP/PNC materials (Duncan, 2011). The AM properties of nanoparticles composed of other materials have been investigated and TiO_2 particles in particular are promising. However, unlike AgNPs, the AM activity of TiO_2 nanoparticles is photocatalyzed and thus TiO_2-based AMs are only active in the presence of UV light.

The ability of phages to specifically interact with and lyse their host bacteria makes them ideal antibacterial agents. The range of applications of bacteriophage can be extended by their immobilization on inert surfaces. Anany et al. (2011) developed a novel method for immobilizing bacteriophages on regenerated cellulose membranes. These membranes effectively controlled the growth of *Listeria monocytogenes* and *Escherichia coli* O157:H7 in ready-to-eat and raw meat, respectively, under different storage temperatures and packaging conditions.

Edible films and coatings have also been studied as carriers for AM agents. The range of matrices for edible films is dominated by the polysaccharides chitosan, alginate, κ-carrageenan, cellulose ethers, high-amylose product and starch derivatives, but protein-based films made with wheat gluten, soy, zein, gelatin, whey and casein have also been produced. AM agents such as benzoic acid, sorbic acid, propionic acid, lactic acid, nisin and lysozyme have been successfully added to edible composite films and coatings, and a recent review (Valencia-Chamorro et al., 2011) provides further details.

The AM activities of packaging systems have been tested mainly with laboratory media, with only a few studies carried out with food systems. To demonstrate the real potential of natural AM agents for packaging applications, their AM activities should be proven with food systems under real storage and distribution conditions (Yildrim, 2011). This will require collaborative research activities between research institutes and food and packaging companies if commercial applications are to be realized. Potential applications of AM packaging for extending the shelf life of meat and meat products have been reviewed by Coma (2008).

15.3.2.5 Flavor/Odor Absorbers and Releasers

The commercial use of flavor/odor absorbers and releasers is controversial due to concerns arising from their ability to mask natural spoilage reactions and hence mislead consumers about the condition of packaged food (Day, 2008). ScentSational® Technologies in the United States released a consumer product called Aroma Water that used smells to replicate flavors. FDA-approved flavors were sealed into a thin layer of plastic on the inside of the bottle cap. Before the seal is broken, the fragrance infused the water with a fruity scent. When a consumer opened the bottle breaking its seal, the fragrance was released into the air, and traveled along the back of the throat to the nasal passage, enhancing the fruity taste.

Active packaging can also be used to remove undesirable taints or odors from packaged food and several such absorbers were released last century to absorb volatile amines from the breakdown of fish muscle, as well as aldehydes from the autoxidation of fats and oils. However, there is no evidence that they are still commercially available, despite being mentioned in some recent reviews and book chapters. Recently, López-de-Dicastillo et al. (2011) reported the use of novel EVOH copolymer films containing β-cyclodextrins to reduce the presence of aldehydes in packaged fried peanuts.

15.3.2.6 Microwave Susceptors

Packaging materials that absorb microwave energy and convert it to heat are called *susceptors* and are described in Section 14.4.2. They qualify as active packaging because they enhance the performance of the package by achieving localized effects such as browning and crisping of the food.

15.3.3 SELF-HEATING AND SELF-COOLING PACKAGES

The concept of a self-heating container is not new, although earlier versions were not without their hazards. The armed services introduced a self-heating can in 1939, which relied on the burning of cordite (a smokeless propellant consisting of 65% gun-cotton, 30% nitroglycerin and 5% mineral jelly) to provide the thermal energy, a design that could hardly be considered safe in untrained hands. More recent designs have all relied on exothermic chemical reactions to generate heat; in most cases, the reaction is between CaO (quicklime) and a water-based solution, although military forces tend to use the more expensive MgO because it heats more quickly. Although the fundamental chemistry is well known, the difficult part is optimizing the reaction and the thermal design of the container to provide an efficient, safe and cost-effective package.

Self-heating cans have been commercially available for decades and are particularly popular in Japan for sake, coffee, tea and ready meals. Recently, several self-heating cans have been developed, all using the same basic heating mechanism, but none were commercially successful.

Not all self-heating packages are cans. Retortable plastic trays based on a six-layer PP-EVOH copolymer structure with an under layer containing CaO have also been commercialized. In another approach using an electrochemical principle, the Flameless Ration Heater (FRH) was developed for the U.S. armed forces to heat Meals, Ready-to-Eat (MREs) for soldiers in the field. The FRH is based on the reaction between Mg and H_2O:

$$\mathrm{Mg} + 2\mathrm{H_2O} \rightarrow \mathrm{Mg(OH)_2} + \mathrm{H_2} + \mathrm{heat} \tag{15.4}$$

Theoretically, 24 g of Mg yields 355 kJ of heat, sufficient to boil a liter of water. In practice, Mg has a protective oxide surface coating that prevents further oxidation, but by mixing the Mg with NaCl and iron, the reaction proceeds, although the role which iron plays is unclear. The food is retorted in an alufoil/plastic pouch and packed in a cardboard carton. To heat the pouch, it is placed inside a plastic sleeve containing an FRH in which the chemicals are contained in a perforated fiberboard box. After water is added, the sleeve is placed inside the carton and as the reaction proceeds, the temperature of a 227 g food pouch increases by up to 55°C in 12 min.

Self-cooling cans have long been commercialized in Japan, utilizing an endothermic reaction based on the dissolution of ammonium nitrate and ammonium chloride in water.

15.3.4 CHANGING GAS PERMEABILITY

Fresh fruits and vegetables when harvested consume O_2 and emit CO_2. When the fruits and vegetables are in a sealed package, the atmosphere will reach equilibrium levels of O_2 and CO_2 depending on the weight of the produce, its respiration rate, temperature and the permeability of the package. A specific beneficial atmosphere exists for each fruit and vegetable that helps preserve the quality and freshness of the produce provided that there is good temperature control. If the temperature increases above the chill range, then the O_2 consumption may increase beyond the rate at which O_2 can permeate through the packaging film and high levels of CO_2 will accumulate inside the package. This is because the respiration rates of fruits and vegetables increase more with temperature than do gas permeabilities of films. Therefore, higher than optimum temperatures can lead to anoxia and seriously damage the produce. As discussed in Chapter 18 (Section 18.3), none of the commercially available common polymer films has the required gas permeability required in this situation. Therefore, when packaging fresh produce, there is a need to provide greater package permeabilities and different selectivities to O_2 and CO_2 so as to maintain the desired atmospheres as the temperature changes.

The adjustable selectivity ratio and temperature switch features of the BreatheWay® membrane technology (from Apio Inc., California) provide the flexibility to meet the specific MA requirements for a wide range of products throughout the total supply chain. This technology is based on an unusual "side chain crystallizable" (SCC) polymer having an internal temperature switch (Clarke, 2011). When elevated to the switch temperature, SCC polymers become molten fluids, which have inherently high gas permeability coefficients. SCC polymers are unique because of their sharp melting transition and the ease with which it is possible to produce melting points in a specific temperature range. In SCC polymers, the side chain crystallizes independently from the main chain. Examples of such polymers are siloxanes or acrylic polymers in which the side chain has eight or more carbon atoms. Varying the length of the side chain can change the melting point of the polymer. Preparation of the acrylic polymers occurs in solution using conventional free radical initiators. By making the appropriate copolymers, it is possible to produce any melting point from 0°C to 68°C.

The SCC polymers are intrinsically highly permeable, but the polymer properties can also be modified by the inclusion of other monomers in order to change the relative permeability of CO_2 to O_2, to alter the temperature switch or other physical properties such as WVTR (Clarke, 2011). The polymers are applied as a coating to a porous substrate, which is then cut into small patches and applied to a bag by a hot-stamping system incorporated into the bag-making process. The patch covers several holes that are cut into the bag material through which gases enter and exit. The use of these highly permeable membranes essentially controls the flow of gases into and from the package. Altering the properties of the polymer provides specific O_2 permeabilities, specific CO_2:O_2 permeability ratios (β) and changes in permeability with temperature.

The membrane is capable of being more than 1000 times more permeable to O_2 and CO_2 than a 50 μm LDPE film while still maintaining the same β ratio. Unlike semipermeable films for respiring produce, which typically allow CO_2 out and O_2 in at a 6:1 ratio, by altering the polymer composition used to coat the membrane, it is possible to obtain β ratios from 2:1 to 18:1, depending on the requirements of the produce in question. The gases enter and exit at a predetermined ratio that maintains an optimal atmosphere. At elevated temperatures, when respiring produce needs more O_2, the polymer becomes more permeable, but at lower temperatures, permeability automatically decreases. In addition to the common gases, the membrane is also highly permeable to volatiles such as ethanol and ethyl acetate, which are generated from anaerobic respiration when produce is packaged in suboptimal atmospheres.

This polymer technology is not intended as a substitute for good temperature control but rather a solution to temporary and unexpected breaks in the cold chain during distribution or display. Despite their relatively high cost, these materials were commercialized during the 1990s, and membranes coated with SCC polymers are currently being employed for a wide range of fresh produce items including mixed cut vegetables, cut broccoli, cauliflower, asparagus, bananas and strawberries.

15.3.5 Widgets

A somewhat unusual example of active packaging is the highly successful foam-producing *widget,* originally developed for stout beer packaged in metal cans. An interesting case study discussing the evolution of the widget has been published (Browne, 1999). A widget is generally defined as a device that is very useful for a particular job, and its synonyms are *gadget* and *gizmo*. Many drinkers of British and Irish beer like their beer to have a low dissolved CO_2 content when poured (i.e., not gassy) but to have a good head, which results from large numbers of gas bubbles produced when pouring. With draught beer, this is easy to achieve by passing the beer through a venturi nozzle to introduce lots of bubbles when poured. However, canned beer needs to have a higher internal CO_2 pressure to ensure that the cans have sufficient strength for stacking and also to provide some form of head when poured. The challenge was to develop a way of getting the dissolved gas out of the solution rapidly when the can was opened to give the creamy head and low gas content preferred by consumers.

In 1986, a system was developed and patented to release more of the dissolved CO_2 when the can was opened to produce the traditional creamy head. The widget itself is a small, plastic or aluminum, N_2-filled sphere with a tiny hole in it. Originally, widgets were inserted into the can before filling but this did not allow the exclusion of O_2 and hence flavor stability was poor. Now widgets can be supplied already attached to the base of the can. Frequently, the floating widget is used since it is less likely to trap O_2 in the can during filling (Briggs et al., 2004).

At filling, a small quantity of liquid N_2 is injected, together with the beer, and the can is rapidly seamed before the N_2 evaporates. After the can is seamed, this liquid N_2 vaporizes and pressurizes the can, forcing a small quantity of beer through the tiny hole of the widget and compressing the N_2 inside. When the can is opened, the pressure inside drops suddenly, the compressed N_2 inside the widget expands, and beer is pushed out through the tiny hole causing the widget to spin and jet the gas and beer down through the can. This expelled beer nucleates a host of very small bubbles from the N_2/CO_2 supersaturated beer, causing the bubbles to rise to the surface and form the desired smooth, creamy head.

Other brewers have since come up with their own widgets and they were introduced to draught beer in 1992, lager in 1994 and cider in 1997. In 2002 canned milk coffee containing a widget was marketed. Recently, Lee et al. (2011) extended the mathematical model of bubble nucleation in carbonated liquids to the case of two gases and calculated that applying a coating of hollow porous cellulose fibers to the inside of a can or bottle could be a potential replacement for widgets.

15.4 INTELLIGENT PACKAGING

Intelligent packaging is defined as *packaging that contains an external or internal indicator to provide information about aspects of the history of the package and/or the quality of the food.*

Intelligent packaging systems can be classified into three categories:

1. Indicate product quality, for example, quality indicators, temperature and TTIs and gas concentration indicators
2. Provide more convenience, for example, during preparation and cooking of foods
3. Provide protection against theft, counterfeiting and tampering

Each of these categories will now be discussed in more detail.

15.4.1 Indicating Product Quality

15.4.1.1 Quality or Freshness Indicators

In this application of intelligent packaging, quality or freshness indicators are used to indicate if the quality of the product has become unacceptable during storage, transport and retailing and in consumers' homes. Intelligent indicators typically undergo a color change that remains permanent and is easy to read and interpret by consumers.

Despite many attempts and several innovative approaches, no quality indicators are in widespread use by the food industry today. Most have been based on detecting volatile metabolites such as diacetyl, amines, ammonia and H_2S produced during the aging of foods. Others have responded to organic acids or volatile biogenic amines formed by microbial degradation of protein-containing foods such as putrescine from arginine, cadaverine from lysine and histamine from histidine.

The RipeSense™ sensor, developed by scientists in New Zealand, enables consumers to choose fruit that best appeals to their taste. The indicator responds to the volatile gases emitted by many fruits as they ripen, that is, not ethylene, but probably the complex mixture of volatiles which include alcohols, esters, aldehyde, ketones and lactones that contribute to the aroma (Mills, 2011). The indicator is red colored for unripe (crisp) fruit, changing through orange to yellow when the fruit is very ripe (juicy). There is a good correlation between the amount of aroma that is produced and the actual softening of the fruit, so that as the fruit softens, it produces more aroma and the sensor changes color. It was initially trialed on pears, and more recently avocados, both fruit whose ripeness consumers have great difficulty in assessing as they do not significantly change their skin color as they ripen.

The label can be attached to a four-piece PET clamshell punnet with a tamper-evident seal that has the added advantage of protecting the fruit from the damage that often occurs as consumers handle produce prior to making their selection. It has also been extended to flow packs which are more cost-effective. Scientists are developing similar sensor labels for subtropical fruits.

15.4.1.2 Time–Temperature Indicators

TTIs are devices which integrate the exposure to temperature over time by accumulating the effect of such exposures and exhibiting a change of color (or other physical characteristic). Many devices which can be attached to food packages to integrate the time and temperature to which the package is exposed have been developed, and the patent literature contains designs of more than 300 such devices. A topical review of the most relevant, recent patents was made, based on the commercial success of the TTIs or their potential commercial viability and the originality of the fundamental principles of the inventions (Maschietti, 2010). Although the majority of these devices were developed specifically for frozen foods, there is now widespread interest in TTIs for most categories of food, especially those where the rate of quality deterioration is highly temperature sensitive. An overview of the major types of TTIs has been presented, together with their application to food quality monitoring (Taoukis, 2011).

TTIs can be divided into two categories: *partial history indicators,* which do not respond unless some predetermined threshold temperature is exceeded, and *full history indicators*, which respond continuously to all temperatures (within the limits of the functioning temperature range of the TTI), thus giving an integrated time–temperature measure relative to the entire life of the product to be monitored. Partial history indicators are intended to identify abusive temperature conditions, and thus there is no direct correlation between food quality change and the response of this class of indicator. The difference in the way the full- and partial-history indicators respond to the same temperature history is shown in Figure 15.1.

ASTM F1416 *Standard Guide for Selection of Time-Temperature Indicators* covers information on the selection of commercially available TTIs for noninvasive, external package use on perishable products such as food and pharmaceuticals. The standard stresses that it is the responsibility of the processor of the perishable product to determine the shelf life of a product at the appropriate temperatures, and to consult with the TTI manufacturer to select the available indicator which most closely matches the quality of the product as a function of time and temperature. British Standard BS 7908 for the performance specification and reference testing of TTIs was issued in 1999 but has since been withdrawn.

TTIs are based on irreversible physical, chemical, enzymic or microbiological changes and their response is usually expressed in a visually quantifiable identifier in the form of mechanical deformation, color development or color movement (Taoukis, 2011). The visible response reflects the cumulative time–temperature history of the package on which they are placed. Examples of the various types of TTIs are discussed below using the classification of Maschietti (2010).

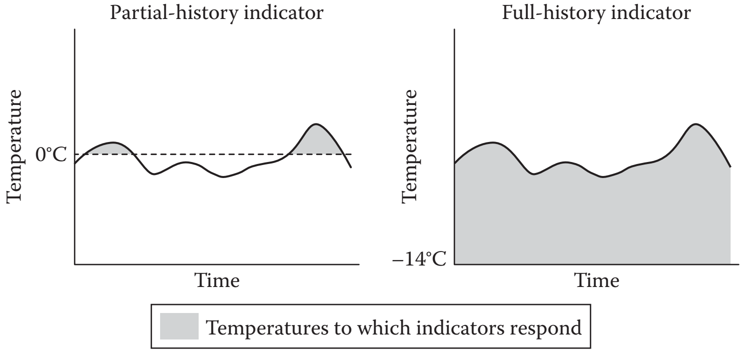

FIGURE 15.1 Two major categories of TTIs.

15.4.1.2.1 Chemical TTIs

Most TTIs are based on a chemical reaction which causes a color change. The rate of color change increases with temperature because the chemical reaction rate increases with temperature. Thus, the intensity of the color can represent a time–temperature integral measurement.

The OnVu™ TTI from BASF Future Business GmbH in Germany is a self-adhesive label composed of a temperature-sensitive, photochromic ink based on benzylpyridines that are activated by UV light, which causes them to turn to a dark blue color. They then turn progressively lighter as time passes and also if and when the ambient temperature rises. When the activated color attains the same shade as the reference, the product has reached the end of its shelf life. The length and temperature sensitivity can be set by controlling the type of photochromic chemical used and the intensity of the UV radiation applied during activation.

The Fresh-Check® TTI from Temptime (formerly LifeLines) is based on a solid-state polymerization reaction and consists of a small circle of polymer surrounded by a printed reference ring. The indicator contains diacetylene monomers ($R–C\equiv C–C\equiv C–R$) which gradually deepen in color to reflect cumulative temperature exposure. Consumers are advised on the package not to consume the food if the polymer center is darker than the surrounding reference ring. The indicators have no means for in-field activation, and are shipped from the manufacturer already activated and responding to storage temperature. To minimize indicator response prior to use, they are stored at −24°C.

15.4.1.2.2 Physical TTIs

TTIs which are not based on chemical reactions are also reported in the patent literature. Some of them are based on diffusion phenomena, that is, the diffusion of colored chemical substances as a function of time and temperature.

The MonitorMark™ TTI from 3M is a partial-history indicator consisting of a pad containing a blue dye within a carrier substance. Removal of the slip-tab brings the pad and a wick into contact, the dye remaining within the pad until the carrier substance undergoes a phase change due to temperature exposure above the response temperature. Indicator response is measured by reading the distance the dye front has migrated past the windows in the indicator.

15.4.1.2.3 Physicochemical TTIs

TTI devices which exploit the chromatic properties of pH indicators by coupling the pH indicator transition to a diffusive mechanism have been patented. The TT Sensor™ TTI from Avery Dennison is based on the diffusion of an organic acid between two polymer layers. The base layer is a rectangular label that includes a circular area (the active zone) containing a fluorescent pH indicator. On the nonactive part of the label, there is a reference pink color. When the activation layer is adhered to the lower active zone, the acid starts to diffuse, resulting in the pH indicator turning progressively from the initial yellow color to the reference pink color.

15.4.1.2.4 Biochemical and Biological TTIs

There have been several patents for TTIs based on biochemical reactions or biological systems which are coupled with pH indicators. In the case of acid-producing bacteria, the color change is caused by the transition of a pH indicator, which must be included in the TTI formula. Such a TTI may comprise a culture medium (a strain of cold-resistant, nonpathogenic acid-producing bacteria, e.g., *Lactobacillus*) and a pH indicator inside a sealed transparent cover which is affixed onto the perishable product packaging. One advantage of such a monitoring system is that the processes which cause the food to deteriorate are the same kind as those occurring in the TTI (i.e., bacterial and enzymic processes), thus allowing the indicator device to accurately mirror the deterioration of the food.

The CheckPoint® TTI from VITSAB (Visual Indicator Tag Systems AB) was previously known as I-POINT™ time–temperature monitor and is a full-history indicator. It is based on the hydrolysis of a lipid substrate (glycerol trihexanoate) in fluid suspension by a proprietary lipase enzyme.

As the hydrolysis reaction proceeds, a pH indicator dye gradually changes color. The color change (from initially deep green to bright yellow, orange and finally red) is compared visually to a reference color scale printed on a paper overlay; it can also be used in automatic optical reading systems.

The (eO)® TTI from CRYOLOG is based on a change in pH expressed as a color change resulting from the growth of selected strains of acid-producing, nonpathogenic bacteria. It consists of a gel made of a nutritive medium and an indicator dye. Lactic acid bacteria are inoculated in the label according to the specifications of the food to be traced, and the label is frozen until it is activated by thawing. Depending on the time–temperature profile, the bacteria in (eO) grow and, as a result, the pH of the medium decreases and the indicator turns from green to red. Patented strains of bacteria which are capable of growing at refrigerated storage temperatures (0°C–8°C) include *Lactobacillus fuchuensis*, *Leuconostoc mesenteroides* and *Carnobacterium piscicola*.

15.4.1.2.5 Applications

In developing an application of TTIs to shelf life monitoring, it is necessary to be able to define and measure quantitatively the key deteriorative reactions that contribute to quality loss in the particular food, and to integrate the expression for quality loss with the TTI response. Paramount to the success of any TTI is recognition of the fact that unless it has the same or similar activation energy (E_A) as the quality-determining deteriorative reaction in the food it is monitoring, then it will overestimate or underestimate the loss of shelf life. The underlying requirement for the reliable prediction of food shelf life using a TTI is that the E_A of the TTI should be within ±25 kJ mol^{-1} of the E_A of the deteriorative reaction (Taoukis, 2011).

Reported results for various TTIs indicate that the MonitorMark has an E_A of 41 kJ mol^{-1}, Fresh-Check® 80–90 kJ mol^{-1}, TT Sensor™ 112–126 kJ mol^{-1}, (eO)® 100–110 kJ mol^{-1}, OnVu™ 90–150 kJ mol^{-1} and CheckPoint® from 50 kJ mol^{-1} for Type C to 195 kJ mol^{-1} for Type L. Apparent E_A*s* of spoilage indices for frozen foods in the temperature range of −12°C to −23°C have been reported and vary from 46 to 64 kJ mol^{-1} for vegetables, 48–61 kJ mol^{-1} for fruit, 54–74 kJ mol^{-1} for meat and 44–49 kJ mol^{-1} for fish, although the E_A of spoilage indices for fish has also been reported as 82 kJ mol^{-1}, so it is important to verify the actual E_A of the specific spoilage reaction rather than rely on published values.

The E_A of the rate constant for the growth and toxin production of nonproteolytic strains (those that grow at refrigeration temperatures) of *C. botulinum* in fresh MAP seafood is 150–200 kJ mol^{-1}. The response of the L5–8 CheckPoint® TTI is within this range and it is being used to monitor the importation of refrigerated seafood into the United States under FDA Import Alert # 16–125 (Taoukis, 2010) that was last published in November 2011.

With increasing incentives for suppliers to deliver high quality food products, better quality control procedures during product transport and improved management of inventory storage will be needed to minimize quality deterioration during distribution. TTIs could play an increasingly important role in monitoring the shelf life of perishable and semiperishable foods. However, despite the clear benefits to be derived from using TTIs in the cold chain, their use is yet to become widespread. Some of the few current applications have been described by Taoukis (2010).

Recently, Tsironi et al. (2011) validated a kinetic model that reliably predicted the shelf life of MAP seabream fillets during refrigerated storage, and selected and programmed an OnVu™ TTI to monitor the quality of fish fillets under any selected storage conditions in the range studied. The growth of lactic acid bacteria in MAP seabream fillets was expressed by an Arrhenius-type model over the range 0°C–15°C and 20%–80% CO_2. The TTI response was tailored to monitor the shelf life of the fish fillets at selected MAP conditions during chill chain storage. A simulation experiment of product distribution and storage in various chill chain conditions showed the applicability of the TTIs as shelf life monitors. Also recently, Ellouze et al. (2011) evaluated the (eO)® TTI as a quality and safety indicator for cold smoked salmon and found that, in the case of poor storage conditions, the TTI could reduce the number of unacceptable products by 50%.

According to Maschietti (2010), the limited use of TTIs is due to the technical difficulties involved in realizing a reliable device which is inexpensive, can be mass-produced and is small enough to monitor single product items. For these reasons, despite the numerous patents and extensive applied research, very few TTIs have been successfully commercialized. The TTIs which are currently on the market still have some scope for improvement, since each of them has some drawback or limitation (e.g., small calibration range, absence of activation system and undesirable influence of parameters other than time and temperature).

15.4.1.3 Gas Concentration Indicators

For many MAP applications (which can include both gas flushing and vacuum), it is helpful to know the gas concentration inside the package headspace and whether or not it is changing over time. Any changes could be as a result of enzymic activity in the food such as respiration of fruits and vegetables, deliberate absorption or generation of gas by added absorbers or generators as discussed earlier or loss of package integrity due to faulty seals or pinholes. The two gases of most interest are O_2 and, to a lesser extent, CO_2.

An *ideal* O_2 indicator for food packaging should be very inexpensive so as to not add significantly to the overall cost of the package, not require an expensive piece of analytical instrumentation for its interrogation and be easily interpreted by an untrained person. It should comprise nontoxic, non-water-soluble components that have food contact approval, since the indicator will be placed inside the food package. In addition, it should have a very long shelf life under ambient, aerobic conditions and, as a consequence, only be active as an O_2 indicator when the package has been sealed and is largely or wholly O_2 free. An ideal O_2 indicator should also exhibit an irreversible response toward O_2 to avoid false negatives. Finally, an ideal O_2 indicator should be easily integrated into the food packaging process and so is best applied as an ink, which must be printable on paper and plastic, either directly to the food package or as a label (Mills, 2009).

The types of gas indicators available commercially are based on either colorimetric changes or luminescence. Many patents exist for colorimetric O_2 indicators and some have been commercialized, but they suffer from high costs and a lack of reliability due to their reversible nature (Mills et al., 2012). For example, the Ageless Eye® (from Mitsubishi Gas Chemical Company in Japan) is an O_2 indicator inserted inside the package that changes from pink when the ambient O_2 concentration is $\leq 0.1\%$ to blue when the O_2 concentration is $\geq 0.5\%$. Such indicators can be included in anoxic packages to indicate the effective absorption of all O_2, and to warn of a breakdown in the O_2 barrier. The presence of O_2 is indicated in 5 min or less, but the change from blue to pink may take 3 h or more at 25°C. At chill temperatures, the response times are much longer. A similar indicator is Wondersensor (from Powdertech in Japan) that also changes in color from pink when the ambient O_2 concentration is $\leq 0.1\%$ to blue when the O_2 concentration is $\geq 0.5\%$. It differs from Ageless Eye® in being a paper type indicator rather than a tablet type indicator.

The Ageless Eye and Wondersensor O_2 indicators are colorimetric redox dye-based indicators, and comprise the redox dye methylene blue (MB) and a strong reducing agent such as glucose in an alkaline medium. In the absence of a significant level of O_2 (i.e., $\leq 0.1\%$), most of the dye lies in its reduced, colorless state, leucomethylene blue (LMB), rather than in its oxidized, more colored form. In contrast, in the presence of a significant level of oxygen (typically $\geq 0.5\%$), most of the dye lies in its oxidized, highly colored form. The reductant and its oxidized form are glucose and gluconic acid, respectively. A nonredox sensitive dye, Acid Red 52, is usually added to provide a background pink color to the indicator. All these components, plus magnesium or calcium hydroxide to provide an alkaline environment, are mixed and, in the case of Ageless Eye, pressed together to form a tablet that is then encapsulated in a clear, O_2 permeable, ion-impermeable plastic sachet to avoid any issue with regard to direct contact; most of the components of the Ageless Eye tablet are water soluble and so susceptible to leaching upon direct contact with foods with a

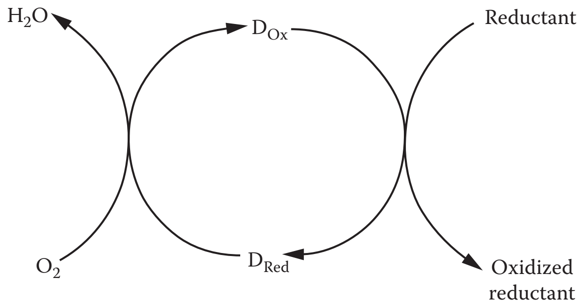

FIGURE 15.2 Schematic illustration of the basic processes associated with a colorimetric redox dye-based O_2 indicator, where D_{Ox} and D_{Red} are the oxidized (usually highly colored) and reduced (usually bleached) forms of the redox dye, respectively. The reductant is usually a reducing sugar in alkali, metal ion (often Fe^{2+}) or ascorbic acid. (From Mills, A., Oxygen indicators in food packaging, in: *Sensors for Environment, Health and Security*, Baraton, M.-I. (Ed.), Springer Science + Business Media B.V., Dordrecht, Netherlands, pp. 371–388, 2009.)

high moisture content (Mills, 2009). The general reaction scheme for this system is shown below and illustrated in Figure 15.2:

$$D_{Ox} + \text{reductant} \rightarrow D_{Red} + \text{oxidant reductant} \tag{15.5}$$

$$D_{Red} + O_2 \rightarrow D_{Ox} + H_2O \tag{15.6}$$

These indicators require storage under anaerobic conditions, because they deteriorate in air via the aforementioned reactions. They are also humidity sensitive, working best under humid conditions, and reversible in response. As a consequence, the use of colorimetric redox dye-based O_2 indicators in the food packaging industry has, for the most part, been confined to package research or the testing of packaging equipment. Cost, reversibility, storage and ease-of-use issues appear major barriers to their general incorporation in O_2-scavenged food packages (Mills, 2009).

Several colorimetric, light-activated O_2 indicators for use with food packaging based on electronically excited dyes such as proflavine, riboflavin and uroporphyrin, by a sacrificial electron donor (SED) like EDTA, have been patented but not commercialized.

The widespread detection of CO_2 by most thin-film, optical indicators has been hindered by their interaction with ambient acidic gas species such as SO_2 and NO_2, which irreversibly acidify and markedly reduce the shelf life of the indicator. A novel CO_2-intelligent pigment with increased stability has been incorporated into flexible LDPE to create a long-lived, CO_2-sensitive indicator film (Mills et al., 2010). The reversible indicator is based on *m*-cresol purple (MCP) that is initially blue but changes to yellow on exposure to CO_2.

Recently a novel “fizziness” indicator based on phenol red was described (Mills and Skinner, 2011), which changes color depending on the headspace pressure of CO_2 above a carbonated liquid. The ink was stable, easy and cheap to prepare and highly reversible. The waterproof indicators, which could be incorporated in a clear bottle cap, would provide a useful guide to the degree of fizziness of carbonated drinks. Neethirajan et al. (2009) reviewed CO_2 sensors for the agri-food industry. Despite many patents and market tests, no indicators are commercially available for reliably indicating the CO_2 level inside packages. Such indicators would be extremely useful in MAP.

Luminescence-based indicators comprise a lumophore dissolved in a solvent, together with a solvent-soluble resin such as a fluoro-silicone polymer. The luminescence associated with the electronically excited lumophore is quenched irreversibly by molecular O_2 (Mills, 2011). OxySense® from Dallas, Texas, is an optical system to measure O_2 noninvasively in the headspace of packages as well as in dissolved liquids, provided that the packaging material can transmit blue and red light (at approximately 470 nm and 610 nm, respectively). The O_2 sensor (Oxy_2Dot®) is based on fluorescence quenching of a ruthenium-based metal organic fluorescent dye encapsulated in a 5 mm diameter, 0.2 mm thick gas permeable, hydrophobic silicone rubber dot that must be attached to the inside of the package. The dot is illuminated with a pulsed blue light from an LED that is absorbed by the dot, red light is emitted and detected by a photodetector and the characteristics of the fluorescence lifetime are measured. Different lifetime characteristics indicate different concentrations of O_2 within the package. The presence of O_2 quenches the fluorescent light from the dye, resulting in a change in the emitted intensity that can be calibrated to provide very accurate O_2 measurements. The sensor is placed in packages prior to filling, and measurements are achieved with a fiber-optic reader pen from outside the package. However, because of cost, it is not possible to place an Oxy$_2$Dot inside every package. There are also possible health and safety issues surrounding the presence of the dot inside packages of food and drink. To date, most applications have been limited to packaging research. Luminescence-based O_2 indicators can be formulated as inks, are reversible in response and tunable with regard to O_2 sensitivity. They do not, however, give an easily discernible response by eye and so require the use of analytical instrumentation in order to be used quantitatively (Mills, 2009).

Recently, the preparation and characterization of a novel, water-proof, irreversible, reusable, UV-activated, O_2-sensitive plastic film was described (Mills et al., 2012). Nanoparticulate pigment particles consisting of the redox dye MB, and a SED (DL-threitol), were coated onto an inorganic support with semiconductor functionality (TiO_2) and extruded in LDPE. The blue-colored indicator was readily photobleached in <90 s using UVA light, whereby MB was converted to its colorless, leuco form, LMB. This form persisted in the absence of O_2, but was reoxidized to MB in ~2.5 days in air under ambient conditions (~21°C, ~65% RH) within the O_2 plastic film; the recovery time at 5°C was about four times longer but not significantly dependent on humidity. The possible application as a "consume-within" or use-by indicator in food packaging was illustrated and discussed briefly.

O_2Sense™ is a range of patent pending O_2-sensing products under development by Freshpoint in Switzerland and aimed at the MAP market. The range consists of an eye-readable indicator that gives a clear, visual indication by means of a color change as to whether the amount of O_2 that is present in a sealed food package is within the specified limits, and a machine readable indicator that elicits a clear electronic signal when read by means of a proprietary optical reader that is placed on a production packaging line.

Recently, a novel colorimetric chemical sensor based on polyaniline (PANI) film for the real-time monitoring of the microbial breakdown products in the headspace of packaged fish was described (Kuswandi et al., 2012). The on-package indicator contains PANI film that responds through a visible color change to a variety of basic volatile amines released during fish spoilage.

15.4.1.4 Radio Frequency Identification

RFID is the use of radio frequencies to read information at a distance with few problems from obstruction or disorientation on a small device known as a *tag* or *transponder* that can be attached to an object (commonly a pallet or corrugated box) so that the object can be identified and tracked (Kumar et al., 2009). Almost all conventional RFID devices contain a transistor circuit employing a microchip, an antenna and a substrate or encapsulation material. The potential in low-cost RFID is split between chip-based technologies and "chipless" tags, which can still be interrogated through a brick wall and hold data, but are cheaper and more primitive in electronic performance than chip tags. To date, most RFIDs have been used to increase convenience and efficiency in supply chain management and traceability, being normally applied to secondary or tertiary packaging. Such RFID tags that simply identify the package are referred to as smart labels and were discussed in Section 9.6.2. To qualify as intelligent packaging, they must contain an indicator that provides information about aspects of the history of the package (e.g., its temperature) or the quality of the food, and such intelligent RFID tags are now being commercialized. If costs can be reduced significantly, then they could find application on individual consumer packages although it is unclear what benefits they might provide to the consumer because a special reader is required to interpret them. However, such readers may be developed as applications for camera phones.

When attached to an RFID chip, a reader can collect data from the label that includes both the aggregate temperature history of the product, and, in the more sophisticated versions that qualify as intelligent packaging, the remaining shelf life left. This provides for intelligent inventory management, and creates an opportunity to dramatically reduce the amount of expired product by first selling those products that the reader shows have the least shelf life left. An increasing number of systems are now available commercially and some are discussed as follows.

TurboTag® T-700 from Sealed Air Corporation, Saddle Brook, New Jersey, is a credit card–sized, battery-powered RFID temperature monitoring tag that captures and delivers the temperature history of any product with which it is associated. PakSense™ Ultra Wireless Labels from Boise, Idaho, are flat and about the size of a credit card, and digitally record the time and temperature of a product's environment during distribution or storage.

The CoolVu™ TTI from Freshpoint in Switzerland shows the total temperature history of the product it is attached to. It consists of a metal label and a transparent label containing an etchant. The label is activated once the etchant label is put on top of the metal layer. The etching process is time and temperature dependent, revealing a visual change at the end of the process. CoolVu can be calibrated for product with a shelf life of days to years and can be designed as a one step or multi step TTI. The CoolVu RF is an add-on to existing RFID systems, enabling electronic monitoring and transmission of the temperature history of the product to which it is attached. CoolVu RF offers both a visual and electronic reading of the temperature history.

Freshtime™ semiactive RFID tags from Infratab Inc. in Oxnard, California, monitor the temperature and integrate it over time to determine the shelf life of a product which can be communicated to a reader. The tags also have a battery and an optional visual display that provides green, yellow and red indicators depending upon the status of the item (e.g., green for fresh and red for unsafe). The range of operation for these tags is from −25°C to 70°C.

The i-Q310 RFID tags from Identec Solutions AG in Lustenau, Austria, have sensors for light intrusion, temperature and humidity as well as shock, and the thresholds for the breach conditions can be specified by the user. It is also available with external sensors and an LED to support visual recognition. It is capable of storing up to 13,000 temperature readings in its memory and it has a battery life of over 6 years.

An exciting, emerging area is that of wireless gas sensors (Potryailo et al., 2011). They are based on different detection principles depending on the type of sensing materials and associated transducers used to provide the required sensitivity, selectivity and stability of measurements. Active wireless sensors have an onboard power supply such as a battery, a supercapacitor or an energy harvester and can transmit signals up to several hundreds of meters. Passive wireless sensors lack an onboard power supply and receive their power from the electromagnetic field generated by the sensor reader. Both active and passive wireless sensors can contain read/write or read-only memory.

Recently, Løkke et al. (2011) reported on the use of wireless sensor networks (WSNs) to determine the respiration rate of oxygen (RRO_2) continuously in fresh-cut broccoli florets at 5°C, 10°C and 20°C and at modified gas compositions (decreasing O_2 and increasing CO_2 levels). WSNs offer the potential to monitor the postharvest RRO_2 of horticultural products during storage and packaging, thereby leading to optimized consumer products.

The polymer PANI has been formulated with camphorsulfonic acid (CSA) and employed for sensing NH_3 and H_2O vapors. The detection limit of PANI-based RFID sensors has been improved down to 500 parts per trillion (ppt) for the monitoring of fish freshness.

15.4.1.5 Biosensors

The demand for new technologies to rapidly detect microbial contamination of food has significantly increased in recent years, due to an increasing number of deaths from food-borne illnesses, as well as the threat of bioterrorism. Traditional methods such as colony counting are excessively time consuming while others, such as PCR, involve complex instrumentation and handling. Biosensors are compact devices that enable detection, recording and transmission of information about biological reactions and offer the potential for real-time pathogen detection. These devices consist of a bioreceptor that is specific for an analyte, and a transducer that converts biological signals into a measurable electrical response. The bioreceptor is an organic or biological material such as an enzyme, antigen, microbe, hormone or nucleic acid. The transducer can assume many forms (such as electrochemical, optical, acoustic) depending on the parameters being measured (Pereira de Abreu et al., 2012). The use of impedance biosensors for detecting foodborne pathogens was recently discussed (Yang, 2011).

Polydiacetylenes (PDAs) have attracted attention for use as sensors, owing to their unique optical properties and rapid response to external stimuli. PDAs are a class of linear conjugated polymers with alternating double and triple bonds that can form vesicles or thin films which change color from deep blue to red in response to different stimuli such as temperature, pH and the presence of biological molecules. The simplicity of PDA synthesis makes this technology a very promising platform for biosensors to detect toxins and bacteria in the food industry. Recently, Pires et al. (2011) developed surfactant-functionalized PDA vesicles to detect *Staphylococcus aureus* and *E. coli* in a culture medium and in apple juice. The vesicles showed great potential as biosensors to detect pathogens in food, but further research is required, especially in relation to their temperature and time stability.

Recently, Duncan (2011) reviewed the use of nanosensors and nanomaterial-based assays for the detection of food relevant analytes including gases, small organic molecules and food-borne pathogens. Several of these techniques could well be adapted for use in food packaging as intelligent biosensors. Also recently, Pérez-López and Merkoçi (2011) reviewed the application of biosensors based on nanomaterials for food analysis which is clearly not intelligent packaging. They concluded that, due to reproducibility problems as well as interferences, their application in real samples is still limited. Furthermore, areas where in their view there does not seem to be a lot of promise for nanobiosensor technology are in situ applications (i.e., implanted sensors) due to stability issues.

15.4.2 PROVIDING MORE CONVENIENCE

Packaging manufacturers have always strived to increase the convenience to the consumer of the package because improved convenience is a value-added function that customers are likely to pay extra for as lifestyles change. Two examples of intelligent packages that increase convenience are described as follows.

15.4.2.1 Thermochromic Inks

Temperature-sensitive thermochromic inks are available and were discussed in Section 9.3. They can be printed onto labels or containers which are to be heated or cooled prior to consumption to indicate the ideal drinking temperature for the product. Depending on their composition, the inks will change color at specific temperatures, and if appropriate colors are chosen, hidden messages such as “drink now” or “too hot” become visible. Thermochromic technology for beverages first became popular with wine labeling, and has been adopted mainly for special occasions and promotions.

The Food Sentinel System™ from SIRA Technologies in Pasadena, California, uses thermochromic ink in a very novel way. Temperature-abused product can be visually identified by an extra-wide, colored bar in the lower bar code which makes it unreadable at the checkout.

15.4.2.2 Microwave Doneness Indicators

MDIs are devices which detect and visually indicate the state of readiness of foods heated in a microwave oven. The utility of such indicators has been recognized for many years because they obviate the need for complicated heating procedures and instructions to the consumer. However, a prerequisite for the use of doneness indicators is a product that heats uniformly enough in order that there is a well-defined stage in the microwave heating sequence at which all the regions within the product simultaneously satisfy the two criteria. In products which heat nonuniformly, the hottest regions (usually around the edges) will trigger a doneness indicator long before the cooler regions have achieved an acceptable temperature.

The requirements for a visual indication of doneness mean that the preferred location for an indicator is on the lid or dome of a container directly above the food. As the food heats in the microwave oven, the space above the food will be heated and, in turn, the heat will be transferred to the lid. The relationship between the temperature of the food and the temperature of the lid forms the basis of an indicator system.

Although there are many temperature indicating papers and labels available that would give a visual indication when the target temperature is reached, most of these devices would be heated by the microwaves, leading to false indications. A solution to this problem is the so-called *shield doneness indicator* discussed as follows.

Because field distributions in microwave ovens are complicated (see Chapter 14), the relationship between the field experienced by the food and the field experienced at the sensor on the lid will generally be different and will vary from oven to oven. As a result, field-sensitive indicator systems would work satisfactorily in some ovens but give false indications in others.

Because the lid temperature generally reaches its equilibrium value before a target temperature has been achieved throughout the product, the sensor must incorporate a time-dependent mechanism. In essence, the detector is activated at a particular temperature and a progressive change in color occurs over the desired time period. Plastic containers of syrup for pancakes can be purchased in the United States that are labeled with a thermochromic ink dot to indicate that the syrup is at the right temperature following microwave heating.

If a temperature sensor is placed in contact with a metallic surface in a microwave oven, it experiences greatly reduced field intensity because the electric fields parallel to the metal surface are very small at or near the surface of the metal. As a result, such a sensor responds primarily to temperature as it has little or no opportunity to absorb microwave energy. Such shielded doneness indicators based on this principle, which incorporate an aluminum foil label on a plastic lid, have been devised but have not been successfully commercialized.

The major limitation of doneness indicators is the difficulty in observing whether or not a color change has occurred without opening the microwave oven. To overcome this limitation, an innovative heating sensor that emitted an audible signal was developed in Japan, consisting of a whistling device on a portion of the lid that generated a sound when gas passed quickly through the device. This indicator worked best when heating foods which had a high moisture content but it has not been commercialized. A Japanese company produced a package with a tuned notch in the lid that whistled like a tea kettle once the product was done. A microchip could possibly be used to provide an audible or visual signal that acts as an indicator but none has been commercialized.

15.4.3 Providing Protection against Theft, Counterfeiting and Tampering

Protection against theft and counterfeiting is a highly developed area for high-value goods such as electronics and clothes. However, it has not found widespread application in the food industry because of the comparatively low unit value of packaged foods. To reduce the incidence of theft and counterfeiting, holograms, special inks and dyes, laser labels and electronic tags have been introduced, but their use in food packaging is minimal, again largely for cost reasons.

Tampering has been a concern for food manufacturers for many years, and there are occasional well-publicized cases where major branded products have been maliciously contaminated with a poisonous substance and the company held to ransom. However, there is no tamper-proof or tamper-evident package that will stop a determined person from contaminating a product. As mentioned earlier, devices such as the button on metal closures attached to glass containers which have been retorted and the tamper-evident band located on the skirt of screw closures attached to glass and plastic bottles have been used for many years but do not qualify as intelligent packaging.

However, intelligent tamper-evident technologies are being developed based on labels or seals which are transparent until the package is opened or tampered with, at which time they change color permanently and/or a word such as “stop” or “opened” becomes visible. Labels or seals which release a dye on being ruptured are also in development, but their widespread use on food packages is unlikely for cost reasons.

15.5 SAFETY AND REGULATORY ISSUES

Despite the intensive R&D and increasing commercialization of active and intelligent packaging systems, no specific methods existed in national and international legislation to determine their suitability in direct contact with foods until recently, when EU regulations were promulgated (see the following text). The result is that legislation which applies to traditional packaging materials has been applied to active and intelligent packaging systems, and countries in the EU consider this to be a satisfactory situation.

The use of some types of active packaging raises safety issues, owing to the effect that such packaging can have on the microbial ecology of the food. For example, packaging that absorbs O_2 from inside the package will affect both the types and growth rate of the microorganisms in foods, and could give rise to the growth of anaerobic pathogenic bacteria such as *C. botulinum*. The inclusion of AM agents in the contact layer of a packaging material may result in a change in the microbial ecology of the food, and the types of microorganisms present on a food will be different from the same food packaged in a conventional manner. AM films which only inhibit spoilage microorganisms without affecting the growth of pathogenic bacteria also raise food safety concerns.

Dainelli et al. (2008) discussed EU legislation and compliance testing of active and intelligent packaging with particular reference to EU Regulation 1935/2004/EC that offered, for the first time, the opportunity for active packaging to be used in Europe by allowing the application of materials with agents that could migrate into foods. This Regulation defined active materials and articles as “materials and articles that are intended to extend the shelf life or to maintain or improve the condition of packaged food.” It also contained general provisions on the safety of active and intelligent packaging and set the framework for the European Food Safety Authority (EFSA) evaluation process.

In 2009, EU Regulation 450/2009/EC detailed specific rules for the safe use of active and intelligent materials and articles, in addition to the general requirements established in Regulation 1935/2004/EC. This new regulation provides a partial explanation for the lack of penetration of active and intelligent packaging in the EU in comparison to Japan, the United States and Australia, where more flexible regulations permitted technological innovations in the food packaging sector. Restuccia et al. (2010) discussed both regulations and summarized the process to obtain approval for all new active and intelligent packaging systems. Based on the outcome of an evaluation by EFSA of a technical dossier containing specified information, the EU Commission (DG SANCO) will grant a petitioner authorization for the submitted active and intelligent ingredients/systems, which will be entered in the Regulation. The authorization is not general but is only for the petitioner. More details are provided in a recent guidance document (EU Guidance to the Commission Regulation (EC) No 450/2009 of 29 May 2009 on active and intelligent materials and articles intended to come into contact with food, 2011).

The EFSA safety assessment will focus on three risks related to the dietary exposure of chemicals. These include migration of active or intelligent substances, migration of their degradation and/or reaction products and their toxicological properties. Nanoparticles should be assessed on a case-by-case basis until more information is known about this new technology (maximum migration limit is 0.01 mg kg^{-1}).

In other countries such as the United States, Australia and Japan, there are no specific regulations related to active and intelligent packaging. A passionate defense of this approach has been provided by Heckman (2007). In his view, as long as a substance used in active packaging does not result in untoward migration into a food, does not give rise to taste or odor problems and is not used to mislead the consumer in any way, it is simply a food contact substance and should be treated as such.

15.6 CONCLUSIONS

Active and intelligent packaging concepts are already in commercial use in many countries, particularly the United States and Japan. In Europe, legislative restrictions, fear of consumer resistance, lack of knowledge about effectiveness and economic and environmental impacts have limited the application of many types of active and intelligent packaging (Day, 2008). Globally, there have been numerous attempts and many highly innovative developments in active and intelligent packaging that have shown great initial promise but have failed to be successfully commercialized. Additionally, attempts are regularly made to commercialize new types of active and intelligent packaging before rigorous scientific evaluations have been undertaken. Even with those systems that have been adopted commercially, the peer-reviewed literature is relatively sparse, making it difficult for food packaging technologists to separate the marketing hype from the technical reality.

Despite this lack of peer-reviewed literature, there is no doubt that the use of active and intelligent packaging systems for food will become increasingly popular and new, innovative applications that deliver enhanced shelf life and greater assurance of safety will become commonplace. However, it would be true to say that the attention and publicity given to active and intelligent packaging is out of all proportion to its use in food packaging.

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16 Modified Atmosphere Packaging

16.1 INTRODUCTION

16.1.1 DEFINITIONS

There is a continuous search for improved methods of transporting food from producers to consumers. It has long been known (see Section 16.1.2) that the preservative effect of chilling can be greatly enhanced when it is combined with control or modification of the gas atmosphere during storage. Such methods have been used commercially for over 100 years for the bulk storage and transport of fresh meat and fruits and are referred to as controlled atmosphere storage (CAS). Since the 1970s and the widespread availability of polymeric packages, this approach has been applied to consumer packs and given the name *modified atmosphere packaging* (MAP) because the atmosphere surrounding the food is modified but not controlled.

MAP can be defined as the enclosure of food in a package in which the atmosphere inside the package is modified or altered to provide an optimum atmosphere for increasing shelf life and maintaining food quality. Modification of the atmosphere may be achieved either actively or passively. *Active modification* involves displacing the air with a controlled, desired mixture of gases, a procedure generally referred to as *gas flushing*. *Passive modification* occurs as a consequence of the food's respiration and/or the metabolism of microorganisms associated with the food; the package structure normally incorporates a polymeric film, and so the permeation of gases through the film (which varies depending on the nature of the film and the storage temperature) also influences the composition of the atmosphere that develops.

Vacuum packaging of respiring foods or foods containing viable microorganisms such as flesh foods is clearly a form of MAP, because after initial modification of the atmosphere by removal of most of the air, biological action continues to alter or modify the atmosphere inside the package. In vacuum packaging, elevated levels of CO_2 can be produced by microorganisms or by respiring fruits and vegetables. Even when no gas is produced inside the package after sealing, vacuum packaging still qualifies as MAP because removing the air has modified the atmosphere inside the package.

Two terms are in widespread use concerning procedures that involve changes in the gas atmosphere in bulk storage facilities. In CAS, the gas composition inside a food storage room is continually monitored and adjusted to maintain the optimum concentration within quite close tolerances. In contrast, the less common *modified atmosphere storage* (MAS) typically involves some initial modification of the atmospheric composition in an airtight storage room, which changes further with time as a result of the respiratory activity of the fresh food and the growth of microorganisms. Because CAS is capital intensive and expensive to operate, it is more appropriate for those foods that are amenable to long-term storage such as apples, kiwifruit, pears and meat.

Controlled atmosphere packaging (CAP) is, strictly speaking, the enclosure of food in a gas-impermeable package inside which the gaseous environment with respect to CO_2, O_2, N_2, water vapor and trace gases has been changed and is selectively controlled to increase shelf life. Using this definition, there are no CAP systems in commercial use. However, the combination of in-package or in-film O_2 and C_2H_4 absorbers, together with CO_2 release agents (i.e., active packaging as discussed in Chapter 15), could be classed as CAP, at least during the early stages of the storage life of the packaged product.

An associated technique is *hypobaric storage*, which consists of placing the food in an environment in which pressure, air temperature and humidity are precisely controlled, and the rate at which air in the storage environment is changed is closely regulated (Burg, 2004). Unlike CAS and MAS, no gases other than air are required. The total pressure within the hypobaric chamber is important because the O_2 concentration is directly proportional to that pressure. Although much research has been carried out into the use of hypobaric conditions for refrigerated storage of flesh foods and horticultural products, it has not been employed commercially to any great extent for the storage or transportation of foods. However, it is used commercially by growers of cut flowers.

16.1.2 History of MAP

The first recorded scientific investigation into the effect of modified atmospheres on fruit ripening appears to have been conducted by Jacques Etienne Berard, a professor at the School of Pharmacy at Montpellier in France, who published his findings in 1821. Berard recognized that harvested fruits utilize O_2 and give off CO_2, and that fruits placed in an atmosphere deprived of O_2 did not ripen as rapidly. There is no record of commercial use of this information for nearly 100 years.

However, a remarkable application of the principles of CAS took place in 1865 in Cleveland, Ohio, when Benjamin Nyce built a reasonably airtight store that used ice for cooling and a special paste for filtering the atmosphere to remove CO_2. He operated this store for a few years but refused to permit others to use his patented procedures; there is no record of expanded use of his system.

The first American scientists to investigate CAS were Thatcher and Booth of Washington State University. Around 1903, they performed 2 years of testing that proved promising but the work was discontinued. In the period between 1907 and 1915, research personnel at the U.S. Department of Agriculture and Cornell University studied the response of several fruits to both lower O_2 and higher CO_2 levels in storage atmospheres. This work was reported in various scientific journals but did not result in commercial applications.

The first intensive and systematic research on CAS of fruits was initiated in England in 1918 by Franklin Kidd (later knighted for his efforts) and Cyril West at the Low Temperature Research Station at Cambridge. Various temperatures and atmospheres were used with apples, pears, plums, strawberries, gooseberries and raspberries. The atmospheres were generated passively by fruit respiration, and were dependent on the O_2 consumed and the CO_2 evolved by the fruit within a gas-tight building. The first commercial CA store appears to have been constructed by a grower near Canterbury in Kent in 1929 and, by 1938, there were over 200 commercial CAS facilities in England.

The knowledge that CO_2 inhibits bacterial growth is not new; in 1877, Pasteur and Joubert observed that *Bacillus anthracis* could be killed using CO_2, and 5 years later, the first paper on the preservative effect of CO_2 on extending the shelf life of beef was published in Germany by Kolbe. During the period from 1880 to late 1920, about 100 reports were published on the inhibitory effects of CO_2 on microorganisms. In 1930, Killefer in England demonstrated that lamb, pork and fish remained fresh twice as long in 100% CO_2 compared with storage in air at chill temperatures, and similar improvements were reported by other English researchers for bacon and beef. In 1933, Haines found that the doubling time of some common bacteria on meat stored in 10% CO_2 at 0°C was twice that in air at the same temperature. Practical application of these results was made in the shipment of chilled beef carcasses from Australasia to England from the early 1930s, with an atmosphere of 10% CO_2 and a temperature of −1°C providing a storage life of 40–50 days without spoilage.

Coyne from the United Kingdom reported in 1932 that fillets and whole fish at ice temperature could be kept twice as long if stored in an atmosphere containing a minimum of 25% CO_2 but that undesirable textural and visual changes occurred if the CO_2 concentration exceeded 80%. Although his results were taken to a semicommercial stage, the technique was never adopted by industry.

A comprehensive study into the use of CO_2-enriched atmospheres for extending the shelf life of poultry meat (chicken portions) was carried out in the United States by Ogilvy and Ayres in 1951. The maximum usable CO_2 concentration was 25% because, above this, the meat became discolored; even at 15%, a loss of bloom was sometimes noted.

In the 1950s, Whirlpool Corporation, the U.S. makers of household washers, driers and refrigerators, tried to develop small gas generators for household food preservation of fresh meats and produce using controlled atmospheres together with refrigeration. Its efforts did not prove successful, but resulted in the Whirlpool Corporation building larger generators (Tectrol® units) for CA warehouses and, later, truck transports for apples, lettuces and a host of fresh foods. In the 1960s, this technology was spun off to a joint venture company called Transfresh (now Fresh Express and owned by Chiquita Brands International), and it is the world's leading producer of fresh cut vegetables (Brody, 2003).

The first patent for MAP of red meat was issued in France in 1969 to Georgala and Davidson, two workers at Unilever. It described an atmosphere containing $\geq$70% O_2 and $\geq$10% CO_2, the balance being an inert gas. Under such an MA in a gas-impermeable container, beef was still in a fresh condition after 15 days at 4°C.

In 1931, Skovholt and Bailey showed that storage of bread in atmospheres containing at least 17% CO_2 delayed appearance of mold, with concentrations of 50% doubling the mold-free shelf life. Aulund from Norway confirmed these findings in 1961, achieving a mold-free shelf life of 16 days for rye bread packaged in an atmosphere of CO_2. During the 1960s, more extensive research was undertaken in the United Kingdom at the Chorleywood Flour, Milling and Baking Research Association into the gas packaging of bakery products using elevated levels of CO_2 to retard mold growth. Unlike flesh foods and fruits and vegetables, baked goods such as bread, pastries and cakes do not benefit from storage at chill temperatures because the rate of staling increases as the temperature is lowered. A large U.K. bakery used MAP in the late 1960s for cake and achieved shelf life extensions of 4–5 days. However, MAP of baked goods did not become significant until the late 1970s when new labeling regulations in Europe required a listing of all preservatives on the label. Adoption of MAP avoided the need to use, and thus list, preservatives and also gave a longer shelf life. Today, there is very little MAP of soft bakery goods in the United States despite the relatively widespread use of MAP for baked goods in Europe.

In the United States, vacuum packaging of poultry was introduced by Cryovac®, followed by the "boxed beef" concept in 1967, both involving vacuum packaging in low O_2 barrier materials. In these circumstances, the atmosphere around the meat becomes depleted in O_2 (often <1% v/v) and enriched in CO_2 (>20% v/v), resulting in microbial changes quite different from those observed during aerobic storage. Vacuum-packaged boxed beef is then distributed to retail outlets where it is converted into consumer units; vacuum-packaged, boxed pork and lamb followed in the 1970s.

In summary, the successful commercialization of MAP in the late 1970s was preceded by over 150 years of scientific research on the inhibitory effects of CO_2 on microbial growth, as well as the effect of gaseous atmospheres on respiring produce. It required the convergence of scientific knowledge, polymeric films, gas flushing and vacuum packaging equipment, and cold distribution chains to achieve the commercial success it enjoys today. Surprising to many is that MAP, in its many manifestations, is now well ahead of the more widely publicized canning, freezing, aseptic packaging, and retort pouch and tray packaging in terms of volume of food preserved (Brody, 2003). Although extension of shelf life is the most apparent advantage of MAP, there are also several other advantages (as well as disadvantages) as shown in Table 16.1.

16.2 PRINCIPLES

MAP is used to delay deterioration of foods that are not sterile and whose enzymic systems may still be operative. With the exception of baked goods, MAP is always used in association with chill temperatures. Chill temperatures are those close to but above the freezing point of fresh foods, and

TABLE 16.1
Advantages and Disadvantages of MAP

Advantages	Disadvantages
Shelf life increase from 50% to 400%	Added costs for gases, packaging materials and machinery
Reduced economic losses due to longer shelf life	Temperature control necessary
Decreased distribution costs, longer distribution distances and fewer deliveries required	Different gas formulations for each product type
Provides a high quality product	Special equipment and training required
Easier separation of sliced products	Potential growth of food-borne pathogens due to temperature abuse by retailers and consumers
Centralized packaging and portion control	Increased pack volume adversely affects transport costs and retail display space
Improved presentation—clear view of product and all-around visibility	Loss of benefits once the pack is opened or leaks
Little or no need for chemical preservatives	CO_2 dissolving into the food could lead to pack collapse and increased drip
Sealed packages are barriers against product recontamination and drip from package	
Odorless and convenient packages	

Source: Adapted from Sivertsvik, M. et al., Modified atmosphere packaging, in: *Minimal Processing Technologies in the Food Industry*, Ohlsson, T. and Bengtsson, N. (Eds), CRC Press, Boca Raton, FL, pp. 61–86, 2002.

are usually taken as −1°C to +7°C. Holding food at chill temperatures is widely used as an effective short-term preservation method, which has the effect of retarding the following occurrences:

1. Growth of microorganisms
2. Postharvest metabolic activities of intact plant tissues, and postslaughter metabolic activities of animal tissues
3. Deteriorative chemical reactions, including enzyme-catalyzed oxidative browning, oxidation of lipids, chemical changes associated with color degradation, autolysis of fish and loss of nutritive value of foods in general
4. Moisture loss

The effect of chilling on the microflora in a particular food depends on the temperature characteristics of the organisms as well as the temperature and time of storage. As the temperature is lowered from the optimum, growth slows and eventually stops. Microorganisms which can grow within the 0°C–7°C range are defined as *psychrotrophs.* The most important psychotropic bacteria as far as chill temperature preservation of food is concerned are from the genus *Pseudomonas,* but the pathogens *Clostridium botulinum* type E, *Yersinia enterocolitica*, *Listeria monocytogenes*, enterotoxigenic *Escherichia coli* and *Aeromonas hydrophila* are also able to grow at or below 6°C. Thus, chill temperatures cannot be relied on absolutely to keep foods safe because of the possible survival and growth of these pathogens at chill temperatures.

If cooling is too fast or if the temperature is reduced too near to the freezing point of the food, then chilling injury can result. This can manifest itself in various ways, for example, cold shortening of muscle and physiological disorders of fruits and vegetables. In general, each food has a minimum temperature below which it cannot be held without some undesirable changes occurring in that food.

The preservative effect of chilling can be greatly enhanced when it is combined with modification of the gas atmosphere. This is because many deteriorative reactions involve aerobic respiration in which the food or microorganism consumes O_2 and produces CO_2 and water. By reducing

O_2 concentration, aerobic respiration can be slowed. By increasing CO_2 concentration, microbial growth can be slowed or inhibited (see the following text).

In addition to the benefits resulting from modification of the atmosphere inside the package, other benefits from MAP for fresh foods can include maintenance of high RH and reduction in water loss, as well as improved hygiene by reducing contamination during handling. In the case of fresh produce, surface abrasions are minimized by avoiding contact between the produce and the shipping container and there is a reduced spread of decay from one item to another. In many cases, the benefits of using MAP relate more to one or more of these positive effects than to changes in the O_2 and CO_2 concentrations inside the package. Negative effects of MAP of fresh produce include a slowing down in the cooling rate of the packaged products, and increased potential for water condensation within the package, which may encourage fungal growth.

Although there is considerable information available regarding suitable gas mixtures for different foods, there is still a need for additional scientific information regarding many aspects relating to MAP, including

1. Mechanisms of action of CO_2 on microorganisms
2. Influence of CO_2 on microbial ecology of a food
3. Safety of MAP packaged food products
4. Interactive effects of MAP and other preservation methods
5. Effect of MAP on nutritional quality of packaged foods

16.3 GASES USED IN MAP

The normal composition of air by volume is 78.08% N_2, 20.95% O_2, 0.93% argon (Ar), 0.03% CO_2 and traces of nine other gases in very low concentrations. The three main gases used in MAP are O_2, CO_2 and N_2, either singly or in combination. Noble or “inert” gases such as Ar are being used commercially for a wide range of products although the literature on their application and benefits is limited (Spencer, 2005). The solubilities in water of these gases are given in Table 16.2. Gases also have significant solubility in the lipid phase of foods. For example, at 0°C and atmospheric pressure, 1 L of vegetable oil can absorb approximately 6 mL of N_2, 12 mL of O_2 and 1 L of CO_2 (Lencki, 2005). Use of carbon monoxide (CO), sulfur dioxide (SO_2) and nitrous oxide (N_2O) in MAP has also been reported.

16.3.1 CARBON DIOXIDE

CO_2 is the most important gas in the MAP of foods, due to its bacteriostatic and fungistatic properties. It inhibits the growth of many spoilage bacteria, with the degree of inhibition increasing with increasing concentration. It is particularly effective against molds and Gram-negative, aerobic spoilage bacteria such as *Pseudomonas* sp., but much less effective in controlling yeasts or lactic acid bacteria.

TABLE 16.2
Solubilities of Gases in Water at Atmospheric Pressure and Various Temperatures

	Gas Solubility (mg kg^{-1})				
Temperature (°C)	**Oxygen**	**Nitrogen**	**Carbon Dioxide**	**Argon**	**Carbon Monoxide**
0	69	29	3350	100	44
5	62	27	2770	89	40
10	58	24	2320	78	36
20	42	18	1690	59	28

Solubilities given for carbon dioxide include all chemical species of the gas and its reaction products with water.

CO_2 is a colorless gas with a slight pungent odor at very high concentrations. It dissolves readily in the aqueous phase and forms a significant quantity of other hydrated carbonate species depending on the pH. At the slightly acidic pH found in many foods, the dissolved CO_2 first hydrates to form carbonic acid H_2CO_3 (Equation 16.1); this is known to disrupt microbial cell membranes and inhibit respiratory enzymes. It then ionizes to release bicarbonate and an H^+ ion (Equation 16.2) that can lower pH depending on the buffering capacity of the food (Lencki, 2005). When the pH of a CO_2 solution rises to 8.0 (most unlikely in foods), the HCO_3^- may even dissociate further to form CO_3^{2-} (Equation 16.3):

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \tag{16.1}$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \tag{16.2}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \tag{16.3}$$

As with all gases, the solubility of CO_2 increases with decreasing temperature and therefore the antimicrobial activity of CO_2 is markedly greater at lower temperatures. This has significant implications for MAP of foods. The high solubility of CO_2 in high moisture/high fat foods such as meat, poultry and seafood can result in package collapse due to the reduction of headspace volume. High levels of CO_2 can also result in increased drip or exudate from flesh foods, and the addition of absorbent pads in the base of the package is used to compensate for this.

16.3.2 OXYGEN

O_2 is a colorless, odorless gas that is highly reactive and supports combustion. It has a low solubility in water. O_2 promotes several types of deteriorative reactions in foods including fat oxidation, browning reactions and pigment oxidation. Most of the common spoilage bacteria and fungi require O_2 for growth. For these reasons, O_2 is either excluded or reduced to as low a concentration as possible. Exceptions occur where O_2 is needed for the respiration of fruits and vegetables or the retention of color in red meat.

16.3.3 NITROGEN

N_2 is an inert gas with no odor or taste. It has a lower density than air and a low solubility in water and other food constituents, making it a useful filler gas in MAP to counteract package collapse caused by CO_2 dissolving in the food. N_2 indirectly influences the microorganisms in perishable foods by retarding the growth of aerobic spoilage microbes but it does not prevent the growth of anaerobic bacteria. MAP mixtures based on N_2 have a similar density to air, and a great deal of turbulence is introduced when such mixtures are used to displace air inside packages as a result of the interaction of two columns of similar density. Sufficient force must be applied to introduce a mass of at least eight times the volume of airspace into the package, although applying a vacuum first can reduce the volume of air that must be displaced (Spencer, 2005).

16.3.4 CARBON MONOXIDE

CO is a colorless, tasteless and odorless gas, which is highly reactive and very flammable. It has a low solubility in water but is relatively soluble in some organic solvents. CO has been studied in the MAP of meat where it has the potential to inhibit metmyoglobin formation and promote metmyoglobin reduction, even when O_2 is present. Lipid oxidation and browning are reduced and the shelf life of the food is prolonged. CO combines with myoglobin to form the bright cherry-red pigment carboxymyoglobin, which is much more stable than oxymyoglobin; a CO concentration of 0.4% in a MAP of meat is sufficient to give a bright red color (see Chapter 17). CO at 5%–10% (combined with less than 5% O_2) is an effective fungistat, which can be used on commodities that do not tolerate high CO_2 levels.

CO has not been approved by regulatory authorities for commercial use in the EU, and is not included in the list of allowed food additives (Directive 95/2/EC). It was legal in Norway for retail packaging of red meat, but Norway has since banned the use of CO in compliance with EU rules. It has been sanctioned for use in the United States to prevent browning in packaged lettuce, and for pretreating meat in a master pack system where it is considered a processing aid. Commercial application has been limited because of its toxicity, its explosive nature at 12.5%–74.2% in air and the fact that it has a limited effect on microorganisms.

16.3.5 NOBLE GASES

The *noble gases* are a family of elements characterized by their lack of reactivity and include helium (He), argon (Ar), xenon (Xe) and neon (Ne). Although the noble gases are chemically inert, it has been suggested that they are biologically active and several patents have been issued for their use in MAP. There has been some research into the biochemical and physiological effects of noble gases on specific enzymes, and the majority of these studies have been related to browning in fresh fruits and vegetables and respiratory metabolism.

For example, although Ar has been considered to be completely inert, some research suggests that it is a competitive inhibitor of respiratory enzymes, including oxidases. It has also been claimed that Ar slows down the rate of production of volatile amino bases in seafood, inhibits enzymic discoloration, delays the onset of textural softening, extends the microbial lag phase, inhibits microbial oxidases and enhances the effectiveness of CO_2 by weakening microbes, thereby enabling the use of less CO_2 in MAP. A possible reason for these effects could be the greater solubility of Ar compared to O_2 and N_2 and its similar atomic size to O_2. It is also claimed that Ar is more effective at displacing O_2 from cellular sites and enzymic O_2 receptors. O'Beirne et al. (2011) suggested that the greater inhibitory effect exhibited by Ar on oxidases was proportional to the greater molecular space occupied by Ar compared to N_2 and was directly related to the van der Waals radius values of Ar against N_2 (1.91 against 1.54 Å).

Ar is a much denser gas than N_2 (1.650 compared to 1.153 kg m^{-3}) and therefore can be made (unlike N_2) to flow in a laminar fashion like a liquid through air space. Thus, if it is introduced into the bottom of a tray, it displaces the air column upward as it fills the tray (Spencer, 2005). For the same reason, Ar is commonly used instead of N_2 to flush the neck of wine bottles immediately prior to corking. Because Ar is denser than N_2 and four times more efficient at displacing air, the difference in cost (Ar costs approximately five times that of N_2) is negligible.

Despite few scientific publications, noble gases are being used in a number of food applications including potato chips, processed meats, nuts, beverages, fresh pasta, chilled prepared meals and lettuce with claims of an average 25% improvement in shelf life. Some products, such as fresh pizza, have shelf life improvements of 40%–50%. At present, nearly 200 different argon-packaged foods can be found on supermarket shelves in the United Kingdom and elsewhere in Europe (Spencer, 2005).

16.3.6 GAS MIXTURES

The gas mixtures used for MAP of different foods depend on the nature of the food and the likely spoilage mechanisms. Where spoilage is mainly microbial, the CO_2 levels in the gas mix should be as high as possible, limited only by the negative effects of CO_2 (e.g., package collapse) on the specific food. Typical gas compositions for this situation are 30%–60% CO_2 and 40%–70% N_2. For O_2-sensitive products where spoilage is mainly by oxidative rancidity, 100% N_2 or N_2/CO_2 mixtures (if microbial spoilage is also important) are used. For respiring products, it is important to avoid too high a CO_2 level or too low an O_2 level, so that anaerobic respiration is prevented.

16.4 METHODS OF CREATING MA CONDITIONS

16.4.1 Passive MA

In this approach (also known as *commodity-generated MA*), an atmosphere high in CO_2 and low in O_2 passively evolves within a sealed package over time as a result of the respiration of the product. Ideally, the gas permeabilities of the packaging film are such that sufficient O_2 can enter the package to avoid anoxic conditions and the occurrence of anaerobic respiration, while at the same time excess CO_2 can diffuse from the package to avoid injuriously high levels. Passive modification is commonly used for MAP of fresh respiring fruits and vegetables. Given the simplicity of this approach and the many interrelated variables which affect respiration rate, considerable research is required to develop appropriate passive MA systems for horticultural products.

16.4.2 Active MA

Several methods can be used to actively modify the gas atmosphere inside a packaged product. These include vacuum packaging where the air is removed under vacuum and the package sealed. This method finds widest application for the packaging of flesh foods, particularly red meat. A two-stage method involves first removing the air inside the package using a vacuum followed by flushing with the desired gas mixture. This creates the desired MA immediately after packaging compared to the passive approach, which may require a week or longer before achieving the same gas composition. In a third active MA method, no vacuum is used but a gas mixture is injected into the package and the air swept or flushed out immediately prior to sealing, resulting in residual O_2 levels of 2–5%. For O_2-sensitive products, the two-stage method is preferred.

Regardless of whether vacuum or gas flush packaging is used to create an MA, the package itself must provide a barrier to permeation over the expected shelf life, otherwise the beneficial effects of reducing O_2 will be lost. In the case of vacuum packaging, the barrier issue relates only to O_2 ingress, but, in gas flushing, both O_2 ingress and N_2 egress must be considered. An elegant analysis of the situation has been presented (Brown, 1992) and is repeated here.

In vacuum packaging, both O_2 and N_2 are potential entrants into the package. O_2 is a faster permeant than N_2 by a factor of about 4–6 (see Table 4.3); however, air contains only a quarter as much O_2 as it does N_2. Therefore, O_2 and N_2 are about equally as likely to enter the package.

On the other hand, gas flush packaging (assuming that only N_2 is used) imposes a 100% N_2 atmosphere inside the package, working against a 79% N_2 atmosphere in the surrounding air. Thus, the driving force for N_2 exiting the package is $1.00 - 0.79 = 0.21$ atmospheres, while the driving force for O_2 to enter is the partial pressure of O_2 in the air ≈ 0.21 atmospheres. Because the driving forces (i.e., the partial pressure differences inside and outside the package) are equal, and the permeation rate for N_2 egress is about a quarter to a sixth that of O_2 ingress, the package will slowly increase in pressure. If the package is made from a flexible film or has a film lid sealed to a plastic tray, a “pillowing” effect is likely to occur. It is important that the reasons for this pillowing effect are clearly understood as it is not uncommon for it to be ascribed by the uninitiated to microbial growth, resulting in perfectly safe product being removed from sale.

In addition to the mechanical methods described earlier, absorbers can be used inside the package, for example, to delay the climacteric rise in respiration for some fruits by adsorbing C_2H_4, to prevent the build-up of CO_2 to injurious levels by adsorbing CO_2 as well as to lower the concentration of O_2 through the use of O_2 absorbers. Obviously, the use of gas absorbers adds considerably to the cost, and therefore their use is limited to those commodities for which it is cost-effective. An alternative method for quickly reducing the O_2 content and increasing the CO_2 content within a package involves the use of ferrous carbonate inside a gas-permeable sachet; in the presence of moist air, the amorphous material oxidizes with the release of CO_2. The quantity of ferrous carbonate used must be carefully calculated since if too much is present inside the package, then anoxic conditions will be established.

The practical upper level of dissolved CO_2 in a food is limited by the degree of filling (DoF) and the flexibility of the chosen packaging material. A high CO_2 level and high DoF is hampered by package collapse. One approach to address this problem is *soluble gas stabilization* (SGS) and involves dissolving CO_2 in the food at low temperature (ca. 0°C) and elevated pressures (>2 atm) prior to packaging (Sivertsvik et al., 2002). This results in packages with smaller gas:product ratios and thus decreased package sizes for a given weight of product. SGS has shown promising results on extending the shelf life of a range of seafood, and has also been used successfully on dairy products. In addition, a mathematical model has been developed to estimate the equilibrium gas composition in MAP and SGS systems (Rotabakk et al., 2008).

16.5 EQUIPMENT FOR MAP

Equipment for MAP must generally be capable of removing air from the package and replacing it with a mixture of gases. There are basically three types of packaging equipment used for MAP: horizontal or vertical form-fill-seal (FFS) machines using pouches or trays, snorkel machines using preformed bags or pouches and chamber machines using preformed pouches or trays.

16.5.1 Form-Fill-Seal Machines

FFS machines can either form pouches (vertically or horizontally), or thermoformed trays with a heat sealed lid, from rollstock. In the pouch version, the desired gas mixture is introduced into the package in a continuous countercurrent flow to force out the air, after which the ends of the web are heat sealed and the packages cut from one another. In the tray version, product is placed in the tray and a vacuum drawn, after which the desired gas mixture is introduced and the top web of film heat sealed to the base tray.

16.5.2 Chamber Machines

Here, the filled package (either a preformed pouch or tray inside a bag) is loaded into a chamber, a vacuum is pulled and the package is then flushed with the gas mixture and heat sealed. This is a batch process, is relatively slow and most suitable for bulk or master packs.

16.5.3 Snorkel Machines

Snorkel machines operate without a chamber. The product is placed inside a large flexible pouch (or bag) and positioned in the machine. Snorkels or probes are inserted into the pouch and remove air, after which the vacuum is broken by the addition of the desired gas mix. The probes are then removed and the package is heat sealed. These machines are used mainly for bulk packaging and for so-called *master packs* in which individual retail packs are packaged in a large MA pouch or bag.

16.6 PACKAGING FOR MAP APPLICATIONS

The main characteristics to be considered when selecting packaging materials for MAP are permeability of the package to gases and water vapor, mechanical properties, heat sealability and transparency. For nonrespiring products, all the common high gas barrier structures have been used in MAP, including laminates and coextruded films containing PVdC, EVOH and PAs as a barrier layer. The inside layer is usually LDPE to provide a good heat seal and moisture vapor barrier.

The OTR of packaging materials used for MAP of chilled products varies extensively with temperature, RH and material thickness after the thermoforming of packages. Gnanaraj et al. (2005) reported OTRs for a range of films at 10°C, 15°C, 23°C, 30°C and 35°C and 0% and 50% RH. The OTRs at 10°C were typically half those at 23°C. Jakobsen et al. (2005) studied two different polymer combinations: an APET-LDPE tray and a PA-LDPE lid. A temperature reduction of 8°C (in the interval 7°C–23°C) caused an OTR reduction of 26%–48%, depending on material type, degree of thermoforming and RH. An increased OTR was observed as a result of material thinning; however, the increase was not always directly proportional to the degree of material thinning. The changes observed in OTR emphasize the necessity of evaluating the performance of packaging materials under realistic storage conditions to estimate the real O_2 content of a chosen package solution. The same comments apply to the TR of other gases used in MAP.

For the MAP of respiring produce such as fruits and vegetables, the choice of suitable packaging materials is much more complex, and no easy solutions are available due to the dynamic nature of the food. Ideally, the packaging material should maintain a low O_2 concentration (3%–5%) in the headspace and prevent CO_2 levels exceeding 10%–20%. Polyolefin films are normally used, but to achieve the desired MAP, it has been necessary to perforate the film or (more recently) use a special patch; O_2 and CO_2 absorbers have also been used on a limited scale. MAP materials for fruits and vegetables are discussed in more detail in Chapter 18.

To prevent condensation of water vapor on the inside of the package as a result of temperature differentials between the package contents and the packaging material, antifogging agents are used. These amphiphilic additives function by decreasing the interfacial tension between the polymer and the condensed moisture vapor, enabling the water droplets to coalesce and spread as a thin transparent layer across the surface of the film. Typical antifogging agents include nonionic ethoxylates or hydrophilic fatty acid esters.

For the trays used in MAP, there are no special requirements other than good thermoformability. Typical tray materials are PS and PVC, although the latter is much less common in Europe because of environmental concerns among consumers. Preformed plastic-coated paperboard trays have also been used. Regardless of the type of tray, it is essential that the lidding film can be adequately sealed onto the tray.

16.7 MICROBIOLOGY OF MAP

The species of microorganisms that cause spoilage of particular foods are influenced by two factors: the nature of the foods and their surroundings. These are known as *intrinsic* and *extrinsic* parameters and were discussed in Chapter 11 (see especially Table 11.4). The two extrinsic factors most relevant in MAP are the gaseous composition of the in-pack environment and the temperature. The specific microbiology of various foods is dealt with in subsequent chapters of this book. However, general comments on the effects of MAs on food spoilage and pathogenic microorganisms will be outlined here.

Microbial food spoilage is characterized by undesirable sensory changes to the odor, color, flavor and sometimes the texture of the food, making it inedible or unsealable. Spoilage is an important safeguard in preventing food poisoning, because the deterioration in food quality normally (but not always) warns the consumer that the food may be unsafe.

Microorganisms have different respiratory and metabolic needs and can be grouped according to their O_2 needs as shown in Table 16.3. The effect of CO_2 on microbial growth is shown in Table 16.4.

Concentrations of CO_2 in excess of 5% v/v inhibit the growth of most food spoilage bacteria, especially psychrotrophic species such as *Pseudomonas*, which grow on a wide range of refrigerated foods. The effect of CO_2 on bacterial growth is complex and the growth inhibition of microorganisms in MA is determined by the concentration of dissolved CO_2 in the product. However, CO_2 does not retard the growth of all types of microorganisms; for example, the growth of lactic acid bacteria is enhanced in the presence of CO_2 and low O_2 concentrations. Another example is *L. monocytogenes* which, although inhibited by 100% CO_2, is unaffected by CO_2 if at least 5% O_2 is present.

Much research has been carried out regarding the safety and the health hazards of MAP of foods, especially on those pathogens able to multiply at chill temperatures and those able to multiply in anaerobic conditions. There are seven food-borne pathogenic bacteria known to be capable of growth

TABLE 16.3
Oxygen Requirements of Some Microorganisms of Relevance in MAP

Group	Spoilage Organisms	Pathogens
Aerobes (require atmospheric O_2 for growth)	*Micrococcus* sp. Molds, e.g., *Botrytis cinerea* *Pseudomonas* sp.	*Bacillus cereus* *Yersinia enterocolitica* *Vibrio parahaemolyticus* *Campylobacter jejuni*
Microaerophiles (require low levels of O_2 for growth)	*Lactobacillus* sp. *Bacillus* spp. *Enterobacteriaceae*	*Listeria monocytogenes* *Aeromonas hydrophila* *Escherichia coli*
Facultative anaerobes (grow in presence or absence of O_2)	*Brochothrix thermosphacta* *Shewanella putrefaciens* Yeasts	*Salmonella* spp. *Staphylococcus* spp. *Vibrio* sp.
Anaerobes (inhibited or killed by O_2)	*Clostridium sporogenes* *Clostridium tyrobutyricum*	*Clostridium perfringens* *Clostridium botulinum*

TABLE 16.4
Effect of CO_2 Atmosphere on Growth

Microorganism	Type of Growth	Effect on Growth in CO_2 Atmosphere
Aeromonas spp.	Facultative	Inhibited (weakly)
Bacillus cereus	Facultative	Inhibited
Campylobacter jejuni	Microaerophilic	Inhibited, survival[a]
Clostridium botulinum proteolytic (A, B, F)	Anaerobic	Unaffected[b]
C. botulinum nonproteolytic (B, E, F)	Anaerobic	Unaffected[b]
Clostridium perfringens	Anaerobic	Inhibited
Escherichia coli	Facultative	Inhibited (weakly)
Listeria monocytogenes	Facultative	Unaffected/inhibited[c]
Plesiomonas spp.	Facultative	Inhibited
Salmonella	Facultative	Inhibited[b]
Staphylococcus aureus	Facultative	Inhibited (weakly)
Vibrio cholerae	Facultative	Inhibited
Vibrio parahaemolyticus	Facultative	Inhibited
Yersinia enterocolitica	Facultative	Inhibited

Source: Adapted from Sivertsvik, M. et al., Modified atmosphere packaging, in: *Minimal Processing Technologies in the Food Industry*, Ohlsson, T. and Bengtsson, N. (Eds), CRC Press, Boca Raton, FL, pp. 61–86, 2002.

[a] The bacteria survive better in CO_2 as compared to air, but growth is (weakly) inhibited.

[b] One report of growth stimulation under CO_2.

[c] Unaffected by CO_2 atmosphere if at least 5% O_2 present; inhibited under 100% CO_2.

at or below 5°C: *C. botulinum* Type E, *L. monocytogenes*, *Y. enterocolitica*, *Vibrio parahaemolyticus*, enterotoxigenic *E. coli*, *Bacillus cereus* and *Aeromonas hydrophila*. Two others are capable of growth at temperatures just above 5°C: *Staphylococcus aureus* at 6°C (10°C for toxin production) and *Salmonella* sp. at 7°C. Thus, it is vitally important that the MAs inhibit the growth of these organisms in foods under refrigerated storage. Fortunately, most of these organisms do not compete well with harmless bacteria, such as the *Lactobacillus* sp., which grow rapidly if temperature abuse occurs.

The spores of *C. botulinum* types B, E and F can grow and produce toxin after 5 weeks at 3°C, 3–4 weeks at 4°C and 2–3 weeks at 5°C. Growth occurs more frequently from spores of type F strains than for types B and E. It has been demonstrated that 100% CO_2 can have an inhibitory effect on the growth of *C. botulinum* at chill temperatures, and an increased inhibitory effect has been observed when combining 100% CO_2 with increased NaCl levels and decreased pH. Of most concern in MAP is the possible growth of *C. botulinum* Type E, which is associated with fishery products. It is tolerant of low temperatures, is anaerobic and may grow and produce a potent neurotoxin on the food before spoilage is detectable by the consumer. Storage at temperatures below 3°C should provide an adequate safeguard for foods where *C. botulinum* may be present.

The concept of barrier or hurdle technology was introduced in the 1980s and refers to combinations of different preservation factors ("hurdles") that are used to achieve multitarget, mild preservation effects. Hurdles that are used in addition to chill temperatures to limit or prevent the growth of psychrophilic pathogens during low temperature storage or limited temperature abuse of the food include CO_2, thermal processing, pH reduction (<5), preservatives, reduced a_w (<0.97) and competitive microflora.

16.8 SAFETY OF MAP

The shelf life and safety of any MAP food is influenced by a number of factors including the nature of the food, the gaseous environment inside the package, the nature of the package, the storage temperature and the packaging process and machinery. In discussing the safety of MAP foods, it is useful to divide them into two categories: those products such as smoked salmon, cured meats, fruits and salad vegetables that are eaten without any prior heat treatment, and those such as fresh fish, raw meats and poultry products that are usually subjected to a sufficient heat treatment to kill all vegetative pathogens (Walker and Betts, 2008). Clearly, the first category presents more risks from a microbiological point of view.

Chilled foods have been subjected to detailed regulatory controls in many countries, particularly with respect to temperature requirements, and at the international level, HACCP-based approaches to hygiene have been established (Codex, 1997, 1999). One of the major concerns of MAP foods is temperature abuse, because the biostatic effects of CO_2 are temperature dependent, and a rise in temperature during storage could permit the growth of microorganisms which had been inhibited by CO_2 at lower temperatures. If O_2 were present in the package, then growth of aerobic spoilage organisms during periods when the food was at nonrefrigerated temperatures would alert consumers to temperature abuse due to the appearance of undesirable odors, colors or slime. However, the absence of O_2 will favor the growth of anaerobic microorganisms (including *C. botulinum*) over aerobic spoilage organisms. It has been demonstrated that anaerobic pathogens can grow at temperatures as low as 3°C and produce toxin without any sensory manifestation of food deterioration.

An area of active research is edible films for use in MAP systems. However, these films can create a very low O_2 environment where anaerobic pathogens such as *C. botulinum* may thrive. Antimicrobial compounds that can be incorporated into the coating are also being investigated.

Successful control of both product respiration and ethylene production by MAP can result in fruit or vegetable products of high sensory quality. However, control of these processes is dependent on maintaining optimum temperature control along the entire food chain continuum, from processing, storage, transportation and retailing to in the home. Maintaining proper storage temperatures is often most difficult at retail and domestic level.

Currently, there is concern with psychrotrophic food-borne pathogens such as *L. monocytogenes*, *Y. enterocolitica* and *A. hydrophila*, as well as nonproteolytic *C. botulinum*, although clearly a number of other microorganisms, especially *Salmonella*, *E. coli* O157:H7 and *Shigella* spp., can be potential health risks when present on MAP produce. Although only two MAP produce products (*C. botulinum* in coleslaw mix in the United States in 1990 and *Salmonella* in ready-to-eat salad vegetables in the United Kingdom in 2001) have been implicated in food-borne illness outbreaks, the potential for growth of pathogens exists. The success and microbiological safety of MAP is dependent on controlled low temperature storage and the product's characteristics.

It is difficult to evaluate the safety of MAP foods solely on the basis of the growth of certain pathogens at abusive temperatures because (1) most food pathogens do not grow at chill temperatures and (2) CO_2 is not highly effective at nonrefrigeration temperatures. To minimize problems with pathogens inside MAP foods, the foods should be of the highest microbiological quality at the time of packing, they should be processed and packaged under high standards of hygiene and sanitation, their temperature should be reduced as rapidly as possible and the temperatures during distribution should be rigidly maintained as low as required to avoid anaerobic pathogen growth. If the aforementioned requirements are compromised in any way, serious public health hazards could result from ingestion of the MAP food.

Predictive microbiology was discussed in Chapter 12 and is being increasingly used as a tool to provide rapid and reliable answers concerning the likely growth of specific organisms under defined conditions. There are many advantages to the use of predictive models with chilled foods, especially in the decision-making processes of HACCP and risk analysis, and reference should be made to a recent review (McClure and Amézquita, 2008).

16.9 REFRIGERATED, PASTEURIZED FOODS WITH EXTENDED DURABILITY AND *SOUS VIDE*

There is an increased interest in "fresh," preservative-free food with extended durability. In addition to foods packaged in MAs, there are refrigerated, pasteurized foods with extended durability (REPFEDs) such as *sous vide* and cook-chill foods that are produced by the following general process. Meals or components of meals (which may include both raw and cooked components) are sealed in a heat-stable pouch and the packaged product cooked at temperatures ranging from 65°C to 95°C. The product is then cooled and stored at refrigeration temperatures (1°C–7°C) and has a shelf life of up to 42 days dependent on the heat treatment and the storage temperature (Gorris and Peck, 1998).

If the pasteurization process is adequately carried out, then all vegetative bacteria present are killed, but bacterial spores can survive this heating process. Since REPFEDs are mostly packed under vacuum or in an anaerobic atmosphere, growth of aerobic microorganisms is restricted while growth of anaerobic bacteria is favored. The ecological niche found in REPFEDs favors colonization by microorganisms that produce heat-resistant spores and grow in the absence of O_2 at refrigeration temperatures. Nonproteolytic *C. botulinum* is the principal microbiological safety concern in REPFEDs (Gorris and Peck, 1998). Proteolytic *C. botulinum* and *Clostridium perfringens* are of concern when the storage temperature exceeds 10°C for a prolonged time.

Hurdle technology has been applied to REPFEDs to control growth of spoilage and pathogenic microorganisms, although each hurdle is insufficient on its own to achieve the same effect. Typical hurdles include $pH \leq 5$, salt concentration $\geq 3.5\%$ and $a_w \leq 0.97$ throughout the food.

A food processing technology known as *sous vide* (literally "under vacuum") has been developed to enhance the shelf life of refrigerated foods and is a particular type of cook-chill process. Though lauded as a revolution by some, it is really the result of an evolution of the conventional cook-chill process. It uses vacuum packaging, heating and rapid cooling, followed (normally) by chilled storage, although two of the largest producers in the United States specialize in frozen *sous vide* products.

The precursor of *sous vide* was first discussed in 1960 (Kohman, 1960) and the name "Frigi-Canning" given to this new process, which involved thermal processing in hermetically sealed cans or jars, followed by rapid chilling since only vegetative forms of microorganisms were destroyed. The first formal application of *sous vide* technology was developed and tested at two hospitals in Sweden from 1960 to 1965, the process being termed the "Nacka System" after one of the hospitals. *Sous vide* technology appeared in France in 1972 for the processing of ham, and the first large-scale application of modern *sous vide* technology was undertaken in 1985 by the French national railway company SNCF (Bailey, 1995). The *sous vide* method was developed for restaurant use in the early 1970s by a French chef George Pralus, who was commissioned to find a way to reduce the shrinkage of *foie gras*; he developed a vacuum packaging and cooking process that not only dramatically reduced shrinkage (from 46% to only 5%) but also enhanced flavor. Today, *sous vide* products range from institutional foodservice to in-home convenience foods to restaurant meals.

Low-acid, refrigerated foods, which are precooked, free of microbial inhibitors and vacuum packaged, present some very serious challenges, because the partial cooking results in the destruction of the vegetative microflora, leaving heat-resistant spores as survivors. However, *sous vide* may be produced safely if proper controls (including HACCP) are in place.

16.10 APPLICATIONS OF MAP

MAP is being successfully used by many food processing companies around the world to extend the shelf life and retain the quality of a wide variety of foods. Table 16.5 gives examples of foods

TABLE 16.5
Examples of Gas Mixtures for Selected Food Products

Product	Temperature (°C)	O_2 (%)	CO_2 (%)	N_2 (%)
Meat products				
Fresh red meat	0–2	40–80	20	Balance
Cured meat	1–3	0	30	70
Pork	0–2	40–80	20	Balance
Offal	0–1	40	50	10
Poultry	0–2	0	20–100	Balance
Fish				
White fish	0–2	30	40	30
Oily fish	0–2	0	60	40
Salmon	0–2	20	60	20
Scampi	0–2	30	40	30
Shrimp	0–2	30	40	30
Plant products				
Apples	0–4	1–3	0–3	Balance
Broccoli	0–1	3–5	10–15	Balance
Celery	2–5	4–6	3–5	Balance
Lettuce	<5	2–3	5–6	Balance
Tomatoes	7–12	4	4	Balance
Baked products				
Bread	RT[a]		60	40
Cakes	RT		60	40
Crumpets	RT		60	40
Crepes	RT		60	40
Fruit pies	RT		60	40
Pita bread	RT		60	40
Pasta and ready meals				
Pasta	4		80	20
Lasagna	2–4		70	30
Pizza	5		50	50
Quiche	5		50	50
Sausage rolls	4		80	20

Source: From Brody, A.L., Modified atmosphere packaging, in: *Encyclopedia of Agricultural, Food, and Biological Engineering*, Heldman, D.R. (Ed.), Marcel Dekker, New York, pp. 666–670, 2003.

[a] Room temperature; staling is accelerated at refrigerated temperatures.

currently packaged in MAs, together with the gas mixtures typically used. A detailed discussion of the MAP of these various foods can be found in subsequent chapters.

Several novel technologies offer the potential of further improvements in the shelf life and safety of MAP foods. These include the use of active and intelligent packaging as discussed in Chapter 15. In particular, O_2 and C_2H_4 absorbers and CO_2 emitters, used either alone or in combination with MAs, are likely to find wider application as more cost-effective and innovative designs are commercialized.

The use of TTIs (also discussed in Chapter 15) on individual MA packs could enable the temperature to be monitored throughout the supply chain and a warning given if the food had suffered temperature abuse. Although not currently practicable due largely to cost, innovative developments enabling each individual package to have its own TTI could make this a commercial reality.

The use of hurdle technology involving MAP in combination with deliberate manipulation of a_w, pH and/or redox potential, as well as the use of preservatives, bacteriocins, ultra high pressure and edible coatings, could lead to better control of potential pathogens and thus a safer product.

In conclusion, MAP is a simple concept and is increasingly applied to many different foods, providing substantial extensions in shelf life and significant economies in production and distribution. However, MAP is not a substitute for good manufacturing practices, HACCP programs and proper temperature control during storage and distribution. Used intelligently and responsibly, MAP is likely to become the dominant form of food preservation in the twenty-first century.

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17 Packaging of Flesh Foods

17.1 INTRODUCTION

There is a continuous search for improved methods of transporting food products from producers to consumers. With the increasing urbanization of society, the problems associated with the keeping quality of fresh flesh foods have become accentuated. Large livestock slaughter and processing facilities have developed in areas where livestock production is highly concentrated; not surprisingly, such areas are well away from the centers of population density. In addition, there is a major world trade in fresh and preserved flesh foods. In all these situations, packaging has a key role to play in protecting the product from extrinsic environmental influences and giving the food the shelf life required in the particular market concerned.

17.2 RED MEAT

In the packaging of red meat, there are two factors of major importance: color and microbiology. Both of these factors will be considered in some detail before specific packaging materials and systems are discussed, because an understanding of red meat color and microbiology is an essential prerequisite to the development of successful packaging for red meat. Color is generally regarded as the first limiting factor in shelf life, but when appropriate hygiene and packaging methods are used, microbial spoilage is the principal determinant of meat product acceptability.

17.2.1 COLOR OF RED MEAT

17.2.1.1 Introduction

The importance of color as a marketing attribute of red meat is well established, especially for self-service retailing. Consumers, used to seeing bright red meat prepared for sale, associate this color with good eating quality, although there is little correlation between the two. This association of the color of red meat (both in the chilled and frozen form) with freshness has been the dominant factor underlying retail meat marketing. The loss of this bright red color, known as loss of "bloom" in the industry, is affected by many factors, although the consumer will usually relate the color loss to bacterial growth. Because of the importance of meat color, various methods of transportation, distribution and packaging have evolved that optimize the maintenance of a desirable meat color.

The color of meat as perceived by the consumer is primarily determined by such factors as the concentration and chemical form of the meat pigment myoglobin, the morphology of the muscle structure and the ability of the muscle to absorb or scatter incident light. However, it is likely that once a decision to purchase beef is made in the market, whether the beef is the red of fresh bloomed beef, the brown of discounted beef or the purple of vacuum-packaged beef, consumer eating satisfaction at home will depend only on the beef quality attributes of tenderness, juiciness and flavor (O'Sullivan and Kerry, 2009).

17.2.1.2 Myoglobin Pigments

Myoglobin is the sarcoplasmic protein that is responsible for meat color. Centrally located within this globular single-chain protein is heme iron, which plays a vital role in the visible color transformations that occur on the surface of meat products (Mancini, 2009). The heme group consists of a flat porphyrin ring with a central iron atom that has six bonding points or coordination links.

Four of these are linked to nitrogen atoms; one is attached to the globin molecule and the remaining linkage is free to bind to other substances, usually water or O_2. The color of myoglobin depends on at least three factors:

1. The oxidation state of the iron atom: it may be in the reduced ferrous form (Fe^{2+}) or the oxidized ferric form (Fe^{3+})
2. The nature of the group at the sixth bonding point of iron
3. The state of the globin: it may be native as in raw meat, or denatured as in cooked meat

The color of fresh meat depends chiefly on the relative amounts of the three pigment derivatives of myoglobin present at the surface: *deoxymyoglobin* (Mb), *oxymyoglobin* (O_2Mb) and *metmyoglobin* (MetMb). Mb is purple in color ($\lambda_{max} = 555$ nm) and predominates in the absence of O_2. O_2Mb is bright red in color ($\lambda_{max} = 542$ and 580 nm) and results when Mb is oxygenated or exposed to O_2, producing the familiar "bloom" of fresh meat. MetMb is brown in color ($\lambda_{max} = 505$ and 635 nm) and exists when the O_2 concentration is between 0.5% and 1%, or when meat is exposed to air for long periods of time. The brown MetMb cannot bind O_2 and is physiologically inactive; the sixth coordination position is occupied by water. The main forms of pigment found in fresh red meat are shown in Table 17.1.

The color reactions of myoglobin are all reversible and dynamic with respect to the three primary forms of myoglobin: Mb, O_2Mb and MetMb. It is rare when all three myoglobin pigments are in the same form; generally, two or more of the pigments will be present with the predominant pigment being most noticeable. Although MetMb is stable and cannot take up O_2, it is slowly reconverted to Mb in *post rigor* meat, primarily by enzymic reactions collectively termed *metmyoglobin reducing activity* (MRA); this is discussed further in Section 17.2.1.3.4. As meat ages, the substrate for these enzymes is gradually used up; MetMb can no longer be reduced and the meat appears brown. The situation is summarized in Figure 17.1.

In extreme conditions, the pigment may be decomposed; the heme portion becomes detached from the protein, the porphyrin ring is disrupted and, finally, the iron atom is lost from the heme structure. Green choleglobin and colorless bile pigments are formed.

During storage, the rate of MetMb accumulation on the surface of red meat is related to many intrinsic factors including pH, muscle type and the age, breed, sex and diet of the animal, as well as extrinsic factors including preslaughter conditions and the processing conditions used (e.g., electrical stimulation, hot boning and chilling mode). During retail display, physical factors such as temperature, O_2 availability, type and intensity of lighting, microbial growth and gas atmosphere surrounding the meat surface influence the shelf life of fresh red meats. A summary of the major factors affecting red meat color is presented in Table 17.2.

17.2.1.3 Role of Oxygen

17.2.1.3.1 Oxygenation and Deoxygenation

The reversible conversion of Mb to O_2Mb is described as oxygenation because O_2 becomes part of the pigment complex. This is not an oxidation reaction, however, because the iron component remains in the ferrous state (i.e., there is no loss of an electron). In the presence of O_2, Mb can exist

TABLE 17.1
Main Forms of Pigment Found in Fresh Red Meat

Pigment	State of Iron	Sixth Linkage	Color
Deoxymyoglobin (Mb)	Fe^{2+}	None	Purple
Oxymyoglobin (O_2Mb)	Fe^{2+}	O_2	Bright red
Metmyoglobin (MetMb)	Fe^{3+}	H_2O	Brown

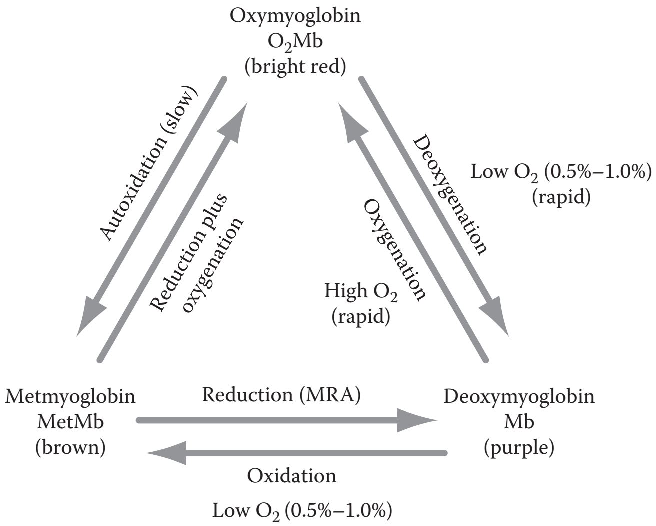


FIGURE 17.1 Interrelationships between the major fresh meat pigments. MRA, metmyoglobin reduction activity.

TABLE 17.2
Summary of Major Factors Affecting Red Meat Color

Storage temperature	
High	Favors greater O_2 scavenging by residual respiratory enzymes, plus other O_2-consuming processes such as fat oxidation
	Enhances dissociation of O_2 from O_2Mb, thereby increasing the tendency for autoxidation of the Mb produced
Low	Promotes increased penetration of O_2 into the surface
	Enhances O_2 solubility in tissue fluids
	Both aforementioned effects increase depth of O_2Mb at the surface
Oxygen partial pressure	
High	Favors formation of O_2Mb
Low	Favors formation of MetMb
Meat pH	
High	Accelerates respiratory activity of meat tissue resulting in thin layer of O_2Mb with underlying Mb more apparent
	Muscle fibers swell thereby reducing O_2 diffusion and therefore formation of O_2Mb
Low	Causes denaturation of the globin moiety and subsequent dissociation of O_2 from the heme
	Promotes oxidation of Mb

either in the O_2Mb or MetMb state depending on the amount of O_2 present. Mb is the dominant form at 0% O_2, MetMb dominates at approximately 0.5%–1% (depending on temperature) and O_2Mb is the dominating form over approximately 4% O_2 (Jacobsen and Bertelsen, 2003). Owing to a lack of O_2, the color of the interior of fresh red meat is purple because of the presence of Mb. The outermost layer exposed to air is red because of the presence of O_2Mb. A thin brown layer of MetMb can be observed between the red and purple regions resulting from a low concentration of O_2. This layer thickens within 1 or 2 days and becomes apparent first by darkening of the translucent surface tissue and later by breaking through to the surface. At lower O_2 partial pressures, the MetMb layer will be nearer the surface until, at the critical partial pressure, it is at the surface. The rate of these changes is strongly influenced by temperature.

Oxygenation of purple Mb to red O_2Mb is rapid, with the surface of beef in air appearing red within half an hour at 5°C. In contrast, oxidation to MetMb is slow; it appears first as a thin brown layer at the limit of O_2 penetration. The red O_2Mb is stable as long as the heme remains oxygenated, although the O_2 is continually associating and dissociating from the heme.

The dissociation of O_2 from the heme (known as *deoxygenation*) is caused by conditions such as low pH (less than pH 5.4), high temperature, UV light, salts and especially low O_2 tensions. The deoxygenation of red O_2Mb results in Mb formation (which is very unstable), which then becomes oxidized to brown MetMb. Surface desiccation increases the salt concentration and promotes the formation of MetMb.

17.2.1.3.2 Oxidation

Oxygen has sufficient oxidation potential to convert O_2Mb and Mb to MetMb. This conversion will occur as NADH and substrates from the glycolytic pathway are depleted. The conditions that cause deoxygenation of O_2Mb to Mb are also responsible for the conversion of unstable reduced Mb to brown MetMb.

The oxidation reaction of O_2Mb to form MetMb, and Mb to form MetMb, involves the loss of an electron from the iron of the heme ($Fe^{2+} \rightarrow Fe^{3+}$) and is termed *autoxidation*; it is a comparatively slow reaction (Young and West, 2001). The maximum rate of MetMb formation has been reported at O_2 partial pressures of 0.75 ± 0.3 cm Hg at 7°C and 0.6 ± 0.3 cm Hg at 0°C for beef (one atmosphere of pure O_2 is 76 cm Hg). Any value is very dependent on temperature, although independent of pH. If meat is held under high O_2 partial pressures (i.e., above 3 cm Hg), then the rate is independent of the O_2 partial pressure and autoxidation of Mb is minimized (Renerre, 2000). These results have led to the development of systems allowing transport of meat at high (>60%) O_2 partial pressures.

17.2.1.3.3 Reduction

Biochemical reduction is a process in which a chemical compound gains an electron; it works in opposition to oxidation. *MetMb reduction* refers to the conversion of Fe^{3+} heme iron to Fe^{2+} heme iron. When this occurs, the concentration of MetMb decreases and that of Mb or O_2Mb increases (Bekhit and Faustman, 2005). MetMb is slowly reconverted to Mb in *post rigor* meat, primarily by enzymic reactions collectively termed MRA. The formation of MetMb in meat can be minimized by packaging in vacuum or high O_2 atmospheres. Some muscles will remain bright red for longer periods of time than other muscles, because any MetMb formed is reduced back to Mb and immediately oxygenated back to red O_2Mb; such muscles are said to have a higher MRA. Loss of reducing activity in meat during storage is a result of a combination of factors including a fall in tissue pH, depletion of required substrates and cofactors (in particular NADH) and, ultimately, complete loss of structural integrity and functional properties of the mitochondria (Renerre, 2000). Grinding (mincing) of meat greatly accelerates enzyme inactivation and depletion of reduced coenzyme NADH (required for MRA) and results in loss of MRA (Gill and Gill, 2010).

In an extensive review, Bekhit and Faustman (2005) characterized the current understanding of MetMb reduction and suggested that the term MetMb reductase is not appropriate to reflect MRA in meat. They discussed the need for a standardized approach for measuring MetMb reduction in order for future research to provide a greater understanding of this important reaction.

17.2.1.3.4 Bacterial Discoloration

Bacteria cause discoloration of meat in their logarithmic growth phase. This is attributed to the high O_2 demand of aerobic bacteria, which reduces the O_2 tension at the meat surface and causes the formation of brown MetMb.

Some bacteria also produce by-products that oxidize the iron molecule. The most common are hydrogen sulfide (H_2S) and hydrogen peroxide (H_2O_2) which react with unstable Mb to produce the green pigments sulfmyoglobin and choleglobin, respectively. H_2S production causes green discoloration on vacuum packaged meat, it is generally found only on meat having a high pH ($pH > 6$). On opening vacuum packaged meat that has green discolorations on it, the green sulfmyoglobin becomes oxygenated to oxysulfmyoglobin, which is red in appearance. However, the color change does not cause any diminution in the H_2S off-odor which resembles rotten eggs. H_2O_2 can either cause greening due to oxidation of heme pigments to form choleglobin, or degradation beyond porphyrins to yellow or colorless bile pigments.

17.2.1.4 Color Intensity

The color intensity of meat is determined by antemortem factors such as species, stress, sex and age of the animal, the postmortem pH rate of decline and the ultimate pH of the meat. During postmortem glycolysis, the pH of normal tissue falls from an in vivo value of 7.2 to an ultimate value of 5.4–5.6. As well as influencing the color, the rate of fall of pH and the ultimate pH value also influence the water holding capacity (WHC) and texture of the meat. Differences in color intensity between species are primarily caused by differing concentrations of Mb. Thus, beef, which has the highest concentration, is the darkest of the meat species. Lamb is intermediate in color and Mb concentration, and pork has the lowest concentration of Mb and, as such, is the lightest in color.

The color intensity of meat is also influenced by pH and morphology of the muscle structure. The pH of a muscle is largely influenced by the conditions that exist immediately prior to or just after slaughter. Short term, violent excitement immediately before slaughter, or the slow cooling of carcasses after slaughter, can result in meat having a low ultimate pH. This is caused by a buildup of lactic acid, which is formed as a metabolic end product in the anaerobic breakdown of glucose and glycogen (Seideman et al., 1984). This condition is known as PSE because it produces *p*ale, *s*oft and *e*xudative meat as a result of an abnormally rapid fall in pH immediately after slaughter, when the combined effects of low pH and high temperature in the muscle lead to denaturation of sarcoplasmic and myofibrillar proteins. Because muscle glycolysis is relatively more rapid in hogs than bovines, PSE is rarely observed in beef animals.

PSE meat causes problems in packaging; the color is abnormally pale due to denatured protein, with the physical structure increasing light scattering and making the meat more opaque. Autoxidation increases, causing color fading. In addition, because of its low WHC resulting from protein denaturation, PSE meat produces excessive drip.

Biochemical conditions directly opposite to those producing PSE meat give rise to another type of abnormal meat from all meat animals but more especially beef cattle and hogs. This condition has been described as even more troublesome than PSE from a packaging point of view. The problem meat, known as dark-cutting or *d*ark, *f*irm and *d*ry (DFD), is translucent and sticky to touch, and unacceptable for retail packaging because of its dark purple color. This meat has a high pH that results from a low residual glycogen level remaining in the muscle at slaughter, which is attributable to excessive stress (such as an extended transit haul) or exercise prior to slaughter. Such treatment causes depletion of the muscle glycogen before death. The low residual glycogen means that insufficient lactic acid is formed by glycolysis during the rigor process to lower the pH. The elevated ultimate pH promotes mitochondrial respiration and competition for O_2 in meat, and results in a low O_2 partial pressure that helps to maintain pigments in a deoxygenated state. In this situation, meat fails to bloom (oxygenate) and does not form the characteristic bright red color associated with fresh meat (Mancini, 2009).

The muscle fibers of DRD meat are swollen and tightly packed together forming a barrier to the diffusion of O_2 and the absorption of light. In addition, the high pH of the meat accelerates respiratory activity of the meat tissue, resulting in a very thin layer of red O_2Mb, with the underlying purple Mb more visually apparent. Moreover, the high pH encourages the growth of putrefactive microorganisms, thereby significantly reducing the keeping quality of this meat. For example, vacuum packaged beef of normal pH can be stored at chill temperatures for periods in excess of 10 weeks, whereas DRD beef held under the same conditions will generally spoil within about

6 weeks. However, it has been shown that both normal and high pH cuts of beef packaged under CO_2 can remain unspoiled at 15 weeks (Gill and Penny, 1986).

17.2.1.5 Role of Carbon Dioxide and Carbon Monoxide

It was reported in the 1970s that meat stored in high concentrations of CO_2 often developed a grayish tinge, supposedly because of the lowering of the pH and subsequent precipitation of some sarcoplasmic proteins. It was therefore recommended that CO_2 not be used in concentrations exceeding 20%. The claim was also made that no MetMb formation occurred in atmospheres containing high concentrations of CO_2, provided that the O_2 partial pressure exceeded 5%. A later report indicating that 50%–80% CO_2 was often found in residual air spaces in vacuum packages with no associated detrimental effect on meat color led to a reevaluation of the effect of CO_2 on red meat color.

The realization that discoloration in high CO_2 atmospheres must be due to O_2 led to the use of 100% CO_2 atmospheres on the grounds that meat color would not be adversely affected if O_2 was rigorously excluded from the packages. In the case of raw red meats, the color was actually improved by enzymic reduction of pigment that oxidized before the meat was packaged. However, the stability of raw meat color on exposure to air decreased as storage life increased, with the color stability at display reaching a minimum value after 12 weeks storage. After that time, acceptable meat color at display was maintained for about 40% of the time that fresh meat retained acceptable color. This was claimed to be an inevitable consequence of prolonged chill temperature storage and not an effect of the 100% CO_2 atmosphere (Gill, 1990). A later review of 36 studies on the effect of CO_2 on red meat color confirmed the importance of excluding O_2 (Jacobsen and Bertelsen, 2002).

Carbon monoxide (CO) has the potential to retard MetMb formation and fat oxidation. CO combines with Mb to form the bright cherry red pigment *carboxymyoglobin* (COMb), which is spectrally very similar to O_2Mb. Because COMb is much more stable toward oxidation than O_2Mb by virtue of the stronger association of CO to the iron-porphyrin site on the myoglobin molecule, the addition of CO at low levels can negate the detrimental color changes associated with the high levels of CO_2 required to maintain wholesomeness over prolonged transit times (Sorheim et al., 1997).

Retail meat can be packaged in gas mixtures containing 60%–70% CO_2, 30%–40% N_2 and <0.5% CO. This gas mixture provides a unique combination of a long microbiological shelf life and a stable, cherry red color of the meat. The shelf life of meat packaged in the CO mixture is longer than that of meat packaged in the commonly used high O_2 atmospheres of approximately 70% O_2 and 30% CO_2 (Krause et al., 2003). A study using 0.4% CO with beef steaks and ground beef found that the COMb formed did not mask microbial spoilage (Hunt et al., 2004). Venturini et al. (2010) reported that MAP with 0.4% CO produced no additional color effect over 0.2% CO; the best atmosphere for maintenance of color stability and microbial quality up to 21 days at 2°C was 69.8% N_2:30% CO_2:0.2% CO plus an O_2 scavenger. Raines and Hunt (2010) found that increased CO concentration in combination with reduced headspace volume had a greater influence on COMb development than molar availability of CO alone. Reducing package headspace reduces the size of the tray, the resources required to make it, the amount of refuse generated, the packaged tray size and the amount of headspace gas per package, making the CO-MAP system more economically feasible and advantageous. A CO headspace of 0.4 L containing 0.8% CO resulted in less CO in the ambient atmosphere than packages with conventional headspaces containing 0.4% CO. Smaller headspaces with higher concentrations of CO (i.e., 0.8% vs. 0.4% CO) optimized the package size while maintaining or improving the appearance of beef packaged in CO-MAP, without compromising consumer safety.

Despite these advantages, CO has not been approved by regulatory agencies for retail use with meats, largely because of safety considerations. In Norway, the packaging of red meat in retail packs with 0.4% CO was permitted from 1985 until 2004; it is reportedly permitted in some Asian countries. In early 2002, the U.S. FDA cleared a system for pretreating meat with 0.4% CO in a master pack system, where the CO was considered as a processing aid and thus did not require labeling. However, the use of sealed retail packages containing CO is precluded in the United States. Similar use has also been approved in New Zealand and Australia where CO is considered a processing aid (Singh et al., 2011).

17.2.1.6 Lighting

Lighting is an important factor when presenting meat and meat products for retail sale. A high percentage of red in the light gives a particularly intense red impression, and products that are already beginning to turn a grayish-red color in daylight appear saturated with red when exposed to reddish lighting.

Incident light is a contributory factor in the discoloration of both fresh and frozen meat as, for example, in a retail supermarket display case. The extent of the effect depends on such factors as the wavelength and intensity of the light, temperature, O_2 partial pressure, meat pH and storage time. Provided that UV wavelengths are avoided, the effect of light is small under normal refrigerated conditions.

17.2.1.7 Effect of Temperature

The optimum temperature for storing chilled meats is the minimum that can be maintained indefinitely without freezing the muscle tissue; in practice, this temperature is in the range −1.5°C ± 0.5°C (Gill, 2003). Discoloration (rather than microbial spoilage) is likely to limit the shelf life of red meats when they are stored in aerobic atmospheres, with the rate of discoloration increasing linearly with temperature. For meats stored in MAs rich in O_2, the effect of temperature on the rate of discoloration does not appear to be well identified in the literature, but it seems likely that it follows a similar pattern as for meat stored in air (Gill, 2003).

When meat is stored anaerobically, the color stability of muscle tissue increases at first (probably related to the relatively rapid loss of respiratory activity) and then declines (probably reflecting the decay of MRA). The rate at which color stability degrades is twice as fast at 5°C and four times as fast at 10°C as at 0°C (Gill, 2003).

17.2.1.8 Effect of Freezing

The color of frozen meat initially depends on the rate of freezing and the resultant size of ice crystals in the surface layer. Slow freezing produces large ice crystals with poor light scattering properties, giving the meat a dark, translucent appearance. Fast freezing, on the other hand, results in the formation of small ice crystals, which scatter light and make the meat surface pale and opaque.

In frozen red meat, the principal deterioration during storage is photooxidation of the pigments. Whereas under direct illumination, chilled meat oxidation begins in the subsurface layer and progresses toward the surface, frozen meat oxidizes from the surface inward. Loss of redness is detrimental to the marketing of frozen as well as chilled meat.

Considerable improvements (in the order of 5–10 times) in the color shelf life of prepackaged frozen beef are possible if the light intensity in a normal retail cabinet is reduced by 90%–95%.

17.2.2 MICROBIOLOGY OF RED MEAT

17.2.2.1 Introduction

Muscle tissue from healthy animals is free of bacterial or viral pathogens. The composition of the flora that is present on meat at the onset of spoilage is affected by the quality of the tissue on which the bacteria are growing, the composition of the atmosphere around the product and the numbers and composition of the microflora on the meat at the time of packaging (Gill, 2004a). The major bacterial pathogens associated with fresh meats are *Aeromonas hydrophila*, *Campylobacter* spp., *Clostridium botulinum*, verotoxigenic *E. coli*, *Salmonella*, *Shigella* spp., *Listeria monocytogenes* and *Yersinia enterocolitica*. These organisms are facultative or obligate anaerobes, or are microaerophilic (Gill and Gill, 2010).

Spoilage flora is generally dominated by those species that can grow most rapidly under the conditions at which the meat is held. At chill temperatures, species of *Pseudomonas* and *Lactobacillus* can outgrow competing species under aerobic and anaerobic conditions, respectively. With the exceptions of *A. hydrophila*, *L. monocytogenes* and *Y. enterocolitica*, the major pathogens associated with meat cannot grow at temperatures below 3°C.

On meat stored aerobically (i.e., in air or in O_2 permeable packaging materials) at chill temperatures (−1°C to +5°C), the flora is usually dominated by species of *Pseudomonas*. These organisms are strictly aerobic and can grow at their maximum rate with O_2 concentrations in the atmosphere of 1% or less. High CO_2 and low O_2 tensions inhibit but do not prevent the growth of pseudomonads. Microbial degradation of refrigerated beef in an aerobic environment produces a gradual elevation in pH, leading to the release of NH_3 following microbial attack on the amino acids. The critical factor is the availability of glucose to the bacteria (Gill, 2004a). Most spoilage species (including the dominant pseudomonads) utilize this substrate preferentially. When bacteria can no longer obtain sufficient glucose, they begin to degrade amino acids, giving rise to NH_3 as well as other odors and highly offensive end products.

Any O_2 remaining in vacuum packages immediately after sealing is converted to CO_2 by meat tissue respiration and bacterial activity. In an anaerobic environment such as exists in vacuum- and some MA-packaged meats, the absence of O_2 inhibits the growth of the putrefying aerobes, and anaerobic and facultative anaerobic strains such as *Lactobacillus*, *Brochothrix thermosphacta* and *Enterobacteriaceae* constitute the dominant microbial flora. However, in many cases, lactic acid bacteria (which include organisms of the genera *Lactobacillus, Carnobacterium* and *Leuconostoc*) become dominant in refrigerated vacuum-packaged meat, and these bacteria do not produce grossly offensive by-products (Gill, 2004a). Inclusion of small amounts of CO in anaerobic atmospheres does not affect development of the spoilage flora (Sorheim et al., 1999).

At least five factors are implicated in slowing or preventing growth of spoilage organisms in vacuum packages: (1) the reduced O_2 concentration, (2) the elevated CO_2 concentration, (3) the normally low (5.5–5.8) pH of meat, (4) the low storage temperature and (5) antimicrobial activities of *Lactobacilli* species.

Raw meat cannot normally be stored for extended periods at chill temperatures because of the proliferation of psychrotrophic food spoilage microorganisms and texture degradation caused by the presence of endogenous proteolytic enzymes.

17.2.2.2 Effect of Temperature

Temperature is of the utmost importance in controlling the types of microorganisms that develop on meats, because these products are normally held at chill temperatures. Essentially, all studies on the spoilage of red meats, poultry and seafood carried out over the past 40 years have dealt with products stored at chill temperatures. The temperature not only determines whether microbial numbers increase or decrease, but also influences the nature of the flora which becomes dominant. Low temperatures select for cold-tolerant organisms (mainly psychrotrophs), and these become the most important component of the spoilage flora. The storage life of meat with or without packaging at 0°C, 2°C and 5°C is about 70%, 50% and 30%, respectively, of the storage life that would be obtained if the product were stored at −1.5°C. Storage at chill temperatures can delay, but not prevent, the ultimate onset of microbial spoilage (Gill, 2003).

It must be emphasized that no matter how good the packaging is, the maximum shelf life of packaged meat will not be achieved unless very close attention is paid to control of the storage temperature. While this can be relatively easily achieved in laboratory trials, the temperature control of commercial quantities of packaged meats is often variable, with the result that product shelf lives are also variable. When the expected shelf life is not achieved, attention should be focused on the temperatures achieved during storage, distribution and retailing, rather than blaming the packaging or those who conducted the laboratory trial.

17.2.2.3 Effect of Gaseous Atmosphere

Any form of packaging changes the environment to which microorganisms are exposed, with the main change being a modification of the gaseous atmosphere. It is the composition of this atmosphere that largely determines the extent and type of spoilage that develops during storage.

Although a number of different gas compositions have been tested and claimed to have preserving properties on flesh foods, pure CO_2 or combinations of CO_2 with O_2 or N_2 are by far the most important. CO_2 is highly soluble in both muscle and fat tissues, the solubility in muscle tissue decreasing with decreasing pH and increasing temperature, and the solubility in fat increasing with increasing temperature within the chill temperature range (Gill and Gill, 2010).

The solubility of CO_2 in muscle tissue of pH 5.5 at 0°C is approximately ~960 mL kg^{-1} of tissue at STP. As the temperature increases, the solubility decreases by 19 mL kg^{-1} for each °C rise. As tissue pH increases, the solubility decreases by 360 mL kg^{-1} for each pH unit. With raw meat, CO_2 at ≈1.5 L kg^{-1} meat is required to saturate the product without the packaging collapsing tightly around the contents (Gill, 1981). The large gas volume initially required can result in pouches at first overfilling the cartons in which they are contained. However, the gas dissolves sufficiently rapidly for the pack volume to fall to its final value during overnight storage (Gill, 1990). Jakobsen and Bertelsen (2003) reported that the CO_2 solubility in meat samples varied with fat content, fatty acid composition as well as temperature between 0.55 and 0.85 L CO_2 kg^{-1} meat when varying these factors.

Models for CO_2 solubility as a function of packaging and storage parameters such as the ratio of product weight to headspace volume, temperature and initial CO_2 levels have been developed (Zhao et al., 1994). The amount of absorbed CO_2 ranges from 0 to 1.8 L CO_2 kg^{-1} of meat depending on the applied CO_2 partial pressure, temperature, pH of the meat and so on. Equilibrium with respect to gas absorption is obtained during the first 1–2 days, although microbial and meat metabolism can cause slight changes in gas composition by consuming O_2 and producing CO_2 (Jakobsen and Bertelsen, 2003).

A large number of papers has been published on the effects of CO_2 on flesh foods and on the inhibitory properties of CO_2 on specific microorganisms. CO_2 is effective when the spoilage microflora is dominated by Gram-negative, aerobic, psychrotrophic bacteria, thus making the use of CO_2 with fresh meats, poultry and seafood efficacious.

CO_2 selectively inhibits the growth of Gram-negative bacteria such as pseudomonads and related psychrotrophs, but has less effect on lactic acid bacteria. The growth rates of pseudomonads decrease with increasing CO_2 concentrations up to about 20%, with concentrations beyond that level doing little to reduce the growth rate provided the atmosphere is aerobic. The maximum reduction in the rates of growth of pseudomonads is about 50%, and this reduction is sufficient to allow lactic acid bacteria to outgrow pseudomonads and dominate the spoilage flora (Gill, 2004b).

There are four major effects of CO_2 on food spoilage:

1. The exclusion of O_2 by replacement with CO_2 may contribute slightly to the overall effect by slowing the growth rate of aerobic bacteria.
2. The ease with which CO_2 penetrates the cell may facilitate its chemical effects on the internal metabolic processes.
3. CO_2 is able to produce a rapid acidification of the internal pH of the cell with possible ramifications relating to metabolic activities.
4. CO_2 appears to exert an effect on certain enzyme systems.

With regard to the optimal concentration of CO_2, there is considerable ambiguity among the reported values of various researchers, as well as variations in methodologies. It is important to appreciate the influence of temperature on the growth-inhibitory effect of CO_2 on microorganisms. Generally, the relative inhibitory effect decreases as the temperature increases. However, because the solubility of CO_2 decreases as the temperature increases, it is necessary to take this into account before interpreting any results. Many results were obtained in liquid media, but the temperature effect may not show the same characteristics in muscle foods where the microbial activity is located at the surface. In this situation, one is dealing with a solid–gas interface rather than a population dispersed in a liquid medium.

The high partial pressure of oxygen-free CO_2 extends the lag phase and the generation time, and slows the growth rate of all spoilage organisms, with the types that cause spoilage being either totally inhibited or subjected to a long lag time of at least 12 weeks at −1°C. The only potent spoilage organism not fully controlled is *Brochothrix thermosphacta*; however, its minimum growth temperature is raised in an oxygen-free CO_2 atmosphere from below the freezing point of meat to above 0°C. As a consequence, even heavily contaminated, high pH meats stored at −1°C will remain unspoiled for at least 3 months (Gill, 2004b).

Unlike CO_2, the solubility of O_2 in muscle and fat tissues is low. However, O_2 is converted to CO_2 by the respiratory activities of both muscle tissue and bacteria. When packaging fresh meat products, an elevated O_2 partial pressure needs to be maintained to ensure that the meat pigment is in the O_2Mb state. Using response surface methodology, it has been shown that the O_2 level has no adverse effect on the color shelf life in the interval between ~40% and 80%. Despite this finding, an O_2 level of 70%–80% is commonly used commercially, even though a level of 40% is sufficient to ensure stability of the bright red color (Jakobsen and Bertelsen, 2003).

The solubility of N_2 in tissues is low and the gas is metabolically inert. Therefore, the only function of N_2 in a package atmosphere is to buffer against changes in the volume of the atmosphere that could lead to package collapse and crushing of the contents (Gill and Gill, 2010).

CO is a potent inhibitor of cytochrome oxidase and hence aerobic respiration of many organisms. However, the effect of low levels (<1%) of CO on the microbiological condition of meat is negligible (Sørheim et al., 1999). This is partly attributable to the fact that CO is removed quickly from the package atmosphere as it reacts rapidly and essentially irreversibly with Mb to form the cherry-red COMb.

17.2.3 Lipid Oxidation

Lipid oxidation is a leading cause of quality deterioration in muscle foods, resulting in rancidity, off-flavors, off-odors as well as color and texture deterioration (Jakobsen and Bertelsen, 2003). It is believed to be initiated in the highly unsaturated phospholipid fraction in subcellular membranes. The major products of lipid oxidation are the hydroperoxides, which break down into secondary products such as aldehydes, alcohols, hydrocarbons and ketones. It is these secondary products which contribute to the off-flavors generated during storage. A distinctive off-flavor that develops rapidly in meat that has been precooked, chill-stored and reheated is termed “warmed-over” flavor and autoxidation of membrane phospholipids is largely accepted as the cause (Jakobsen and Bertelsen, 2003).

Mechanisms of myoglobin-induced oxidation/peroxidation of polyunsaturated fatty acids are still a matter of dispute (Baron and Anderson, 2002). At pH values of relevance for meat and meat products, both MetMb and O_2Mb have been shown to be major initiators of lipid oxidation and peroxidation. An in-depth knowledge of the relationship between lipid and protein oxidation might reveal important information regarding the oxidative stability of meat and meat products. More recently, Faustman et al. (2010) reviewed mechanistic bases of myoglobin and lipid oxidation interactions to explain quality deterioration in meat, and also for developing strategies such as the inclusion of antioxidants to maintain optimal sensory qualities.

Lipid oxidation is not usually a limiting factor in conventional retail trays of meat over-wrapped with a polyolefin film, as such films are permeable to gases and allow odor volatiles to escape. However, with MA packs, the volatile products are retained within the package and can be clearly detected by consumers when opened (O’Sullivan and Kerry, 2010). Storage of meat in high O_2 atmospheres leads to a limited shelf life due to lipid oxidation (Jakobsen and Bertelsen, 2003).

17.2.4 Vacuum Packaging of Fresh Meat

In the United States, prior to 1967, beef carcass shipments were traditionally made to retail outlets where carcasses were fabricated into retail items by butchers in individual stores. The “boxed beef” concept was developed by French scientists as early as 1932 to prolong the shelf life of frozen meat used as military provisions (O'Sullivan and Kerry, 2010). It was introduced in the United States in 1967, dramatically changing beef processing, distribution and retail fabrication, without affecting retail presentation to the consumer. The basis for the boxed beef concept was vacuum packaging into plastic bags with low gas permeabilities.

The introduction of vacuum packaging for the distribution and storage of chilled beef was one of the greatest innovations in meat handling. Beef carcasses are broken down into primal and subprimal cuts, separated into boneless and bone-in cuts and then vacuum packaged. Because only about two thirds of a beef carcass is usable meat, there are clear advantages in reduced refrigerated space for transportation and storage and less packaging material when boneless beef rather than bone-in or carcasses are stored and distributed. Another advantage is that the tenderness of the beef can be improved by aging without the evaporative weight loss incurred when carcasses are hung in the conventional manner.

It is now common practice to butcher beef carcasses at the slaughter house into primal joints, which are then vacuum packaged. In these circumstances, the atmosphere around the meat becomes depleted in O_2 (often <1% v/v) and enriched in CO_2 (>20% v/v), resulting in microbial changes quite different from those observed during aerobic storage. Vacuum packaged boxed beef is then distributed to retail outlets where these primals and subprimals are fabricated into consumer units, overwrapped in O_2-permeable film on PS foam or PVC trays and displayed for sale (Tewari et al., 1999). Although consumers prefer raw meats of bright red color, vacuum packaged beef and pork primal cuts with dull, purple colors imparted by Mb are now also offered for retail sale in some countries. Most U.S. beef carcasses are fabricated and converted to vacuum packaged, primal and subprimal cuts within 64 h of entering the chill cooler, and normally appear in retail markets 14–28 days after fabrication (Smith et al., 2000).

Because the a_w of chilled meat is very high, unpackaged meat will lose weight by evaporation and its appearance will deteriorate. Further weight loss will occur when meat is cut, because the exposed surfaces exude liquid, which detracts from the appearance of packaged meat. This can be overcome by including an absorbent pad in the base of the package. Although efficient chilling can reduce the quantity of exudate, a certain amount will always be present when meat cuts are held for retailing. This unattractive, bloody exudate found in vacuum packaged beef is referred to as "purge," "weep" and "drip"; 1%–2% purge is considered acceptable, while 4% is considered excessive. Values of 2%–4% purge can have substantial economic implications if not controlled.

Vacuum packaging achieves its preservative effect by maintaining the product in an O_2-deficient environment (nominally <500 ppm). Any residual O_2 is rapidly consumed by meat and muscle pigments, and CO_2 is produced as the end product of tissue and microbial respiration. In anoxic conditions, potent spoilage bacteria are severely or totally inhibited on low pH (<5.8) meat. However, their growth on high pH muscle tissue, or extensive fat cover of inevitably neutral pH, will result in relatively rapid spoilage in a vacuum pack. Vacuum packaging can therefore extend the shelf life of primal cuts composed largely of low (normal) pH muscle tissue such as beef and venison by about fivefold over that achieved in air. Typical shelf lives of normal pH meat are 12–14 weeks at 0°C. For other meats and small cuts, only a twofold extension of shelf life can be safely anticipated (Gill, 1990).

17.2.4.1 Vacuum Packaging Systems

Vacuum packaging involves enclosing meat in flexible plastic containers (usually bags) to prevent moisture loss and exclude O_2 from the meat's surface. Packing under a vacuum reduces the volume of air sealed in with the meat. The plastic materials used for vacuum packaging must have low moisture and gas permeabilities and be strong enough to hold the meat. In packaging fresh meat primals, many cuts contain bones which are often sharp and abrasive and readily puncture the flexible plastic materials used in vacuum packaging. To overcome bone puncture, a material consisting of a wax-impregnated and coated cotton scrim is sometimes employed.

Reported O_2 permeabilities of packaging films are usually measured at ambient temperatures and moderate humidities (typically 23°C and 50% RH), but both temperature and humidity affect the rates at which gases are transmitted through films. Data on the O_2 permeabilities of packaging films at chill temperatures are sparse, and those that do exist often do not include a complete specification of the film under test, or the test conditions. This is further complicated by the variety of test methods and units used. The O_2 permeabilities at subzero temperatures of two plastic films used for the vacuum packaging of meat have been reported (Lambden et al., 1985). One film was a PA-LDPE laminate, while the other was an EVA copolymer-PVdC copolymer laminate. Their OTRs at −1°C were 0.42 and 0.13 mL m^{-2} day^{-1}, respectively, approximately one-fiftieth of the values obtained at 23°C and 90% RH.

Once meat has been vacuum packaged in an O_2 barrier material with an OTR (at 23°C and 75% RH) less than 10 mL m^{-2} day^{-1} and adequately sealed to prevent air reentry, the shelf life of the meat is very much the same regardless of the packaging material. Therefore, the significant differences between high O_2 barrier packaging materials and systems are not so much in the structure as they are in the physical properties, the production speeds of the system and the abuse resistance of the package itself. The relationship between O_2 permeability and storage life of vacuum packaged beef is shown in Table 17.3 and clearly indicates the advantages in terms of shelf life of using a high O_2 barrier package.

The O_2 in the small volume of residual air inside a vacuum package is quickly consumed by meat respiration so that, within 2 days, the O_2 partial pressure at the surface of the meat drops below 1 cm Hg. At these very low partial pressures, the penetration limit of O_2 is very near the surface, and the thin brown layer of MetMb which develops cannot conceal the underlying Mb; therefore, the visible color of vacuum packaged beef is purple (Taylor, 1985).

The efficacy of vacuum packaging depends on close contact between a film of low gas permeability and all product surfaces. If there are vacuities within the pack, these will develop an O_2-containing atmosphere as gases permeate into the package during storage. Bacterial growth will accelerate and product color will deteriorate, because of oxidation of Mb at meat surfaces exposed to such an atmosphere. In addition, when the meat surface is large relative to the meat mass, an extensive film surface is presented for O_2 permeation and color deterioration can also occur. Consequently, vacuum packaging is relatively ineffective for preserving products such as carcasses whose shapes preclude close application of the packaging film to all surfaces. Furthermore, because the anoxic conditions within the package result in the formation of purple Mb, vacuum packaging for retail display packages of red meat has not met with wide success because of negative perceptions by consumers of the color purple.

Four basic methods are available for vacuum packaging meats, which are now discussed in turn.

TABLE 17.3
Relationship between OTR of Vacuum Packs and the Storage Life of Normal pH Beef at 0°C

Film OTR (mL m^{-2} day^{-1} at 25°C)	Storage Life (Days)
0	105
40	105
61	77–105
112	42–63
172	24–42
193	14–28

Source: Adapted from Newton, K.G. and Rigg, W.J., *J. Appl. Bacteriol.*, 47, 433, 1979.

17.2.4.1.1 *Shrink Bag Method*

The shrink bag method involves placing the meat into a heat shrinkable barrier bag (typically a triple-layer coextruded film constructed from EVA copolymer-PVdC copolymer-EVA copolymer, but sometimes PA is used as the barrier layer with an ionomer as the inner or outer layer). The bag is then evacuated prior to sealing. In the past, this was achieved by applying a metal clip around the twisted neck of the bag, but today, heated jaws are used. The bag is then heat shrunk by placing in water at 90°C. After shrinking, the bag conforms closely to the meat and produces a tight vacuum pack. Very high vacuum levels are achieved on rotary single-chamber machines, which also heat seal shrink bags, and owing to their improved productivity and versatility, these machines have become the industry standard. Large primal cuts up to 205 mm high and 460 mm wide can be vacuum packaged using this type of equipment.

17.2.4.1.2 *Nonshrink Bag Method*

In this technique, meat is placed into a preformed plastic bag, which is then put in an enclosed chamber and evacuated. When a predetermined low pressure has been reached, heated jaws close and weld the mouth of the bag. Typical bag constructions consist of laminates or coextrusions, which include PET as the outside layer to provide strength, PA as the middle layer to provide a good O_2 barrier and inner layers of LDPE, ionomer or EVA copolymer, which are good moisture barriers and can be easily heat sealed. A typical structure would be ionomer-PA-EVA copolymer.

Because the bags used in this system are not heat shrinkable, purge tends to accumulate in corners during storage. Secondary sealing (also referred to as *self-welding*) has been introduced to overcome this problem, and involves passing the vacuum packs through a heating tunnel. Because of the ease with which these films are heat sealed, the excess area of film around the meat is sealed. If performed perfectly, then the packaging material size can be reduced or sealed to a point that approximates the surface area of the meat inside. This prevents purge from spreading into the film wrinkles, folds and corners as well as providing a wider heat seal, which reportedly reduces the incidence of leaking bags.

17.2.4.1.3 *Thermoforming Method*

In this method, deep trays are thermoformed in-line from a base web of plastic. Meat is placed in the trays and an upper web of plastic is heat sealed under vacuum to form a lid. Generally, the materials used for thermoforming are laminates of PA, PET or PVC, sometimes with a PVdC copolymer coating and heat sealing layers such as LDPE, EVA copolymer or ionomer.

17.2.4.1.4 *Vacuum Skin Packaging*

Vacuum skin packaging (VSP) involves production of a skin package in which the product is the forming mold. It was first introduced using an ionomer film, which softens on heating to such an extent that it can be draped over sharp objects without puncturing. In this technique, meat portions are skin packed in a barrier film material, the top web of which is softened by heating before applying a vacuum and sealing. During this operation, the soft film molds itself to the shape of the meat to give a skintight package, the meat thus being held under anaerobic conditions. It forms closely around the meat and seals to the base film. Although this type of vacuum pack is an excellent method of presentation, the meat remains in an unoxygenated state, which is not accepted by most consumers, even although it will still oxygenate to the customary red color when exposed to air.

In a comparison with MAP meat (Taylor et al., 1990), it was found that VSP meat remained microbiologically acceptable for up to at least 2 weeks after packing, during which time the color, although not red, was unchanged. However, the meat retained its ability to develop a bright red color when exposed to air for at least 2 weeks during storage at 1°C. As is typical for vacuum packaged meat, lactic acid bacteria predominated on VSP samples on which spoilage bacteria grew slowly, if at all, resulting in a long, odor-free shelf life. Off-odors developed much more rapidly in MAP packs than in VSP. In choosing between MAP and VSP, it was concluded that the retailer must balance the attractive red color achieved over a relatively short period by MAP against the longer-term stability (albeit with an unaccustomed purple meat color) afforded by VSP. Because long term stability can be achieved only at the expense of color, the authors were unable to see a ready compromise between these two divergent packaging systems. A red color can be maintained by meat in vacuum packs if the meat is exposed to an atmosphere containing CO to allow extensive formation of COMb before the meat is packaged (Aspé et al., 2008).

17.2.4.2 Shelf Life of Vacuum Packaged Red Meats

In any discussion of the shelf life of packaged meats, it must be borne in mind that comparisons of published data are difficult. Moreover, making generalizations is foolhardy because there are a large number of variables which interact to determine the actual shelf life. The most important of these variables is temperature, and the statement that samples of vacuum packaged meat were held at a particular temperature is not especially helpful, unless the range of temperatures encountered by the samples during storage is specified. Generally, it can be said that laboratory scale trials control temperatures over a much smaller range compared to commercial scale trials, and this is frequently the reason for the longer shelf life obtained in laboratory scale trials compared to that obtained in commercial production.

Other important variables include the microbiological status of the meat at the time of packing and the method used to determine the end of shelf life of the meat. These methods range from objective assessments of microbial counts to subjective assessments by taste panels consisting of trained or untrained members. Clearly, attempting to draw generally applicable conclusions from numerous published reports where the magnitude of these variables differs (or is not even specified) would only be misleading.

17.2.4.2.1 Beef

Vacuum packaged beef of normal pH can be stored at chiller temperatures for periods in excess of 10 weeks. However, high pH, DRD beef held under the same conditions will generally spoil within about 6 weeks (Taylor, 1985). The degree of vacuum has been reported as having no effect on sensory panel ratings of vacuum packaged beef cuts. There are also advantages in aging beef in vacuum packages as opposed to carcass aging, including less loss due to water evaporation, less necessity for trimming of exposed surfaces and more efficient use of refrigerated space.

17.2.4.2.2 Lamb and Pork

Although for many years vacuum packaging was only applied to chill beef, it is now also applied to lamb and pork. Because of their relatively small size, pork and lamb carcasses are only partially boned before packaging, and the presence of bone can lead to puncturing of the package unless precautions are taken.

In contrast to beef cuts, much of the surface of lamb cuts is adipose (rather than muscle) tissue. Adipose tissue has pH values close to neutrality and has no significant respiratory activity. Packaged lamb can therefore present a heterogeneous environment for microbial growth. This different microbial environment of high pH and, possibly, relatively high O_2 concentration probably accounts for the shelf life of only 6–8 weeks reported for vacuum packaged lamb, whereas 11–12 weeks is routinely attainable with beef. The longer shelf life of vacuum packaged beef is due to its flora being dominated by lactobacilli, which overgrow other spoilage organisms in the low temperature, low pH, low O_2, high CO_2 environment of the package.

Various conflicting reports have appeared in the literature concerning the chill temperature shelf life of pork joints. For example, figures of little more than 2 weeks at 1°C and 3–4 weeks at 2°C were reported in an extensive review (Taylor, 1985). However, it appears that limited use is being made of vacuum packaging for wholesale cuts of pork, where the attraction is likely to be convenience in butchery rather than savings in weight loss.

17.2.5 MODIFIED ATMOSPHERE PACKAGING OF FRESH MEAT

Vacuum packaging has the inherent disadvantage that both package and meat are subjected to mechanical strain. Mechanical pressure on the meat may increase drip loss, and if bone is present and not adequately covered with a suitable material, the pack may be ruptured. As an alternative to vacuum packaging, attempts have been made to store meat under various gaseous atmospheres, a process referred to as *modified atmosphere packaging* or MAP. The strain on the packaging material can be alleviated by introducing another gas or mixture of gases after evacuation and before sealing. Typical polymers used for the packaging of chilled meat (both vacuum and MAP) are presented in Table 17.4.

The first patent for MAP of red meat was issued in 1969. The intention has generally been to preserve the fresh meat color (O_2Mb) and prevent anaerobic spoilage by using high concentrations of O_2 (50%–100%) along with 15%–50% CO_2 to restrict the growth of *Pseudomonas* and related bacteria. O_2 at concentrations of 75% penetrates almost twice as far into the surface of meat as it does at the 21% level in air. The resultant thick layer of oxygenated tissue allows red meat to retain its bright red color for up to 5–6 days in normal retail display cabinets. In practice, however, the storage life in packs containing high concentrations of O_2 is usually less than in conventional vacuum packs.

Master packaging in gas-impermeable bags (backflushed with CO_2 or N_2) of meat in retail trays overwrapped with high O_2-permeable film has the potential to provide sufficient shelf life to facilitate centralized meat cutting and packaging operations (Tewari et al., 1999). However, permanent discoloration can occur if residual O_2 is high enough to exhaust the MRA of the muscle. The use of O_2 scavengers inside the retail trays has been shown to improve the shelf life of retail-ready meat cuts by achieving an O_2 concentration of $\leq$500 ppm in the pack atmosphere (Tewari et al., 2002).

TABLE 17.4
Typical Materials Used for Packaging Chilled Meat

Pack Type	Bottom Web Materials	Top Web Materials (Where Applicable)
Flexible vacuum pack	PA-LDPE, co-extruded as 5 layer film	
Flexible MAP pack	PA-LDPE	OPA-LDPE
	PA-EVOH-LDPE	
	PA-EVOH-PA-LDPE	PET-PVdC-LDPE
	PP-EVOH-LDPE	
	LDPE-EVOH-LDPE	
Rigid vacuum pack	APET	OPA-LDPE
	PVC or PVC-LDPE	PET-PVdC-LDPE
	PS-EVOH-LDPE	OPA-LDPE-EVOH-LDPE
		PET-LDPE-EVOH-LDPE
Rigid MAP pack	PVC	OPA-LDPE
	PVC-LDPE or PVC-EVOH-LDPE	PET-PVdC-LDPE
	APET	OPA-LDPE-EVOH-LDPE
	APET-LDPE or APET-EVOH-LDPE	PET-LDPE-EVOH-LDPE
	PS-EVOH-LDPE	
Skin packs	PVC-LDPE	Several combinations of up to seven or more layers but incorporating EVOH as gas barrier
	PS-EVOH-LDPE	
	APET	
	APET-LDPE	

Source: Mondry, H., Packaging systems for processed meat, in: *Meat Quality and Meat Packaging*, Taylor, A.A., Raimundo, A., Severini, M., and Smulders, F.J.M. (Eds), ECCEAMST (European Consortium for Continuing Education in Advanced Meat Science and Technology), Utrecht, Holland, pp. 323–356, 1996.

Because containers for gas packaging are good gas barriers, the internal atmosphere will be modified by the meat during storage. The relative volumes of gas and meat are therefore important in determining the progress of the changes in concentration of gases during storage, and the high solubility of CO_2 compared to the relatively low solubility of O_2 and N_2 in meat must be taken into account. In addition, the safety aspects of MAP must be fully appreciated before use is made of this technology.

Eilert (2005) reviewed the major influencers that are driving change in meat packaging. These included the continued evolution to case ready packaging and a higher degree of convenience in the meat case. Belcher (2006) identified three trends that continue to drive developments in meat packaging: (1) the need to reduce labor in the back of retail stores; (2) the need for fresh, high quality, convenient meat items and ready meal entrees; and (3) the need to deliver a safe food item to customers every time. While a tremendous amount of work has been done inside the meat plants to eliminate pathogens and improve the quality of the product, packaging has played a pivotal part in several advances and these were reviewed.

In a review of MAP for meat, McMillin (2008) noted that it provides too many advantages of cost, shelf life, tamper evidence, product uniformity, label information and supply chain integration for most industrialized countries to return to in-store cutting and packaging to supply self-service meat cases. In his view, MAP will continue to be used for meat in the future, most probably with several different MAP formats in use around the world. Mechanistic, logistical and perception obstacles will require effort and ingenuity to overcome existing package and system difficulties and promote implementation of processing and packaging technologies.

MAP of fresh meat can be classified into three categories: high O_2, low O_2 and ultra-low O_2.

17.2.5.1 High Oxygen MAP

High O_2 MAP systems that have atmospheres of 20%–30% CO_2, 60%–80% O_2 and up to 20% N_2 are used to both extend the color stability and delay microbial spoilage of display-packaged meat. Although both the color stability and the time to spoilage are approximately doubled by high O_2 MAP, this extension in shelf life is not wholly adequate for many commercial purposes (Gill, 1990).

Studies (Taylor, 1985), following the changes in gas volume and composition when beef was stored in completely impermeable containers with mixtures of CO_2 and relatively high concentrations of O_2, showed that an initial O_2 concentration of 80% was depleted to approximately 65% within 2 days in a typical commercial package where headspace volume was roughly equal to meat volume. The CO_2 level changed only slightly during this time, because the gas dissolving in the meat was balanced by CO_2 from tissue respiration. If packages with O_2-rich atmospheres are to be stored for relatively long times, then the volume of the pack atmosphere should be about three times the volume of the product, to avoid excessive decreases in O_2 concentration (Gill, 2003). In many retail situations, a package that meets these requirements is impractical.

The O_2 level during storage determines the effectiveness of color retention. The depth of oxygenation with 80%, 60% and 40% concentrations is shown in Table 17.5 and indicates the time when the

TABLE 17.5
Thickness of Oxygenated Layer in Beef Samples Stored in Different Mixtures of O_2 and CO_2

	Thickness of Oxygenated Layer (mm)				
Gas Mixture	**1 Day**	**2 Days**	**5 Days**	**8 Days**	**12 Days**
80% O_2 + 20% CO_2	11	11	14	14	—
60% O_2 + 20% CO_2 + 20% N_2	9	9	8	—	—
40% O_2 + 20% CO_2 + 40% N_2	8	7	—	—	—

Source: Taylor, A.A., Packaging fresh meat, in: *Developments in Meat Science,* Lawrie, R.A. (Ed.), Vol. 3, Elsevier Applied Science Publishers, Essex, U.K., pp. 107–131, 1985.

surface color is no longer considered red. Many workers have concluded that mixtures of 75%–80% O_2 with 25%–15% CO_2 are the most effective, but there have been reports of off-odors and rancidity in meats stored in high O_2 concentrations (Taylor, 1985). High O_2 MAP provides a shelf life at chill temperatures of only 5–10 days. Recently, Kim et al. (2010) compared high O_2 MAP with vacuum packaging of beef steaks. The steaks in high O_2 MAP had significantly lower tenderness and juiciness scores, and higher off-flavor scores compared to steaks in vacuum packs.

Their results suggested that the high O_2 MAP system may negatively affect meat quality characteristics by inducing lipid and myoglobin oxidation, and cross-linking/aggregation of myosin by protein oxidation.

For the aforementioned reasons, use of high O_2 MAP for display packaging depends largely on commercial circumstances.

17.2.5.2 Low Oxygen MAP

17.2.5.2.1 Carbon Dioxide Gas Flush

In these packages, the air is largely displaced by CO_2, either by itself or mixed with N_2. In general, the shelf life extension is similar to that achieved with vacuum packaging, with higher concentrations of CO_2 leading to a longer shelf life. N_2 is inert and plays no active part. Because of the low O_2 concentrations, the formation of O_2Mb on the meat surface is precluded or hindered, and red meats rapidly discolor due to the formation of MetMb. Thus, a low O_2 MAP system is unsuitable for use in retail packs of red meat.

17.2.5.2.2 Nitrogen Gas Flush

As an inert gas, N_2 is convenient for gas packaging; it is generally considered to be a neutral filler because it influences neither the color of the meat nor its microbiological quality. If the air in the package is removed prior to the addition of N_2, the effect on meat is similar to that of vacuum packaging, except that residual O_2 is diluted and MetMb formation on the surface should be less pronounced than with a vacuum (Taylor, 1985). However, although the formation of MetMb on the surface is reduced, the N_2 also dilutes the CO_2 produced by tissue respiration, prolonging the time required for the concentration to accumulate to levels sufficient to inhibit growth of spoilage bacteria.

Although there is little commercial use of N_2 flushing with fresh meat, several studies have confirmed that 100% N_2 is as effective as a vacuum for storing fresh meat joints; the only advantage is reduced exudate owing to less mechanical pressure on meat compared with vacuum packaging.

17.2.5.2.3 Argon

Ruiz-Capillas and Jiménez-Colmenero (2010) investigated the effect of MAP with 20% CO_2 and 80% N_2, or 30% CO_2 and 70% Ar, on the microbiological and physicochemical characteristics of fresh pork sausages during refrigerated storage (1°C ± 1°C) in the dark, and compared the results with vacuum and aerobic overwrap packaging. There was no significant difference in microbial counts or color parameters between the two lots in MAP, both of which had a beneficial effect on sensory quality during the 28 day storage period. The non-MAP sausages were rejected after 11 days of storage. There have been no other reports on the use of Ar in MAP of fresh meat.

17.2.5.3 Ultra Low Oxygen MAP

This type of MAP could also be described as high or saturated CO_2 MAP. It has been identified by some experts (Gill, 2003) as controlled atmosphere packaging (CAP). However, CAP implies that an atmosphere of known, desired composition is established within a package and is controlled (i.e., remains unchanged) during the life of the package. Because in this type of package no control is extended over the package atmosphere after sealing with respect to its volume or composition, it is misleading to describe it as CAP; ultralow O_2 MAP is a preferable term.

CO_2 is highly soluble in both water and oils. Therefore, when CO_2 is applied to meat in a rigid pack, the gas will be absorbed by the muscle and fat tissue until equilibrium is attained. At equilibrium, the partial pressure of CO_2 will be less than that of the original gas mixture, and the total gas pressure will also be less than that at which the gas mixture was initially applied (Gill, 1981).

Similar considerations apply in flexible packaging systems. If CO_2 alone is added, the pack will collapse around the meat as gas is absorbed, unless CO_2 is added in excess of the quantity required to saturate the meat (1.5 L CO_2 kg^{-1} meat at atmospheric pressure). In general, meat will absorb approximately its own volume of gas in an atmosphere of 100% CO_2 (Gill, 2003).

As noted earlier in this chapter, red meat color is not adversely affected by high CO_2 atmospheres if O_2 is rigorously excluded from the package. To ensure that the package is impermeable to O_2, the package is constructed from a laminate containing aluminum foil or two webs of metalized film (Gill, 1990; Bell, 2001). Such a packaging system incorporating specialized gassing equipment has been developed, initially for achieving a long shelf life for chilled lamb. A filled pouch is evacuated in a chamber under reducing external pressure to maintain free pathways for the exhaustion of air. The pouch is then collapsed by mild external pressure to expel residual air and subsequently inflated under increasing external pressure to minimize stress during gassing of the pack. With this type of relatively elaborate filling procedure, residual O_2 levels of <0.05% (500 ppm) can be reliably obtained provided that the CO_2 gas contains 0.03% or less O_2 (Kropf, 2000). With O_2-free CO_2, residual O_2 concentrations after pack sealing of 100 ppm have been obtained. However, even 100 ppm O_2 can result in discoloration of meat, although such discoloration is generally transient. MetMb is usually reduced to Mb within 4 days as anoxic conditions are established and maintained (Gill, 2003).

This system (known as CAPTECH) was initially developed to allow convenient sea shipment of chilled lamb primal cuts and whole lamb carcasses from New Zealand to northern hemisphere markets. After 24 weeks storage for lamb carcasses and 20 weeks for lamb primal cuts at −1°C, the product was still acceptable, whereas vacuum packaged controls began to spoil after 11 weeks. The end of shelf life of the CAPTECH products was not microbial spoilage but the development of excessive meat tenderness. Maintaining a storage temperature of −1°C under commercial conditions without allowing the meat to freeze presents a serious challenge. However, this system is increasingly being used commercially for the aforementioned applications, as well as for the prolonged storage of shelf ready consumer packs of beef and lamb which have shelf lives at −1°C of 18 and 20 weeks, respectively. Trials also demonstrated that it is suitable for the prolonged storage of pork, poultry, venison, offal, fish, cooked meats, blanched vegetables and complete meals (Gill, 1990).

17.2.6 PACKAGING OF FROZEN AND RESTRUCTURED MEATS

Frozen meat is stored and displayed between −10°C and −30°C, at which temperatures microbiological growth is arrested (Taylor, 1985). Therefore, the changes in meat most influenced by packaging are those associated with appearance, with color and the absence of frost inside the package being the two most important features in this regard.

If a bright red color is required, then it must be produced by oxygenation of the meat surface before freezing, followed by packaging in a material which is relatively permeable to O_2. It has been claimed (Taylor, 1985) that ionomer film will keep the bright red color for at least a year if the meat is stored in the dark at −20°C. However, when exposed to light, the red color begins to darken after about a week. This is caused by light-activated oxidation of the pigment in the meat surface, and is inevitable in meat which has been frozen in the bright red state and subsequently exposed to light.

When frozen meat and meat products are stored without an adequate moisture vapor barrier, an opaque dehydrated surface known as freezer burn is formed. Freezer burn is caused by the sublimation of ice on the surface of the product when the water vapor pressure of the ice is higher than the vapor pressure in the surrounding air inside the package. Histological studies have revealed that the spongy freezer burn area in frozen muscle and liver possesses microscopic cavities which scatter light; these cavities were previously occupied by ice crystals.

The key to avoiding freezer burn and lessening oxidative deterioration during frozen storage is to eliminate or reduce the headspace in the package, which should also serve as an effective barrier to O_2 and water vapor. Freezer burn can occur even when using a packaging material which is an excellent barrier to moisture vapor if the package headspace has not been essentially eliminated. Oxidative changes are even more effectively reduced through exclusion of air by means of vacuum packaging.

Several packaging systems are available that satisfy the aforementioned requirements for frozen meat. Vacuum packing followed by heat shrinking of the package has been available for many years, as has VSP. Because there is no space between the meat and the packaging material, frost cannot develop to mask the attractive appearance. Some systems can handle either chilled or frozen cuts of meat, whereas others can only pack meat which is already frozen. When the meat is frozen prior to VSP, the final radiant heat sealing operation glazes the surface of the frozen meat and produces an appearance similar to that of chilled meat (Taylor, 1985).

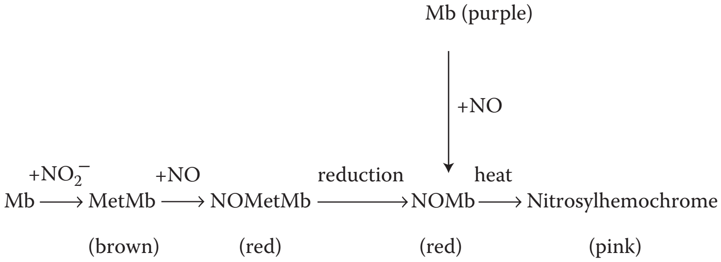
Restructured meat products can be manufactured by three methods: (1) chunking and forming, (2) flaking and forming and (3) tearing and forming. Chunked and formed products are normally either cured and heat processed or fresh frozen. Cured products include sausages and loaves; fresh products are shaped by stuffing into casings or forming into logs. Flaking and forming processes are normally used only to make fresh products such as steaks, cutlets, chops and roasts. Tearing and forming produces products similar to those made by flaking and forming (Harte, 1987).

There are four major problems related to the packaging of restructured meat products: (1) microbial spoilage, (2) change in color, (3) lipid oxidation and (4) moisture loss (Harte, 1987). Because most restructured meat products are distributed frozen, microbial spoilage is generally limited to cured meat products which are discussed in the next section.

Frozen, restructured meat products have traditionally been packaged in bags, pouches, trays, overwraps and plastic-coated paperboard, with polyolefins being the most common material used. Of course, they must contain appropriate plasticizers or, more commonly, comonomers such as butene or octene so that their mechanical properties are not impaired at subzero temperatures. VSP is also used for frozen, restructured meat products. Typically, a heat-softened ionomer film is draped over the product, which is supported on a lower web of the same material. Air is withdrawn from between the two webs and the webs heat sealed together, resulting in a package that is sealed skintight to the edge of the product, regardless of its contour or size. Because there are no empty spaces for moisture condensation to occur, freezer burn is virtually eliminated during frozen storage (Harte, 1987).

17.3 CURED AND COOKED MEATS

A significant volume of meat products are cured; therefore, an understanding of the changes meat pigments undergo during the curing process is important. A cured meat is one to which NaCl has been added and in which the native meat pigment Mb is, as a result of reaction with nitric oxide (NO), mainly in the nitroso-form. The precursor of NO is either $NaNO_2$ or KNO_2, which may be added directly or result from nitrate reduction. Nitrite is also an oxidizing agent and rapidly converts Mb to MetMb. NO then combines with MetMb to form nitrosylmetmyoglobin (NOMetMb), which is then reduced by various reducing agents such as added ascorbate to nitrosylmyoglobin (NOMb). NO also reacts directly with Mb to form NOMb:



$$\begin{tikzcd} & & & \text{Mb (purple)} \arrow[d, "+\text{NO}"] & \\ \text{Mb} \arrow[r, "+\text{NO}_2^-"] & \underset{\text{(brown)}}{\text{MetMb}} \arrow[r, "+\text{NO}"] & \underset{\text{(red)}}{\text{NOMetMb}} \arrow[r, "\text{reduction}"] & \underset{\text{(red)}}{\text{NOMb}} \arrow[r, "\text{heat}"] & \underset{\text{(pink)}}{\text{Nitrosylhemochrome}} \end{tikzcd}$$

The attractive red color of cured meats before cooking is essentially that of NOMb; it has the red color characteristic of fresh meat O_2Mb. Heating converts NOMb to denatured globin nitrosylhemochrome, which is stable and characteristically red-pink in cooked, cured meats. Residual nitrite is required at the time of cooking, and bacon with low or zero nitrite at the time of frying may be gray after cooking. In traditional processes, nitrate was the only source of nitrite, which was formed by the action of bacteria (mainly micrococci) on the nitrate. However, in modern rapid-cure processes, nitrite is added directly to the brine and a proportion of nitrate may also be included.

During storage, cured meats deteriorate, firstly because of discoloration, secondly because of oxidative rancidity in the fat and thirdly on account of microbial changes, the latter having become of somewhat greater importance since the advent of prepackaged methods of sale (Lawrie, 2006).

Although the pigment of cured meats (NOMb) is stable in the absence of O_2 or under vacuum, its oxidation to MetMb is very rapid when O_2 is present. The rate of NOMb oxidation increases directly with increasing O_2 tension, unlike Mb itself where the rate of oxidation is maximal at 0.4 cm Hg O_2 partial pressure. The most common and effective antioxidants used are ascorbate and erythrobate, which are either incorporated into the curing brine or sprayed onto the surface of the product after maturing.

NOMb and nitrosylhemochrome are much more susceptible to light than Mb, and cured meats can fade after 1 h under retail display lighting conditions. Because light accelerates oxidative changes only in the presence of O_2, vacuum or inert gas packaging can eliminate this effect. Holding vacuum packaged meats in the dark for 1–2 days before exposing them to display lights allows residual surface O_2 to be depleted by microorganisms and tissue activity, thus reducing subsequent color deterioration. Several other techniques can reduce light-related color damage (Harte, 1987). The most efficient way is environmental control, that is, changing the type of light or using light shields, but this is usually impractical. Modification of the package can also result in less light damage. This can be achieved by the addition of additives to the package such as coloring agents, UV absorbers and other materials that decrease transmission by increasing opaqueness of the film. Packages can be designed to reduce the total exposed area by adding labels, printing on the film and increasing film thickness. In addition, the product can be stored with the clear side facing down in the display case. However, all these techniques decrease the ability of customers to view the product inside the package.

To inhibit color changes in cured meat products, a lower level of available O_2 than that required to shift the microbial population from aerobic to anaerobic is required. In cooked beef roasts, N_2 packaging significantly improves appearance by retarding greenish discoloration. Light increases the frequency of green discoloration of vacuum packaged samples after 28 days of storage.

Smoke, traditionally produced by the slow combustion of sawdust derived from hard woods, inhibits microbial growth, retards fat oxidation and imparts flavor to cured meats. Today, however, smoke essences are frequently used instead of actual smoke, and they contribute largely only flavor to cured meats.

TABLE 17.6
Factors Influencing the Form of Microbial Spoilage of Cured Meats

Product Characteristic	Environmental Factors
Nature of tissue (fat, lean, etc.)	Storage atmosphere (O_2; CO_2)
pH of tissue	Storage temperature and time
Moisture content	Heat treatment
Levels of curing salts (NaCl, nitrite, nitrate)	
Smoke components	
Polyphosphates, sugars and other curing adjuncts	

Source: Gardner, G.A., Microbial spoilage of cured meats, in: *Food Microbiology: Advances and Prospects*, Roberts, T.A. and Skinner, F.A. (Eds), Academic Press, London, U.K., pp. 179–197, 1983.

Cured hams undergo a different type of spoilage from that of fresh or smoked hams, due primarily to the fact that curing solutions pumped into hams contain sugars, which are fermented by the natural flora of the ham, and also by those organisms such as lactobacilli, which are pumped into the product in the curing solution (Jay et al., 2007).

A study (Møller et al., 2003) on the factors affecting light-induced oxidative discoloration of cured ham (CO_2:N_2 20:80) during 14 days storage at 5°C drew attention to the important effect of headspace volume, which directly influences the total amount of O_2 available for oxidation. As well as keeping the headspace O_2 level low, the headspace volume should also be small. A packaging film with an OTR of 0.1 mL m^{-2} day^{-1} was recommended.

Currently, there is widespread production of sliced, cooked, vacuum packaged cured meats including cooked ham, corned beef, emulsion-type sausages and luncheon meats. The salt contents are usually in the range 2%–4%, pH values are normally >6.0 and residual nitrite levels vary from 10 to 200 μg g^{-1}, but are mostly <100 μg g^{-1} (Gardner, 1983). Bacterial spoilage of these products is largely influenced by the nature of the meat, together with environmental factors (see Table 17.6) and the degree and composition of the initial microflora.

Semipreserved cured meats include hams, bacons and sausages packaged either in metal containers or plastic films and cooked after packaging to an internal temperature of between 65°C and 75°C. This destroys most vegetative microorganisms and gives the product a keeping quality of 6 months if held below 5°C. There is a concern over the safety of these types of products in environments where rigid temperature control cannot be guaranteed.

In contrast, shelf stable canned cured meats (SSCCMs) have shelf lives comparable to canned meat products. However, compared to canned meat products whose safety depends on heat treatment alone (provided that there is no postprocess contamination), the thermal process for SSCCM is relatively mild and allows the survival of a significant number of bacterial spores. These must be adequately inhibited from outgrowth by the NaCl/nitrite combination.

17.4 POULTRY

Raw poultry meat is a perishable commodity of relatively high pH (5.6 for breast muscle and up to 6.4 for leg muscle), which readily supports the growth of microorganisms when stored under chill or ambient conditions. The shelf life of such meat depends on the combined effects of certain intrinsic and extrinsic factors, including the numbers and types of psychrotrophic spoilage organisms present initially, the storage temperature, muscle pH and type (red or white) as well as the kind of packaging material used and the gaseous environment of the product.

Poultry muscle generally has low concentrations of Mb and high rates of O_2 consumption, which means that little O_2Mb is formed when poultry muscle is exposed to air. Consumers are accustomed to the appearance of poultry meat where Mb and MetMb pigments are dominant. Therefore, while the color of poultry meat is not enhanced by storage under high O_2 atmospheres, the appearance of the meat is not grossly degraded by its exposure to anaerobic conditions or low concentrations of O_2 that would cause red meats to lose their attractive red color (Gill, 2003).

The major factor limiting the shelf life of poultry is microbial spoilage, especially growth of *Pseudomonas* and *Achromobacter* species and enterobacteria, the latter causing putrid spoilage of the product after relatively short storage times. These Gram-negative aerobic spoilage organisms can be effectively inhibited by CO_2 concentrations of 20%.

The main pathogenic organisms associated with poultry and poultry products are *Salmonella* spp., *Staphylococcus aureus* and *Clostridium perfringens*. Most studies on the extension of shelf life using CO_2 in MAs have concentrated on the suppression of spoilage organisms rather than the survival and growth of pathogens.

As the color of poultry meat in anoxic packaging is acceptable to consumers, VSP using upper and lower films with low OTRs (typically less than 2 mL m^{-2} day^{-1}) can be used to extend the storage life by inhibition of aerobic spoilage flora, provided that the packs are held under chill conditions (Kartika et al., 2003). Vacuum packaging of poultry meat leads to the development of mainly lactic acid bacteria, sometimes accompanied by cold-tolerant coliforms. Although vacuum packaging may be used to encourage the development of an atmosphere around the product which delays microbial spoilage, other systems currently in use involve addition of at least 20% CO_2 to either individually packaged items or bulk packs of varying size in an O_2-impermeable plastic film.

Based on research in the United States in the 1950s, it was considered for many years that the maximum usable CO_2 concentration for poultry was 25% because, it was claimed, above this level the meat became discolored with grayish tinges; even at 15%, a loss of bloom was sometimes noted. However, gas compositions of 25%–50% CO_2 and 50%–75% N_2 are used commercially, and it appears that the occasional discoloration problems may be due to high residual levels of O_2 rather than the concentration of CO_2 (Gill, 1990).

Although the number and types of microorganisms found on stored poultry is an important factor when determining the shelf life, the real determinant is the sensory quality of the raw and cooked product. Unfortunately, most published studies have not included sensory tests, but one study (Hotchkiss et al., 1985) did evaluate the quality of raw and cooked poultry stored under MA and refrigeration. Their data indicated that MAP (80% CO_2) poultry would be quite acceptable to consumers for up to 4–6 weeks depending on the temperature of storage. They noted that commercial poultry processors may not get as long a shelf life because of difficulties in controlling the packaging process and temperature under production conditions.

TTIs were used to monitor the quality of MAP broiler chicken cuts stored under different temperature conditions (Smolander et al., 2004). It was found that microbiological shelf life could be considerably improved when the cold chain was carefully maintained. Temperature had a critical effect on the numbers of *Enterobacteriaceae*, proteolytic bacteria, H_2S-producing bacteria and clostridia—the microbial groups likely to have an effect on the sensory quality.

In a study of broiler carcasses packaged under vacuum in film of low O_2 permeability, or under CO_2 in gas-impermeable packages (Gill et al., 1990), shelf life was a function of storage temperature, packaging and O_2 availability. Putrid spoilage in gas-impermeable packages after 7 weeks storage at 3°C or 14 weeks storage at −1.5°C was attributed to *Enterobacteriaceae*. In vacuum packages with OTRs of 30–40 mL m^{-2} day^{-1}, putrid odors were detected after 2 weeks storage at 3°C and 3 weeks storage at −1.5°C.

Concerning the safety of MAP chicken, the possible problem organisms would be *C. jejuni*, which may be able to survive better in a MAP product, and *L. monocytogenes* and *A. hydrophila*, which, because of the extended storage lives of the MAP products, may have additional time to grow to potentially high numbers. Although *C. perfringens* may be able to survive better in some MAs as compared with air, it would not be able to grow at the chill temperatures commonly used for MAP products. Thus, it is unlikely to be a health hazard in a MAP product unless the product is temperature abused, because high numbers of the organism must be ingested to cause illness (Farber, 1991).

Salmonella is one of the leading causes of human foodborne illnesses originating from meat and poultry products, and cross contamination from raw to cooked products continues to be problematic in the food industry. Kudra et al. (2011) combined irradiation with 99.5% CO_2:0.5% CO-MAP to improve the control of *Salmonella* Typhimurium on chicken breast meat. They demonstrated that irradiation was an effective means of reducing *Salmonella* on meat or poultry, but packaging in either vacuum or MAP had little impact during subsequent refrigerated storage. Shin et al. (2011) evaluated the effectiveness of controlled released ClO_2 sachets and MAP (30% CO_2:70% N_2) to control the growth of *S.* Typhimurium and *L. monocytogenes* on raw chicken breast during storage at 4°C for up to 21 days. The fresh chicken samples were inoculated with one or the other of the pathogens at 10^4 cfu g^{-1}; the maximum reduction in the MAP plus ClO_2 samples (compared with MAP alone) was 0.68 log cfu g^{-1} for *S.* Typhimurium and 1.87 log cfu g^{-1} for *L. monocytogenes*. The ClO_2 caused a negative color change in the chicken meat and the pH decreased from 5.79 to 5.45.

A wide range of manufactured poultry products has been developed including rolls, roasts, burgers and sausages. However, in most cases, very little information is available on either keeping quality or the influence on shelf life of particular packaging materials. Conte-Junior et al. (2010) showed that MAP (CO_2: N_2 80:20) inhibited the growth of the psychrotrophic pathogen *Y. enterocolitica* in fresh poultry sausage, but MAP itself was not able to eliminate this pathogen. They recommended that fresh poultry sausage not be packaged in 100% air or 100% N_2.

Most studies on possible methods of extending shelf life of poultry meat have been on chicken with little attention to other poultry species. It cannot be assumed that the keeping quality and shelf life characteristics of turkeys and ducks are the same in all respects as those of chickens, particularly in relation to flavor changes under different storage conditions, which do not always correlate with off-odor development. Recently, Fraqueza and Barreto (2011) evaluated the effect of 0.5% CO in MAP of turkey meat stored in the dark at 0°C for up to 25 days. The presence of CO in anoxic gas mixtures with CO_2 inhibited microbial flora in general, with particular action on *Brochothrix thermosphacta*. It also gave turkey meat the bright pink color preferred by consumers without leading to the appearance of undercooked meat.

Recently, Rocculi et al. (2011) reported on the effect of MAP (100% CO_2 or 100% N_2) at 25°C for 28 days on the functional properties of albumen in eggs. Packing eggs in CO_2 promoted an improvement in meringue crispness and could ameliorate the quality characteristics of albumen-based food products. They suggested that commercially, CO_2 MAP could provide an albumen-based ingredient tailored to maximize the characteristics needed in the final product (e.g., fresh shell eggs for meringue preparation) that could give an added value to the product.

17.5 SEAFOOD

17.5.1 Types of Spoilage

Flesh foods such as fish and shellfish are highly perishable due to their high a_w, relatively high pH and the presence of autolytic enzymes which cause the rapid development of undesirable odors and flavors. The chemical composition and microbial flora of seafood vary considerably between species, different fishing grounds and seasons, but the pH of most fish is >6.0. The flesh of most marine fish and shellfish contain large amounts of nonprotein nitrogen (NPN), including the compound trimethylamine oxide (TMAO). After death, TMAO can serve as a terminal electron acceptor for some spoilage bacteria, enabling them to grow when O_2 levels are depleted; the ammoniacal substances trimethylamine (TMA), dimethylamine (DMA) and formaldehyde are released as a consequence and are responsible for the strong, characteristic fishy odors (Davis, 1998). Nonfatty fish such as cod and haddock have lipid contents of 1%–2% in contrast to fatty fish such as herring and mackerel, which can have lipid contents of more than 30%. The high degree of unsaturation which gives fish oils their nutritional significance also makes them very vulnerable to oxidation. The ready oxidation of fish oils adds rancid off-odors to the fishy odors, and the nutritional benefits of the omega-3 fatty acids are lost over time.

It is generally accepted that the internal flesh of healthy, live fish is sterile; microorganisms that exist on fresh fish are generally found in the gills, the outer slime and the intestines. The postmortem changes leading to spoilage depend principally on the chemical composition of the fish, its microbial flora and subsequent handling, processing and storage. The spoilage of salt and fresh water fish appears to occur in essentially the same manner. Spoilage results from changes brought about by (1) reactions due to autolytic enzymes, (2) the metabolic activities of microorganisms and (3) chemical reactions such as oxidation.

Immediately postmortem, a whole series of tissue enzyme reactions begin the process of autolysis (basically self-digestion of the fish muscle), which leads eventually to spoilage. The autolytic enzyme reactions predominate for 4–6 days at 0°C, after which the products of bacterial activity become increasingly evident with the appearance of undesirable odors and flavors. The rates of autolytic changes are determined by many factors, but the most important are temperature, pH, availability of O_2 and the physiological condition of the fish before death.

As spoilage proceeds, there is a gradual invasion of the flesh by bacteria from the outer surfaces. Because bacteria can generally use only very basic nutrients as food, bacterial spoilage does not normally commence in whole fish until autolysis is well advanced. Breakdown of the muscle structure occurs only after spoilage has proceeded well beyond the point of rejection. The development of objectionable slimes, odors and flavors results mainly from bacterial activity. Although there is a great variation in the species of microorganisms present on fresh fish, only a select few—the so-called specific spoilage organisms (SSOs)—are responsible for the offensive off-flavors associated with seafood spoilage (Gram and Dalgaard, 2002). Gram-negative fermentative bacteria (such as *Vibrionaceae*) spoil unpreserved fish, whereas psychrotolerant Gram-negative bacteria such as *Pseudomonas* spp. and *Shewanella* spp. grow on chilled fish.

Fish from warm sea waters generally carry larger numbers of bacteria than fish from colder waters, with Gram-positive organisms forming a large or predominant fraction of the flora, along with Gram-negative organisms of the types found on fish from colder waters. The major spoilage organisms found on temperate fish stored under aerobic conditions are dominated by psychrotrophic Gram-negative bacteria belonging to the genera *Pseudomonas*, *Moraxella*, *Acinetobacter*, *Shewanella*, *Vibrionaceae*, *Clostridium*, *Lactobacillus* and *Corynebacterium* (Giatrakou et al., 2008). As mentioned earlier, some of these organisms can utilize TMAO and continue with oxidative metabolism under anaerobic conditions. *Photobacterium phosphoreum* is responsible for spoilage of cod fish under anaerobic conditions, but it is not known if this bacterium is the general SSO for all marine temperate fishes (Sivertsvik et al., 2002). Lactic acid bacteria and *Brochothrix thermosphacta* have been identified as the typical SSOs of freshwater fish and fish from warmer waters (Sivertsvik, 2003).

Macé et al. (2012) characterized the spoilage microbiota in raw salmon steaks stored under vacuum or MAP (CO_2:N_2 50:50) after storage for 3 days at 2°C, a cold chain break at 20°C for 2 h and then 7 days at 8°C, according to the shelf life evaluation protocol monitored by industrial plants. At the onset of spoilage, 65 bacterial isolates from 13 different genera or species were identified. At the beginning of storage, *Pseudomonas* sp. dominated the raw salmon microbiota, but in the following days (7 and 10), *Photobacterium phosphoreum* and *Lactococcus piscium* were identified as the main bacterial groups.

The third type of spoilage is chemical spoilage—primarily oxidation of the fatty compounds leading to the development of rancid flavors. The rate of rancidity development is closely related to the temperature of storage and the reactions can still occur at freezer temperatures as low as −30°C. Some substances such as salt and some processes such as drying and smoking can aggravate the oxidation problem, and therefore frozen smoked fish has a shorter shelf life than unsmoked fish of the same species.

Shellfish are divided into two main groups: crustaceans (which include shrimp, prawn, lobster, crabs and crayfish) and mollusks (which include oysters, clams, squid, cockles, mussels and scallops). The microbial flora of shellfish reflect the waters from which they are caught, contaminants from the deck and handlers and the quality of the washing waters used. Mollusks differ from crustacean shellfish and nonfatty fish in having a significant content of carbohydrate material and a lower total quantity of nitrogen in their flesh. Because the carbohydrate is largely in the form of glycogen, the spoilage of molluscan shellfish is largely fermentative (Jay et al., 2007). This results in a progressive fall in tissue pH as spoilage develops, from pH 5.9 to 6.2 in fresh mollusks to less than about pH 5.5 in spoiled mollusks.

17.5.2 Vacuum and Modified Atmosphere Packaging

Because of the high pH of most fish muscle, growth of *S. putrefaciens* is not prevented by vacuum packaging, and this organism may dominate the spoilage process in vacuum-packaged fish (Gill and Gill, 2005). However, *P. phosphoreum* has been identified as the organism responsible for spoilage of fish such as cod in vacuum and MA packs (Sivertsvik, 2003). The rates of growth of both these organisms are not greatly reduced by anaerobic conditions and, consequently, the extension of shelf life achieved by the vacuum packaging of fish is often small. In contrast to *S. putrefaciens,* which is greatly inhibited by high concentrations of CO_2, *P. phosphoreum* has been shown to be relatively insensitive to CO_2 and may alone spoil fish in MAP after a minimally longer storage life than that of the same product stored in air (Gill and Gill, 2005).

The first extensive research on seafood stored in CO_2 was reported in the early 1930s in the United Kingdom, the United States and Russia. In a 100% CO_2 atmosphere, fish kept fresh two to three times longer than control fish in air at the same temperature (Stammen et al., 1990). The absorption of CO_2 altered the pH of fish from 6.6 to 6.2, but it was reversed on subsequent exposure to air (Sivertsvik et al., 2002).

Many of the reported studies on MAP of seafood do not specify the gas volume to product weight ratio (DoF). For a given gas mixture, a high gas-to-fish ratio will present a very different chemical balance from a low ratio. Moreover, changes in the CO_2 and O_2 levels inside the package headspace during storage are seldom measured, making comparison between different studies difficult. While any chemical effects on fish tissues will be affected by the amount of CO_2 that dissolves, the bacteriostatic effect is more likely to be influenced by the residual atmosphere because most spoilage organisms are present on the surface.

The effects of MAP on seafood are similar to those described earlier in this chapter for meat and poultry. Vacuum and MAP (including flushing with N_2 and CO_2) suppress the normal spoilage bacteria that cause off-odors and -flavors, thereby extending the shelf life of seafood. Microorganisms not usually involved in aerobic spoilage eventually predominate. These microorganisms such as lactobacilli are less affected by the elevated CO_2 atmosphere and grow more slowly than the normal aerobic spoilage bacteria. Because the microorganisms which predominate under MAP cause less noticeable and less offensive organoleptic changes, the net result is a significant extension of shelf life under MAP at refrigeration temperatures, compared with packaging under air. However, a review concluded that MAP confers little or no additional increase in shelf life compared with vacuum packaging. The best effect of MAP storage on shelf life has been obtained with fish from warm waters, with the spoilage flora being dominated by Gram-positive microorganisms (Sivertsvik et al., 2002).

Effective gas compositions vary according to fish species, with low O_2 concentrations being used with fatty fish which are susceptible to oxidative rancidity. Fish species with a high proportion of red muscle tissue require the presence of O_2 to maintain good color. This is especially important for high value species, such as tuna, that are also prone to histamine formation. Fortunately, there was a strong inhibitory effect on formation of this compound in an atmosphere of 40% CO_2:60% O_2 recommended for tuna (Emborg and Dalgaard, 2008). Generally, gas mixtures for nonfatty fish and shellfish are 25%–35% O_2, 35%–45% CO_2 and 25%–35% N_2, and for smoked and fatty fish 35%–45% CO_2 and 55%–65% N_2 (Day, 2001). Problems caused by too high a CO_2 level include pack collapse, increased drip, CO_2 taint (which gives an acid flavor to certain species of fish) and clouding of the eyes, which consumers often use as an indicator of freshness.

Sivertsvik (2007) investigated the optimal gas mixture to maintain the quality of farmed, pre-*rigor* cod at the highest possible level as measured by sensory, microbiological, chemical and physical attributes using a gas:product ratio of 2:1 and storing at 0°C. Somewhat surprisingly, the optimum gas composition was determined to be 63 mL O_2 and 37 mL CO_2 per 100 mL gas mixture. Bacterial growth decreased and formation of exudates increased with increased CO_2 levels. H_2S-producing bacteria were not present or unable to grow on the cod under any gas mixture. Reduction of odor scores, TMAO and formation of TMA increased with decreasing CO_2 and O_2 levels. The optimal gas mixture minimized formation of exudate, TMA and total volatile bases, and inhibited microbiological growth, while at the same time maintaining a high odor score and TMAO content in packaged cod. The findings suggested that the O_2 level in the gas mix is at least as important as the CO_2 content when packaging pre-*rigor* farmed cod.

Siah and Tahir (2011) evaluated the shelf life of red tilapia fillets under MAP (80% CO_2: 20% N_2) at 2°C ± 2°C using four different films whose OTRs and CDTRs were determined at 23°C and 0% RH. A shelf life of 14 days was obtained for fillets packed in 60 μm LLDPE-EVOH-LLDPE and 70 μm BON-LDPE, compared to 9 days in 60 μm OPP-PP and 6 days in HDPE. The CDTRs of the four laminates were 11, 320, 4,749 and 17,469 mL cm^2 day^{-1}, respectively, confirming the importance of using a package for MAP with a good barrier to CO_2.

The use of CO in MAP of fish has been practiced for some time, with a book devoted solely to this topic (Otwell et al., 2006). Many authors have found that CO improved fish shelf life, but there were some risks to its use with many samples of CO-treated tuna having high histamine levels, which could lead to sickness in the consumer (Slattery, 2010). A recent review by Prester (2011) on biogenic amines in fish, fish products and shellfish should be consulted for further details of this potentially fatal side effect. Filtered smoke containing 30%–40% CO is permitted for pretreatment of fish in the United States and some other countries. Recently, Bjørlykke et al. (2011) reported that Atlantic salmon exposed to CO prior to killing had a significantly deeper red color of both gills and fillets 10 days postmortem.

Rotabakk et al. (2008) evaluated the suitability of soluble gas stabilization (SGS) to extend the microbial shelf life of Atlantic halibut compared with traditional MAP. It was possible to dissolve CO_2 in the fillet prior to packaging by using SGS. SGS treatment increased headspace volume and CO_2 as compared to MAP, with increasing SGS pressure and time. Drip loss was reduced, most likely because of less pressure in the package as a result of increased headspace volume. The SGS treatment did not affect the color or pH of the halibut fillets.

"Superchilling" or "partial freezing" involves reducing the temperature of the food to 1°C–2°C below its freezing point (Kaale et al., 2011). Sivertsvik et al. (2003) compared the use of MAP (CO_2:N_2 60:40) of salmon with storage in air at normal chilled (4°C) and superchilled (–2°C) temperatures. The shelf life of MAP salmon at −2°C (24 days) was 2.5 times that of MAP salmon at 4°C, and 3.5 times that of salmon at 4°C stored under air. It was suggested that the synergistic effect of MA and temperature may be caused by increased solubility of CO_2 at the superchilled temperature.

It is evident from the published literature that MAP can extend the shelf life of a variety of fish and fish products. However, MAP is not equally effective for extending the shelf life of all fish products. Most studies of MAP of seafood indicate a shelf life extension from a few days up to a week or more compared with air storage, depending on species and temperature. Differences in spoilage microflora and pH are mainly responsible for the observed differences in shelf life, provided similar gas to product ratios are used (Sivertsvik et al., 2002). Although some claims have been made of a shelf life of up to 3–4 weeks for the refrigerated storage of MAP fish, this is generally considered to be unrealistic unless superchilled temperatures are used. General target shelf lives of these products are in the range of 10–14 days, but may reach 18–20 days if the temperature is controlled very tightly just above freezing point.

Recently, Sone et al. (2012) were able to classify fresh salmon fillets stored under different atmospheres (air, CO_2:N_2 60:40 and 90% vacuum) according to the type of packaging used during storage at 4°C for up to 16 days postmortem. The successful classification (88.3 ± 4.5%) was largely dependent on spectral characteristics at the wavelengths 606 and 636 nm and may be related to the different oxidation states of the heme proteins in the muscles.

17.5.3 SAFETY ASPECTS OF PACKAGED SEAFOOD

Fish and shellfish are vehicles for transmission of foodborne diseases. There is a large body of evidence which indicates that fresh fish may be contaminated with the anaerobe *C. botulinum*, either as a result of the organisms being present in the microbiota of the fish ecosystem, or as a result of postcatching contamination during processing. Conditions for growth of *C. botulinum* occur only a few mm below the surface of fish flesh, where spores may arise through gaping, knife cuts and other punctures (Davis, 1998). Foodborne botulism outbreaks caused by fish are predominantly a result of type E strains of *C. botulinum* in products which are consumed without further heat processing. Because many fish products are not cooked prior to consumption, the hazard from heat labile botulinal toxin is real. Skinner and Reddy (2006) discussed the hazards associated with *C. botulinum* in MAP of fish and fishery products.

It is now recognized that the growth of *C. botulinum* in foods does not depend on the total exclusion of O_2, nor does the inclusion of O_2 ensure that growth of *C. botulinum* is prevented (Sivertsvik et al., 2002). A summary of recent results on the growth and toxin production by *C. botulinum* is presented in Table 17.7. While some studies have detected botulinal toxin in MAP fish prior to the products being considered spoiled, other challenge studies have shown MA or vacuum packaged fish spoil prior to, or in parallel with, toxin production. Despite these inconclusive results, there is a potential threat for a packaged fish product to become toxic prior to spoilage at storage temperatures of 8°C or above (Gibson et al., 2000; Sivertsvik et al., 2002).

While the presence of CO_2 does not lead to an increase in growth of *C. botulinum*, replacing air with N_2 produces anaerobic conditions and an increased susceptibility to the growth of *C. botulinum* in advance of spoilage signals resulting from spoilage microflora. Vacuum packaging in high barrier films produces the same growth conditions as replacing air with N_2. However, if an O_2-permeable film is used for vacuum packaging, then distinct spoilage signals will be produced if the pack is held at abuse temperatures because of the ingress of O_2 into the package (Ashie et al., 1996).

High temperature abuse (21°C–27°C) for periods of 12–24 h is a major concern because MAP fish generally do not become overtly spoiled under these conditions yet may be toxic, whereas fish held at the same temperatures under similar aerobic conditions start to become putrid before toxin production occurs. If MAP fish are held at very high chill temperatures (greater than 10°C), then strong spoilage signals may not develop in advance of *C. botulinum* toxin production.

Vacuum and MAP alone are not capable of providing the safety required for extended storage of seafood with respect to outgrowth and toxin production by *C. botulinum* type E. A fail-safe mechanism by which storage temperature can be maintained at or below 3°C is required. In order to effectively utilize the extended shelf life aspect of vacuum packaging and MAP, some intervention is needed to assure the delay of toxin production if even mild temperature abuse should occur.

In an extensive 5 year study involving 927 experiments and 18,700 samples, nonproteolytic *C. botulinum* types B, E and F in a variety of fresh fish stored between 4 and 30°C for up to 60 days were evaluated (Baker and Genigeorgis, 1990). A general formula that provides the most conservative model for the prediction of lag times was developed, and its utility was demonstrated by its ability to predict the time before toxigenesis of *C. botulinum* in inoculated fish stored under different MAs. Models based on lag times are regarded as most appropriate for pathogens with zero growth tolerance, such as *C. botulinum*, *Salmonella* and *Listeria*.

TABLE 17.7
Growth and Toxin Production by *Clostridium botulinum* in Packaged Fishery Products

Type of Fishery Product	Storage Temperature (°C)	Atmosphere CO_2:N_2:O_2	Toxin Detection (Days)	Shelf Life (Days)
Salmon fillet	16	Air	4	4
	16	75:25:0	4	5–6
	16	Vacuum	3	3
	8	Air	17	13–17
	8	75:25:0	24	20–24
	8	Vacuum	10	>6, <10
	4	Air	>66	24–27
	4	75:25:0	>80	55–62
	4	Vacuum	>66	34–38
Tilapia fillets	16	Air	4	3
	16	75:25:0	4	4
	16	Vacuum	3	3
	8	Air	20	6
	8	75:25:0	40	17
	8	Vacuum	17	10
	4	Air	>47	10
	4	75:25:0	>90	80
	4	Vacuum	>90	47
Catfish fillets	16	Air	3	3
	16	75:25:0	4	4
	16	Vacuum	3	3
	8	Air	9	6
	8	75:25:0	18	13
	8	Vacuum	6	6
	4	Air	>54	13
	4	75:25:0	>75	38–40
	4	Vacuum	46	20–24
Cod fillets	16	Air	>7	3–4
	16	75:25:0	7	6
	16	Vacuum	7	3–4
	8	Air	>41	13–17
	8	75:25:0	>60	24–27
	8	Vacuum	17	13
	4	Air	>60	20–24
	4	75:25:0	>90	55–60
	4	Vacuum	>5	24–27
Rainbow trout fillets	10	Vacuum skin packaging	6	3
	4	Vacuum skin packaging	<21	12
Channel catfish	10	Air	4	4–6
	10	80:20:0	4	2–6
	4	Air	9	9
	4	80:20:0	18	9–12

Source: Sivertsvik, M., Jeksrud W.K., and Rosnes T., *Int. J. Food Sci. Technol.*, 37, 107, 2002.

Another study (Graham et al., 1997) found growth and toxin production from spores of *C. botulinum* types B, E and F after 5 weeks at 3°C, 3–4 weeks at 4°C and 2–3 weeks at 5°C. Growth occurred more frequently from spores of type F strains than for types B and E.

The use of active packaging technologies such as O_2 scavengers and CO_2 emitters does not improve microbial safety above that obtained by traditional MAP and gives little or no additional shelf life to fresh seafood products compared to MAP and vacuum packaging (Sivertsvik, 2003).

The only effective way to assure the safety of chilled vacuum packaged or MAP fish products would be to either (1) keep the product at or below 3°C at all times, (2) heat the product sufficiently to destroy spores of all strains or (3) heat the product sufficiently to inactivate the nonproteolytic spores and then keep the product well below 10°C (Farber, 1991). The latter two points may be effective from a theoretical standpoint but, in practice, it may be difficult in a fish processing environment to avoid postprocessing contamination with spores of *C. botulinum* (Notermans et al., 1990). As mentioned earlier, many seafood products are eaten in the raw state; this makes the application of heat as a method of ensuring their microbiological safety an unacceptable approach. When chill storage is the only controlling factor, storage at temperatures between 5°C and 8°C should be limited to 5 days; shelf lives up to 10 days could be assigned for storage temperatures at 5°C or below.

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18 Packaging of Horticultural Products

18.1 INTRODUCTION

Fresh fruits and vegetables are essential components of the human diet as they contain a number of nutritionally important compounds such as vitamins and pigments that cannot be synthesized by the human body. A fruit or vegetable is a living, respiring and edible tissue that has been detached from the parent plant. Fruits and vegetables are perishable products with active metabolism during the postharvest period. In simple terms, the shelf life of fruits and vegetables can be extended by retarding the physiological, pathological and physical deteriorative processes (generally referred to as postharvest handling) or by inactivating the physiological processes (generally referred to as food preservation). Packaging has an important role to play in both the handling and preservation approaches to maximizing the shelf life; this chapter will primarily focus on the former since the packaging requirements of the preservation processes are not unique to horticultural products.

Difficulties arise when attempts are made to draw a clear line between fruits and vegetables. Fruits and vegetables cannot be clearly delineated botanically or morphologically as they encompass numerous organs in vegetative or reproductive stages and belong to a large number of botanical families. Fruits tend to be restricted to reproductive organs arising from the development of floral tissues, with or without fertilization, while vegetables consist simply of edible plant tissues. Thus, some fruits are included as vegetables and *vice versa*. Table 18.1 classifies horticultural produce according to the plant organ used, based mainly on the form in which the product is handled such as root, tuber, stem or leaf.

18.2 POSTHARVEST PHYSIOLOGY

Growth, maturation and senescence are the three important phases through which fruits and vegetables pass, the first two terms often being referred to as *fruit development*. *Ripening* (a term reserved for fruit) generally begins during the later stages of maturation and is considered the beginning of *senescence*, a term defined as the period when anabolic or synthetic biochemical processes give way to catabolic or degradative processes leading to aging and final death of the tissue.

18.2.1 RESPIRATION

Respiration involves the oxidation of energy-rich organic substrates normally present in cells such as starch, sugars and organic acids, to simpler molecules (CO_2 and H_2O) with the concurrent production of energy (ATP and heat) and other molecules which can be used by the cell for synthetic reactions. The principal carrier of free energy is ATP. The greatest yield of energy is obtained when the process takes place in the presence of molecular O_2. Respiration is then said to be aerobic. If hexose sugar is used as the substrate, then the overall equation can be written as follows:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy} \tag{18.1}$$

TABLE 18.1
Classification of Horticultural Produce according to the Plant Organ Used

Class	Commodities (Examples)
Root vegetables	Carrot, garlic, horseradish, onion, parsnip, radish, turnip
Tubers	Potato, yam, Jerusalem artichoke
Leaf and stem vegetables	Brussels sprouts, cabbage, celery, chicory, Chinese cabbage, cress, green onion, kale, lettuce, spinach
Flower vegetables	Artichoke, broccoli, cauliflower
Immature fruit vegetables	Bean, cucumber, gherkin, okra, pea, pepper, squash, sweet corn
Mature fruit vegetables	Melon, tomato
Reproductive organs	Most fruits

This transformation actually takes place in a large number of individual stages with the participation of many different enzyme systems. The water produced remains within the tissue but the CO_2 escapes and accounts for part of the weight loss of harvested fruits and vegetables, typically in the range of 3%–5%. When 1 mol of hexose sugar is oxidized, 36 mol of ATP (each possessing 32 kJ of useful energy) are formed. This represents about 40% of the total free energy change, the remainder being dissipated as heat. Rapid removal of this heat is usually desirable and it is important that the packaging assists, rather than impedes, this process.

The rate of respiration is often a good guide to the storage life of horticultural products: the higher the rate, the shorter the life; the lower the rate, the longer the life. Table 18.2 classifies vegetables according to their respiration intensities.

It is possible to evaluate the nature of the respiratory process from measurements of CO_2 and O_2. The ratio of the volume of CO_2 released to the volume of O_2 absorbed in respiration is termed the *respiratory quotient* (*RQ*). Values of *RQ* range from 0.7 to 1.3 for aerobic respiration, depending on the substrate being oxidized: $RQ = 1$ for carbohydrates, $RQ < 1$ for lipids and $RQ > 1$ for organic acids (Kader and Saltveit, 2003a).

Anaerobic respiration (sometimes called *fermentation*) involves the incomplete oxidation of compounds in the absence of O_2 and results in the accumulation of ethanol and CO_2:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2 + \text{energy} \tag{18.2}$$

Much lower amounts of energy (2 mol of ATP) and CO_2 are produced from 1 mol of hexose sugar than that produced under aerobic conditions. In addition, compared to aerobic respiration, very little

TABLE 18.2
Classification of Vegetables according to Respiration Intensity

Class	Respiration Intensity at 10°C; mg CO_2 kg^{-1} h^{-1}	Commodities
Very low	Below 10	Onion
Low	10–20	Cabbage, cucumber, melon, tomato, turnip
Moderate	20–40	Carrot, celery, gherkin, leek, pepper, rhubarb
High	40–70	Asparagus (blanched), eggplant, fennel, lettuce, radish
Very high	70–100	Bean, Brussels sprouts, mushroom, savoy cabbage, spinach
Extremely high	Above 100	Broccoli, pea, sweet corn

energy (~5%) is produced for a given amount of carbohydrate oxidation in anaerobic respiration. The O_2 concentration at which a shift from aerobic to anaerobic respiration occurs varies among tissues and is known as the extinction point (Kader and Saltveit, 2003a). Very high RQ values (>1.3) usually indicate anaerobic respiration.

18.2.1.1 Internal Factors Affecting Respiration

Variations in the rate of respiration occur during organ development; as fruits increase in size, the total amount of CO_2 emitted increases, although the respiration rate calculated on a per unit weight basis decreases continually. A majority of studies on gas exchange in plant tissues indicate that the skin represents the main significant barrier to diffusion. Clearly, the rate at which the three gases O_2, CO_2 and C_2H_4 diffuse through the tissue will have a significant effect on the rate of respiration.

Fruits may be divided into climacteric and nonclimacteric types. Climacteric fruits are those in which ripening is associated with a distinct increase in respiration and C_2H_4 production, with the respiration rate rising up to the climacteric peak and then declining. Such an increase can occur either while the fruit is attached to or separated from the plant. A further distinguishing feature is that treatment of climacteric fruits with C_2H_4 or propylene stimulates both respiration and autocatalytic C_2H_4 production. Low temperatures greatly reduce the magnitude of the climacteric. The climacteric generally coincides with changes associated with ripening such as color changes, softening, increased tissue permeability and the development of characteristic aromas. Typical climacteric fruits include apples, pears, peaches, nectarines, bananas, mangoes, plums, tomatoes and avocados.

In nonclimacteric fruits, ripening is protracted and the attainment of the ripe state is not associated with a marked increase in respiration or C_2H_4 production. Treatment of nonclimacteric fruits with C_2H_4 stimulates respiration only; there is no increase in autocatalytic C_2H_4 production. Citrus, strawberries and pineapples are examples of nonclimacteric fruits.

Generally, vegetables do not show a sudden increase in metabolic activity that parallels the onset of the climacteric in fruit, unless sprouting and regrowth is initiated.

18.2.1.2 External Factors Affecting Respiration

18.2.1.2.1 Temperature

Temperature is the most important environmental factor in the postharvest life of horticultural products because of its dramatic effect on the rates of biological reactions including respiration (Kader and Saltveit, 2003a). Typical Q_{10} (the ratio of the respiration rates for a 10°C interval) values for vegetables are 2.5–4.0 at 0°C–10°C, 2.0–2.5 at 10°C–20°C, 1.5–2.0 at 20°C–30°C and 1.0–1.5 at 30°C–40°C. Taking mean Q_{10} values, it can be calculated that the relative rate of respiration would increase from 1.0 at 0°C to 3.0 at 10°C, 7.5 at 20°C, 15.0 at 30°C and 22.5 at 40°C. These figures dramatically illustrate the need to reduce the temperature of fresh fruits and vegetables as soon as possible after harvesting in order to maximize the shelf life.

The rate of increase in respiration rates declines with an increase in temperature up to 40°C, with the Q_{10} becoming less than 1 as the tissue nears its thermal death point (about 50°C–55°C) when enzyme proteins are denatured and metabolism becomes disorderly (Kader and Saltveit, 2003a).

The storage life of some fruits and vegetables, primarily those of tropical or subtropical origin, can be limited by chilling injury, a disorder induced in whole plants or susceptible tissues by low (0°C–12°C) but nonfreezing temperatures. The extent of the chilling injury is influenced by the temperature, the duration of the exposure to a given temperature and the chilling sensitivity of the particular fruit or vegetable. The symptoms of chilling injury may not be evident while the produce is held at chill temperatures, only becoming apparent after transfer to a higher temperature. Chilling injury prevents some fruits from ripening and increases their susceptibility to fungal spoilage. Chilling injury is generally associated with necrosis of groups of cells situated either externally, leading to the formation of depressed areas, pitting and external discoloration or internally leading to internal browning.

TABLE 18.3
Classification of Fruits according to Their Maximum Ethylene Production Rate

Ethylene Production Rate μL kg^{-1} h^{-1} at 20°C	Fruits
Very low: 0.01–0.1	Cherry, citrus, grape, pomegranate, strawberry
Low: 0.1–1.0	Blueberry, kiwifruit, peppers, persimmon, pineapple, raspberry
Moderate: 1.0–10.0	Banana, fig, honeydew melons, mango, tomato
High: 10.0–100.0	Apple, apricot, avocado, plum, cantaloupe, nectarine, papaya, peach, pear
Very high: >100.0	Cherimoya, mamey apple, passion fruit, sapote

Source: Kader, A.A., *Food Technol*., 34(3), 51, 1980.

18.2.1.2.2 Ethylene

Ethylene is a natural plant hormone and plays a central role in the initiation of ripening. It is physiologically active in trace amounts (<0.1 ppm). The capacity to produce C_2H_4 varies greatly among fruits as shown in Table 18.3, with those fruits exhibiting moderate-to-very-high production rates generally being classified as climacteric fruits. Vegetables also produce C_2H_4, although data are comparatively scarce. Some typical figures in μL kg^{-1} h^{-1} at 20°C range from 0.04 for whole carrot roots, 0.02 for potato slices, 0.6 for intact cabbage head, 1.1 for summer squash, 1.7 for cauliflower head, 2.3 for Brussels sprouts, to 3.3–27.0 for broccoli head. Some fruit–vegetables such as tomatoes and melons are climacteric, while other fruit–vegetables such as cucumbers are not. The production of C_2H_4 by edible floral parts such as cauliflower and broccoli may be quite high and comparable with that of tomatoes.

When climacteric fruits are exposed to C_2H_4 during their preclimacteric stage, the time to the start of the climacteric rise in respiration is reduced. The magnitude of the final respiratory rise is controlled by the fruit's endogenous C_2H_4 production and is not influenced by added C_2H_4. A reduction in C_2H_4 production and sensitivity associated with modified atmospheres can delay the onset of the climacteric and prolong the storage life of these fruits.

When nonclimacteric tissues are exposed to C_2H_4, a climacteric-like rise in respiration is induced, proportional to the C_2H_4 concentration. Respiration rates return to their pretreatment level when the C_2H_4 is removed. Nonclimacteric fruits and vegetables can benefit from reduced C_2H_4 sensitivity and a lower respiration rate attributed to modified atmospheres.

The potent effects of C_2H_4 on plant growth, development and senescence mean that this gas, which is commonly found in the environment, can greatly reduce the storage life of perishable commodities sensitive to it. Important effects of C_2H_4 in hastening the deterioration of perishable commodities include accelerated senescence and loss of green color in leafy vegetables and some immature fruits (e.g., cucumbers, squash), accelerated ripening of fruits during handling and storage, russet spotting on lettuce, formation of a bitter compound (isocoumarin) in carrots, sprouting of potatoes, abscission of leaves (e.g., in cauliflower and cabbage) and toughening (lignification) of asparagus.

In addition to C_2H_4, several other hydrocarbons such as propylene and acetylene mimic the effects of C_2H_4 on respiration rates of fruits and vegetables (Kader and Saltveit, 2003a). Ethylene production is reduced by low O_2, high CO_2, or both and the effects are additive.

In 1994, it was discovered that the cyclic olefin 1-methylcyclopropene (1-MCP) was a specific inhibitor of ethylene action. Since that time, it has been used during postharvest storage to maintain quality by delaying ripening of partially ripe fruit through its effects on respiration, suppression of C_2H_4 production, volatile production, chlorophyll degradation and other color changes, protein and membrane changes, softening, disorders and diseases, acidity and sugars (Blankenship and Dole, 2003; Huber, 2008). It is complexed with γ-cyclodextrin to form a stable powder and when the powder is dissolved in water, 1-MCP is easily released as a gas (effective concentrations range from 0.25 to 1 μL L^{-1}) (Watkins, 2006). Treatment with 1-MCP is often combined with modification of the atmosphere.

18.2.1.2.3 Oxygen and Carbon Dioxide Concentration

A simple consideration of Equation 18.1 would suggest that if the CO_2 in the atmosphere were augmented (or the O_2 decreased), the respiration rate would be decreased and the storage life would be extended. Such is the case and the application of this approach is considered further in Section 18.3. However, fresh fruits and vegetables vary greatly in their relative tolerance to low O_2 concentrations (see Table 18.4) and elevated CO_2 concentrations (see Table 18.5), and optimum concentrations must be determined for each if modification of the atmosphere is to be successful.

Reduction of the O_2 concentration to less than 10% provides a tool for controlling the respiration rate and slowing down senescence, although an adequate O_2 concentration must be available to maintain aerobic respiration. Vegetable crops usually require a minimum O_2 content of 1%–3% in

TABLE 18.4
Classification of Fruits and Vegetables according to Their Tolerance to Low O_2 Concentrations

Minimum O_2 Concentration Tolerated (%)	Commodities
0.5	Tree nuts, dried fruits and vegetables
1.0	Some cultivars of apples and pears, broccoli, mushroom, garlic, onion, most cut or sliced (minimally processed) fruits and vegetables
2.0	Most cultivars of apples and pears, kiwifruit, apricot, cherry, nectarine, peach, plum, strawberry, papaya, pineapple, olive, cantaloupe, sweet corn, green bean, celery, lettuce, cabbage, cauliflower, Brussels sprouts
3.0	Avocado, persimmon, tomato, pepper, cucumber, artichoke
5.0	Citrus fruits, green pea, asparagus, potato, sweet potato

Source: Kader, A.A. et al., *CRC Crit. Rev. Food Sci. Nutr.*, 28, 1, 1989.

TABLE 18.5
Classification of Fruits and Vegetables according to Their Tolerance to Elevated CO_2 Concentrations

Maximum CO_2 Concentration Tolerated (%)	Commodities
2	Apple (Golden Delicious), Asian pear, European pear, apricot, grape, olive, tomato, pepper (sweet), lettuce, endive, Chinese cabbage, celery, artichoke, sweet potato
5	Apple (most cultivars), peach, nectarine, plum, orange, avocado, banana, mango, papaya, kiwifruit, cranberry, pea, pepper (chili), eggplant, cauliflower, cabbage, Brussels sprouts, radish, carrot
10	Grapefruit, lemon, lime, persimmon, pineapple, cucumber, summer squash, snap bean, okra, asparagus, broccoli, parsley, leek, green onion, dry onion, garlic, potato
15	Strawberry, raspberry, blackberry, blueberry, cherry, fig, cantaloupe, sweet corn, mushroom, spinach, kale, Swiss chard

Source: Kader, A.A. et al., *CRC Crit. Rev. Food Sci. Nutr.*, 28, 1, 1989.

the storage atmosphere and, at O_2 contents below 2%, most vegetables react with a sudden increase in CO_2 production. Glycolysis results in the formation of acetaldehyde, CO_2 and finally ethanol. Both acetaldehyde and ethanol are toxic to plant cells.

Elevated CO_2 levels can inhibit, promote or have no effect on C_2H_4 production by fruits. However, CO_2 has been shown to be a competitive inhibitor of C_2H_4 action, delaying fruit ripening by displacing C_2H_4 from its receptor site. The respiration rate of most root- or bulb-type vegetables when stored under elevated CO_2 levels is stimulated and, at concentrations above 20%, a significant increase in anaerobic respiration occurs which can irreversibly damage plant tissue.

Low O_2 and/or high CO_2 can reduce the incidence and severity of certain physiological disorders such as those induced by C_2H_4 (scald of apples and pears) and chilling injury of some commodities (e.g., avocado, citrus fruits, chili pepper and okra). On the other hand, O_2 and CO_2 levels beyond those tolerated by the commodity can induce physiological disorders such as brown stain on lettuce, internal browning and surface pitting of pome fruits and blackheart of potato (Kader et al., 1989).

18.2.1.2.4 Stresses

Physical damage such as surface injuries, impact bruising and vibration bruising can stimulate respiration and C_2H_4 production rates, depending on the variety of fruit or vegetable and the severity of the damage. The extent of the increase in respiration rate is usually proportional to the severity of bruising. However, the commercial implications of the bruising (i.e., the fact that consumers prefer not to purchase bruised fruits and vegetable) are of far greater importance than its effect on the respiration rate.

Water stress resulting from loss of water to the surrounding atmosphere can stimulate the respiration rate, although once the water loss exceeds 5%, the respiration rate may be reduced, coinciding with noticeable wilting and shriveling of the tissue (see next section).

18.2.2 TRANSPIRATION

18.2.2.1 Introduction

All fruits and vegetables continue to lose water through transpiration after they are harvested, and this loss of water is one of the main processes that affect their commercial and physiological deterioration. If transpiration is not retarded, it induces wilting, shrinkage and loss of firmness, crispness and succulence, with concomitant deterioration in appearance, texture and flavor. Most fruits and vegetables lose their freshness when the water loss is 3%–10% of their initial weight. As well as loss of weight and freshness, transpiration induces water stress which has been shown to accelerate senescence of fruits and vegetables.

18.2.2.2 Factors Influencing Transpiration

Several factors such as the surface area to volume ratio, nature of the surface coating, RH, temperature, atmospheric pressure and extent of any mechanical damage influence the transpiration process in fruits and vegetables.

The surface area to volume ratio can range from 50 to 100 $cm^2\ mL^{-1}$ for individual edible leaves to 5–10 $cm^2\ mL^{-1}$ for small soft fruits such as currants, 2–5 $cm^2\ mL^{-1}$ for larger soft fruits such as strawberries, 0.5–1.5 $cm^2\ mL^{-1}$ for tubers, pome, stone and citrus fruits, bananas and onions, to 0.2–0.5 $cm^2\ mL^{-1}$ for densely packed cabbage (Burton, 1982). Other factors being equal, a leaf will lose water and weight much faster than a fruit, and a small fruit or root or tuber will lose weight faster than a larger one.

While O_2, CO_2 and C_2H_4 diffuse mainly through air-filled stomata, lenticels, floral ends and stem scars, water vapor preferentially diffuses through the liquid aqueous phase of the cuticle (Zagory and Kader, 1988). In addition, there can be significant water vapor loss from cut tissues such as asparagus and celery ends.

Mechanical damage and physical injury, such as bruising, scratches and surface cuts, greatly accelerate the rate of water loss from fruit and vegetable tissue. Some tuber and root vegetables such as onions and potatoes retain the capacity to seal off wound areas after harvest when held at the appropriate temperatures and humidities (a process known as *curing*).

As mentioned earlier, respiration generates heat, which is dissipated through direct heat transfer to the environment and through evaporation of water. The heat of respiration raises the tissue temperature and therefore increases transpiration.

The ambient RH is not a very reliable guide to likely water loss and it is more useful to calculate the water vapor pressure deficit (WVPD) at the particular temperature and humidity. The WVPD of the air is defined as the difference between the water vapor pressure of the ambient air and that of saturated air at the same temperature (Ben-Yehoshua and Rodov, 2003). Thus, the drier the air, the greater the WVPD and the more rapidly any produce held in that environment will transpire. To minimize transpiration, produce should be held at low temperature, high RH and as small a WVPD as possible. Alternatively, packaging materials that have very low WVTRs can be used. However, the problem in these situations is that decay processes are favored.

18.2.3 Postharvest Decay

Once microorganisms are established in plant tissue, they can proliferate and secrete enzymes to bring about quality deterioration. Frequently, there is a lag period between infection and any manifestation of the presence of microorganisms. The most common pathogens causing harvested vegetables to rot are fungi such as *Alternaria*, *Botrytis*, *Diplodia*, *Monilinia*, *Penicillium*, *Phomopsis*, *Rhizopus* and *Sclerotinia* and the bacteria *Erwinia* and *Pseudomonas*. The majority of these can only invade damaged tissue such as bruised structures and fractured cells. The development of postharvest decay is favored by high temperatures and high humidities, with the latter often a result of condensation which may affect spore germination and can cause tissue anaerobiosis.

Acidic fruit tissue is generally attacked and rotted by fungi, while many vegetables with a tissue pH above 4.5 are more commonly attacked by bacteria. Initially only one or a few pathogens may invade and break down the tissues, followed by a broad spectrum attack of several weak pathogens which results in complete loss of the produce.

18.3 MODIFIED ATMOSPHERE PACKAGING OF FRESH HORTICULTURAL PRODUCE

18.3.1 Introduction

As stated earlier, a simple consideration of Equation 18.1 would suggest that if the CO_2 in the atmosphere were augmented (or the O_2 decreased), then the respiration rate would decrease and the shelf life would be extended. This is the basis of modified atmosphere packaging (MAP) as discussed in Chapter 16. The recommended concentrations of O_2 and CO_2 for fruits and vegetables can be found in the published literature, and a very effective way of plotting this data with CO_2 concentration as the ordinate and O_2 concentration as the abscissa is presented in Figures 18.1 and 18.2 (Kader et al., 1998). The windows represent the boundary of recommended gas concentrations; the smaller the window the more rigid the design requirement. Thompson (2010) reviewed the increase in shelf life for a wide range of fruit and vegetables packaged under MAP.

The permselectivity ratio β (permeability coefficients of CO_2:O_2) for air is ~0.8 (Table 18.6) and this is represented as line A–D in Figures 18.1 and 18.2. An otherwise impermeable package with a few small holes can be used to create atmospheres along this line; no vegetable windows fall on this line but it does pass through the window for berry fruits and figs. Line A–B is plotted for a β of 5.0 which is approximately the value for LDPE and PVdC copolymer films. This line bisects several windows indicating that these films could be used successfully for some fruits and vegetables.

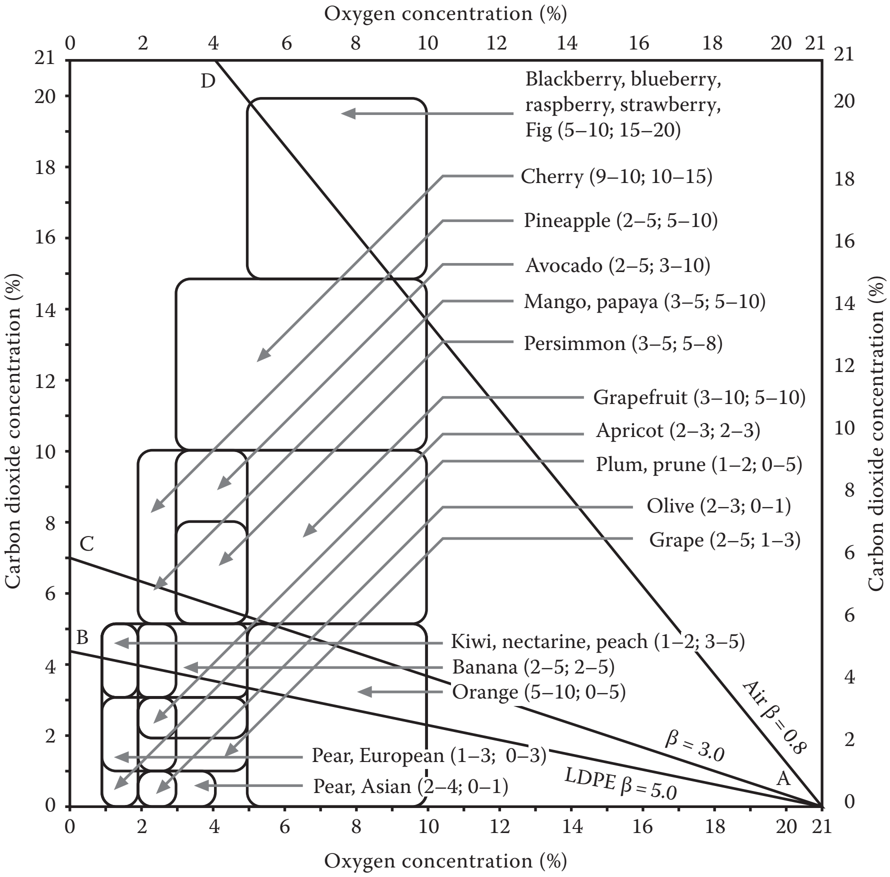

FIGURE 18.1 Recommended modified atmospheres for storage of fruits. (From Kader, A.A. et al., Technologies to extend the refrigerated shelf life of fresh fruits, in: *Food Storage Stability*, Taub, I.A. and Singh, R.P. (Eds), CRC Press, Boca Raton, FL, pp. 419–434, 1998).

However, PVdC copolymer is suitable only for produce with very low respiration rates because it has such low gas permeabilities (Table 18.6). The CO_2-O_2 atmospheres that lie between the lines A–B and A–D may be created by using packages made from LDPE film with perforations or microporous windows. The permselectivity ratios are not constant for a given polymer but increase as the temperature is lowered. For example, β for LDPE has been reported to range from 5.08 at 0°C to 3.45 at 20°C and β for PVC from 6.0 at 5°C to 4.0 at 40°C. Line A–C is plotted for a β of 3.0.

Since the 1960s, attempts have been made to create and maintain modified atmospheres within plastic polymeric films (Varoquaux and Ozdemir, 2005). As discussed in Chapter 15, the availability of absorbers of O_2, CO_2, C_2H_4 and water provides additional tools for the packaging technologist to use to maintain a desired atmosphere within a package. Details of such systems are now discussed.

18.3.2 Factors Affecting MAP

The conditions created and maintained within a package are the net result of the interplay among several factors, including those related to the specific fruit or vegetable and those related to the surrounding environment (Zagory, 1995).

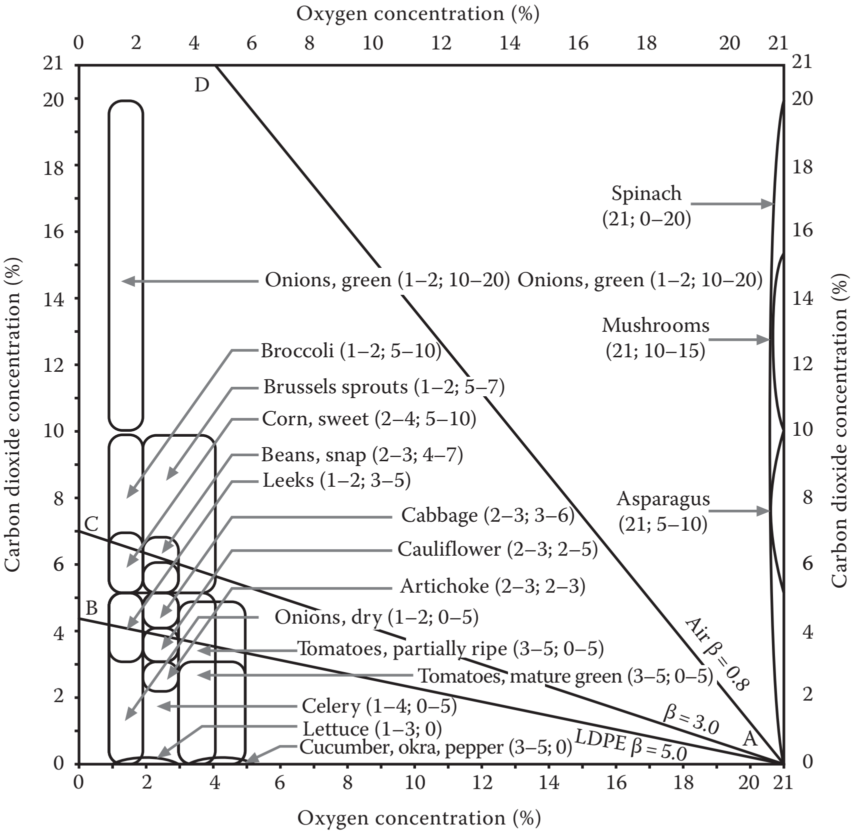

FIGURE 18.2 Recommended modified atmospheres for storage of vegetables. (From Kader, A.A. et al., Technologies to extend the refrigerated shelf life of fresh fruits, in: *Food Storage Stability*, Taub, I.A. and Singh, R.P. (Eds), CRC Press, Boca Raton, FL, pp. 419–434, 1998).

18.3.2.1 Resistance to Diffusion

Movement of O_2, CO_2 and C_2H_4 in fruit tissue occurs by diffusion of the gas molecules under a concentration gradient. O_2 in the environment immediately surrounding the external surface of the tissue diffuses in the gas phase through the dermal system and into the intercellular system; it then diffuses from the intercellular atmosphere into the cellular solution (cell sap) from where it diffuses in solution within the cell to centers of consumption. CO_2 and C_2H_4 produced in the cell sap diffuse outward to the ambient environment under a concentration gradient.

The rate of gas movement depends on the properties of the gas molecule, the magnitude of the gradient and the physical properties of the intervening barriers. Both the solubility and diffusivity of each gas are important for its diffusion across barriers, with CO_2 moving more readily than O_2; CO_2 and C_2H_4 have similar diffusion rates (Kader and Saltveit, 2003b).

Different commodities have different total amounts of internal air space; for example, potatoes have only 1%–2% while tomatoes have 15%–20% and apples have 25%–30%. A limited amount of air space could lead to a significant tissue resistance to gas diffusion. In addition, the cell wall appears to present some resistance to gas diffusion and thus a gradient between the cells and the intercellular space may be expected to develop (Kader et al., 1989).

Internal concentrations of O_2 and CO_2 in plant tissues depend on the stage of maturity at harvest, respiration rate, temperature, composition of the external atmosphere and added barriers (Kader and Saltveit, 2003b).

TABLE 18.6
Average Permeability Data[a] and Permselectivity Ratios of Some Polymeric Films, Air and Water to O_2 and CO_2 at 25°C and 5°C and 0% RH

	P in *barrer*		Permselectivity Ratio	Activation Energy E_P (kJ mol^{-1})	
Polymer	O_2	CO_2	β	O_2	CO_2
Low density polyethylene	4.9	21	4.3	43	39
	1.4	6.8	4.9		
High density polyethylene	0.9	3.1	3.4	35	30
	0.3	1.3	4.3		
Polypropylene	1.6	9.2	5.8	48	38
	0.4	3.1	7.8		
Poly(vinyl chloride) film	0.06	0.52	8.7	56	57
	0.01	0.10	10		
Poly(ethylene terephthalate)	0.13	0.26	2.0	38	28
(amorphous)	0.04	0.11	2.8		
(40% crystalline)	0.024	0.14	5.8	32	18
	0.009	0.08	8.9		
Poly(lactic acid) (98% *L*)	0.34	1.88	5.5	41	16
	0.10	1.18	11.8		
PVdC copolymer	0.006	0.029	4.8	67	52
	0.0009	0.006	6.7		
Perforated film (air)	2.5×10^7	1.9×10^7	0.76	3.6	3.6
	2.3×10^7	1.7×10^7	0.74		
Water	90	2.1×10^3	23.3	15.8	15.8
	57	1.3×10^3	22.8		

[a] Values taken from Table 4.3 and recalculated for 5°C using Equation 4.27.

A majority of studies on gas exchange in plant tissues indicate that the skin represents the main significant barrier to gas diffusion. Skin resistance to water vapor diffusion is much lower than resistance to O_2, CO_2 or C_2H_4 diffusion. As plant organs advance into the senescent stage, cell walls and membranes begin to break down, flooding some of the intercellular space with cell sap. In addition, the peel of some fruit may shrivel after prolonged exposure to lower water vapor concentrations. Consequently, the resistance of tissue to gas diffusion increases and may become significant (Kader et al., 1989).

18.3.2.2 Respiration

The respiration rate of a commodity inside a polymeric film package depends on the kind of commodity, its stage of maturity and physical condition, the concentrations of O_2, CO_2 and C_2H_4 inside the package, the quantity of product within the package, temperature and possibly light (Kader et al., 1989). These factors were discussed earlier in Section 18.2.1. Suffice it to say that the interplay of these factors leads to a complex situation about which it is difficult to make quantitative predictions (see Section 18.3.4).

18.3.2.3 Temperature

It is impossible to make any specific predictions about the magnitude of the effect of a change in temperature on MAP since a number of key, interrelated factors are involved. Any change in temperature will affect the respiration rate; it will also affect gas diffusion between the cell sap and the intercellular spaces, with the solubility of gases in liquids decreasing with increasing temperature. In addition, any change in temperature will affect the permeability of the plastic film surrounding the fruit or vegetable.

It is extremely unlikely that, as a result of any change in temperature, the change in respiration rate will match the change in gas permeability rates of the film. For a match to occur, the activation energy of permeation E_P would have to equal the activation energy of the respiration process and this is most unlikely. For example, Lakakul et al. (1999) reported, E_P for O_2 in LDPE as 37 kJ mol^{-1} and apparent E_A's for respiration of apple slices of 75 kJ mol^{-1} at 16 kPa O_2 and 55 kJ mol^{-1} at 0.5 kPa O_2, three times higher than for intact fruit. Exama et al. (1993) reported that E_A values for common fruits and vegetables in air range from 29.0 to 92.9 kJ mol^{-1}.

If the activation energies are not approximately equal, the equilibrium gas concentrations inside the package will change, which in turn will affect the respiration rate. If the temperature stabilizes, new equilibrium conditions will be established; however, if the temperature continues to change, steady-state conditions will never be reached. It is the complex nature of this dynamic situation that makes modeling of MAP so difficult (see Section 18.3.4).

18.3.3 Methods of Creating MA Conditions

The two methods for creating MA conditions are either passive or active and they were discussed in Chapter 16. Passive MA creation relies on the respiration of the produce and the gas permeability properties of the film to achieve the desired MA. Active MA creation involves gas flushing and gas scavenging technology by adding, for example, CO_2 and N_2, and/or removing O_2 during packaging. Although the passive method was the traditional approach taken with horticultural produce, the active approach is increasingly common. The main reason for this is the time required to achieve the desired MA: a week or longer may be necessary using the passive approach as shown in Figure 18.3. Such a delay is particularly unacceptable for fresh cut (minimally processed) produce where, for example, enzymic browning reactions need to be inhibited as soon as possible.

18.3.4 Design of MAPs

18.3.4.1 General Concepts

The selection of suitable packaging materials and the evaluation of MAP for fresh fruits and vegetables have traditionally been a largely empirical, trial-and-error exercise that is time-consuming, subjective and often without unifying principles to guide the research and development efforts. This empirical approach can lead to long testing times, high development costs, costly over packaging and the absence of a mechanism to fine-tune a packaging system once it has been developed. In an attempt to put the design of MAP on an analytical basis, a number of research groups have proposed and tested mathematical models (Yam and Lee, 1995; Mahajan et al., 2007) and these have been reviewed by Rodriguez-Aguilera and Oliveira (2009) and Zhang et al. (2011); few are used commercially. University College Cork in Ireland has developed the web-based software

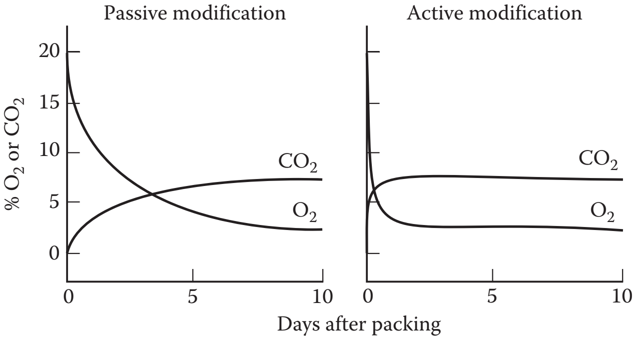

FIGURE 18.3 Relative changes in O_2 and CO_2 concentrations during passive modification and active modification of packaged horticultural products. (From Zagory, D. and Kader, A.A., *Food Technol.*, 42(9), 70, 1988).

tool PACK-in-MAP™ that helps in designing MAP for fresh and fresh-cut fruits and vegetables (www.packinmap.com). A practical software simulation tool to predict the amount of O_2 permeating into the package headspace during storage for a variety of multilayer packaging configurations was described by Van Bree et al. (2010).

In order to predict what the equilibrium gas concentrations will be and how long it will take to achieve equilibrium, a model should take into account the following factors (Zagory and Kader, 1988):

1. The effects of changing O_2 and CO_2 concentrations on the respiration rate
2. The possibility that the *RQ* is not equal to 1
3. The permeability of the film to O_2 and CO_2
4. The effect of temperature on film permeability
5. The surface area and headspace of the package
6. The resistance of the commodity to diffusion of gases through it
7. The optimal atmosphere for the commodity of interest
8. The gas concentrations which are likely to be deleterious to the commodity and if they are likely to be reached before or after equilibrium

The key part of any model is the relationship between the rate of respiration by the commodity and the permeation rate of respiratory gases through the package. As the O_2 supply within the plant cells begins to decrease as a result of respiration, the partial pressures of O_2 between the cells and the package interior and exterior atmospheres become unbalanced, causing some O_2 to diffuse into the package. When the rate of O_2 consumption exceeds the rate of O_2 permeation into the package, the O_2 concentration in the package decreases. This, in turn, further slows the respiration rate to the point where the rate of O_2 consumed equals the rate of O_2 permeation through the package film.

True equilibrium in the package would be reached when the gas flux due to respiration equaled the gas flux due to permeation; that is, O_2 was being consumed at the same rate at which it was entering the package, and CO_2 was being produced at the same rate at which it was leaving the package. However, unless the package is held under very closely controlled temperature conditions, it is doubtful if true equilibrium is ever achieved. This has not stopped some authors from referring to equilibrium MAP or EMAP when they mean the optimum or target atmosphere, for example, Del-Valle et al. (2009). Furthermore, since no polymeric film has the same permeability to O_2 as to CO_2, and because anoxic conditions and resultant anaerobic respiration are to be avoided at all costs, steady-state conditions inside a package are generally taken to be when the rate of O_2 consumption equals the rate of O_2 permeability through the film. In such situations, the concentration of CO_2 inside the package will increase over time, because the partial pressure difference of CO_2 across the package film will, at least in the early stages, be so low as to result in negligible gas flux to the external atmosphere.

The real challenge in designing and developing MA packages for fresh produce is to determine the O_2 consumption and CO_2 evolution rates under the variable atmosphere conditions existing in the package. These values can be found in the literature for many products under normal atmosphere but not under abnormal atmosphere conditions.

In examining the factors listed earlier, several important aspects must be remembered. The standard approach to measuring the gas permeabilities of films (see Chapter 4) uses Fick's law with some simplifying assumptions, the most salient in the present context being that there is a constant partial pressure difference across the film of the gas under consideration. Clearly, in MAP, this is not the case until (if ever) equilibrium is reached. Thus, the use of traditional film permeability data (if it is available at the temperatures of interest) to calculate likely gas fluxes will require accurate data on the pressure gradients across the package at any particular time.

18.3.4.2 Developing a Predictive Model

Because the shelf life of fresh horticultural produce can be extended by packaging in an atmosphere of reduced O_2 and elevated CO_2, it is of practical importance to be able to design a package to maintain the desired concentrations of O_2 and CO_2 inside a single retail package of fresh produce. A predictive model makes the design process more focused and rapid (Hertog and Banks, 2003).

The influx of O_2 and efflux of CO_2 at a specific temperature are determined by the permeability of the package, the thickness and surface area of the film, and the partial pressure gradients of O_2 and CO_2 inside and outside the package. The first three parameters should be specified by the designer of the package, while the partial pressure gradients are dictated by the desired atmospheric composition inside the package and the ambient atmosphere.

The starting point for the development of a predictive model for MAP is the application of Fick's law to the package system. From Equation 4.15, the flux of O_2 through a polymeric film can be described as follows:

$$Q_{\mathrm{O}} = \frac{P_{\mathrm{O}}}{X} A(p_{\mathrm{Oo}} - p_{\mathrm{Oi}}) \tag{18.3}$$

where

Q_{O} is the diffusive flux of O_2 through the package in unit time
P_{O} is the O_2 permeability coefficient of the package at the temperature of storage
A is the surface area of the package
X is the thickness of the film
p_{Oo} is the partial pressure of O_2 outside the package (0.209 atm)
p_{Oi} is the partial pressure of O_2 inside the package

A similar expression can be written for the flux of CO_2 through the package:

$$Q_{\mathrm{C}} = \frac{P_{\mathrm{C}}}{X} A(p_{\mathrm{Ci}} - p_{\mathrm{Co}}) \tag{18.4}$$

where

Q_{C} is the diffusive flux of CO_2 through the package in unit time
P_{C} is the CO_2 permeability coefficient of the package at the temperature of storage
p_{Ci} is the partial pressure of CO_2 inside the package
p_{Co} is the partial pressure of CO_2 outside the package (0.0003 atm but essentially zero)

The flux of O_2 into the fruit or vegetable is a function of the respiration rate (RR_{O}), which in turn is a function of the O_2 (and maybe CO_2) concentration within the package (Fonseca et al., 2002):

$$Q_{\mathrm{f}} = RR_{\mathrm{O}}W \tag{18.5}$$

where

Q_{f} is the flux of O_2 into the fruit per unit time
RR_{O} is the respiration rate or O_2 uptake of the fruit (mL kg^{-1} h^{-1}) as a function of O_2 partial pressure inside the package
W is the weight of fruit in the package

At equilibrium, the O_2 flux through the film and into the fruit should be equal; that is, $Q_O = Q_f$. On rearranging Equations 18.3 and 18.5,

$$\frac{P_O A}{X} = \frac{RR_O W}{(p_{Oo} - p_{Oi})} \tag{18.6}$$

Thus, Equation 18.6 enables the prediction of the O_2 permeability requirements provided RR_O, the relationship between the respiration rate and O_2 concentration, is known. Inspection of Equation 18.6 indicates that the equilibrium concentration of O_2 (p_{Oi}) is independent of time; this is understandable since the time to equilibrium depends on the free or headspace volume of the package. The smaller the free volume, the faster equilibrium or steady-state conditions are reached.

The effect of changing the surface area of the package or the weight of produce in the package can be calculated by rearranging Equation 18.6:

$$\frac{A}{W} = \frac{RR_O X}{P_O(p_{Oo} - p_{Oi})} \tag{18.7}$$

Similar calculations can be made to calculate the effect of changing the thickness of the film X.

A similar equation to Equation 18.6 can be derived for CO_2:

$$\frac{P_C A}{X} = \frac{RR_C W}{(p_{Ci} - p_{Co})} \tag{18.8}$$

Equations 18.6 and 18.8 can be rearranged to make A/WX the subject of each equation and then combined:

$$\frac{A}{WX} = \frac{RR_O}{P_O(p_{Oo} - p_{Oi})} = \frac{RR_C}{P_C(p_{Ci} - p_{Co})} \tag{18.9}$$

and

$$(p_{Ci} - p_{Co}) = \frac{P_O}{P_C}(p_{Oo} - p_{Oi})\frac{RR_C}{RR_O} \tag{18.10}$$

If gas concentrations (c), rather than partial pressures (p), are used (for example, 10% O_2 (v/v) = 0.1 atm = 10.13 kPa), RQ is the respiratory quotient RR_C/RR_O and the permselectivity ratio of P_C to P_O is designated as β, then

$$c_{Ci} = \frac{1}{\beta}(c_{Oo} - c_{Oi})RQ + c_{Co} \tag{18.11}$$

and

$$c_{Ci} = \left[c_{Co} + \frac{RQ}{\beta}c_{Oo}\right] - \frac{RQ}{\beta}c_{Oi} \tag{18.12}$$

For a specific film and RQ, the terms inside the bracket are all constant and there is a linear relationship between c_{Ci} and c_{Oi} with a slope equal to $-RQ/\beta$.

The intercept on the *y* axis can be calculated by letting $c_{\text{Oi}} = 0$ and assuming that $RQ = 1$ and $\beta = 5$. Then,

$$c_{\text{Ci}} = c_{\text{Co}} + \frac{RQ}{\beta} c_{\text{Oo}}$$

$$= 0.0003 + \frac{0.21}{5} = 0.0423 = 4.23\%.$$

Similarly, when $\beta = 0.8$,

$$c_{\text{Ci}} = 0.0003 + \frac{0.21}{0.8} = 0.2628 = 26.3\%.$$

Using Equation 18.12, it is possible to construct lines for various β values. For example, for LDPE film where $\beta \approx 5$ at 5°C (Table 18.6) and assuming that $RQ = 1$, results in the straight lines A–B in Figures 18.1 and 18.2, both with a slope of −1/5. The implication is that only the modified atmospheres falling along the line A–B can be generated by LDPE film, for example, 2.2% CO_2 and 11% O_2, or 1.4% CO_2 and 16% O_2. Clearly the value of the respiratory quotient *RQ* affects the slope of the line A–B; *RQs* greater than unity will result in slopes greater than $-1/\beta$ and *vice versa*.

It is helpful to understand the importance of film thickness and surface area on MAP. Consideration of Equations 18.3 and 18.4 indicates that doubling the thickness of a film will halve the amount of gas that can move across the film in a given amount of time; making the film thinner will have the opposite effect. Once the β of the film is known, the thickness of the film will help determine where on the β line the actual gas concentrations in the package will lie (Figures 18.1 and 18.2). Increasing the thickness or decreasing the surface area of the film will move the gas equilibrium concentrations up the β line owing to reduced gas movement across the film. Increasing the weight of produce inside the package will have a similar effect because more produce will consume more O_2 and produce more CO_2.

The quantitative relationship between these factors can be expressed by rearranging Equation 18.6 and substituting concentrations for partial pressures:

$$P_{\text{O}} = \frac{RR_{\text{O}}WX}{A(c_{\text{Oo}} - c_{\text{Oi}})} \tag{18.13}$$

Equation 18.13 enables calculation of the desired permeability of a plastic film to supply sufficient O_2 to a product in order to prevent anaerobic conditions, provided the product respiration rate at the desired O_2 concentration is known; such data can often be found in the scientific literature (Zagory, 1995).

The aforementioned concepts were used in the development of a model to analyze the effect of the key parameters on the design of polymeric MA packages (Kader et al., 1998). The design parameters selected were *W*, *A*, *X*, P_{O} and P_{C}, the last three parameters being fixed when a specific film of given thickness is selected, leaving only *W* and *A* as design variables.

If the ratio *W*:*A* is denoted by τ, then Equations 18.6 and 18.8 can be rearranged to yield

$$c_{\text{Oi}} = c_{\text{Oo}} - \frac{XRR_{\text{O}}}{P_{\text{O}}} \tau \tag{18.14}$$

$$c_{\text{Ci}} = c_{\text{Co}} - \frac{XRR_{\text{C}}}{P_{\text{C}}} \tau \tag{18.15}$$

If the respiration rates do not change with gas concentrations, then any changes in τ simply move the gas compositions inside the package along the line A–B. As τ increases, the O_2 concentration decreases and the CO_2 concentration increases. Thus, the package atmosphere moves toward B on the line A–B in direct proportion to the increase in τ.

However, the respiration rate usually decreases as the package atmosphere moves toward B, and therefore the actual change in package atmosphere is smaller than that dictated by the increase in τ alone. Similarly, the effect of any decrease in τ will also be moderated. Therefore, the effect of any errors made in the selection of τ will be moderated to a large extent by the response of respiration rate to the change in package atmosphere (Kader et al., 1998).

Equation 18.6 can be rewritten as follows:

$$P_O = \frac{RR_O WX}{A(p_{Oo} - p_{Oi})} \tag{18.16}$$

Similarly for Equation 18.8:

$$P_C = \frac{RR_C WX}{A(p_{Co} - p_{Ci})} \tag{18.17}$$

Assuming that $RR_O = RR_C$ and substituting for P_O and P_C yields the following equation:

$$\beta = \frac{P_C}{P_O} = \frac{p_{Oo} - p_{Oi}}{p_{Ci} - p_{Co}} \tag{18.18}$$

If air surrounds the package, then p_{Oo} is approximately 0.21 atm and since p_{Co} is essentially zero, Equation 18.18 can be simplified to

$$\beta = \frac{0.21 - p_{Oi}}{p_{Ci}} \tag{18.19}$$

Table 18.6 lists average values for P_O and P_C and the corresponding β values for some common polymeric films as well as air and water. The values at 5°C were obtained from the values at 25°C using the appropriate activation energy for permeation E_P as the following example demonstrates.

Example 18.1

Equation 4.27 can be written for each temperature:

$$P_5 = P_o \exp\left(\frac{-E_p}{RT_5}\right)$$

$$P_{25} = P_o \exp\left(\frac{-E_p}{RT_{25}}\right)$$

On dividing the first equation by the second:

$$P_5 = P_{25} \exp\left(\frac{-E_p}{R\left[1/T_5 - 1/T_{25}\right]}\right)$$

The temperatures must be converted from °C to K:

$$\frac{1}{T_5} = \frac{1}{(273+5)} = \frac{1}{278} = 0.003597$$

$$\frac{1}{T_{25}} = \frac{1}{(273+25)} = \frac{1}{298} = 0.003356$$

To calculate the O_2 permeability of PVdC copolymer at 5°C and E_P = 67,0000 J mol^{-1}

$$P_5 = 0.006 \exp\left(\frac{-67{,}000}{8.314\left[0.003597 - 0.003356\right]}\right)$$

$$= 0.006 \exp(-8059 \times 0.000241)$$

$$= 0.006 \exp(-1.9422)$$

$$= 0.006 \times 0.1434$$

$$= 8.6 \times 10^{-4}\, \textit{barrer}$$

That is, P is seven times greater at 25°C than at 5°C.

Example 18.2

Assume that a company wanted to package sweet corn in a MA and store it at 5°C. From Figure 18.2, the optimum atmosphere is 2%–4% O_2 and 5%–10% CO_2. Taking the midpoint concentrations for both gases and substituting in Equation 18.19:

$$\beta = \frac{0.21 - p_{\text{Oi}}}{p_{\text{Ci}}} = \frac{0.21 - 0.03}{0.075} = 2.4 \tag{18.20}$$

From Table 18.6, it can be seen that at 5°C there are no films that have a β value of 2.4, although amorphous PET is close at 2.8. If the β value is recalculated for 2% O_2 and 5% CO_2, a value of 3.8 is obtained; for 4% O_2 and 10% CO_2, the β value is 1.7. Given this wide range of values for β, it is clear that such calculations provide only a rough guide to selecting suitable films for MAP of fruits and vegetables. Once a candidate film has been selected, trials are required to confirm the choice and ensure that the desired atmospheres are in fact achieved.

In the case where the film has similar permeability coefficients to both O_2 and CO_2 (i.e., $\beta = 1$), the sum of the partial pressures of O_2 and CO_2 inside the package will equal 0.21 atm. The final volume concentrations of O_2 and CO_2 inside the package will be ~21%, the exact value depending on the *RQ* of the product. Therefore, products requiring optimum atmospheres of say 5% O_2 and 15% CO_2 could achieve this by using a perforated package. From Figure 18.1, it can be seen that blackberries, blueberries, figs, raspberries, strawberries and cherries are suitable for packing in perforated packages.

However, because in reality the permeability coefficients of commercial films are different for O_2 and CO_2 (P_C is typically 3–6 times P_O as shown in Table 18.6), the sum of the partial pressures will be less than 0.21 atm. Although the partial pressure of CO_2 inside the package increases and the partial pressure of O_2 decreases, the total pressure of these two gases will be less than 0.21 atm. Given that according to the gas laws, the total pressure times the volume is a constant, the volume of the package will decrease. As the volume of the package decreases, the partial pressure of N_2 inside the package will exceed the partial pressure of N_2 outside. This results in the permeation of N_2 through the package to the outside and, in certain situations, the reduction in package volume is such that the film adheres to the surface of the fruit or vegetable. In other situations, such as the onset of anaerobic respiration where there is a rapid buildup of CO_2, the total pressure inside the package may increase, causing the package to bulge. This would cause the partial pressure of both O_2 and N_2 inside the package to decrease and favor permeation of these gases into the package. The actual scenario depends on whether the package is rigid or flexible. In a rigid package, the free volume remains constant, while the total pressure may change, whereas in a perfectly flexible package, the total pressure remains constant while the free volume may change (Talasila and Cameron, 1997).

It is not only the permselectivity ratio which is important, but also the actual magnitude of the permeability values. If the permeability coefficients are very small, then the gas fluxes will be very low and there is the possibility of anoxic conditions or undesirably high concentrations of CO_2 developing inside the package.

As is evident from Table 18.6, the β value for a particular film is not constant but varies with temperature; the higher the temperature, the lower the β value. In a study based on 122 permeability measurements of LDPE film, β values at 0°C, 5°C, 10°C, 15°C and 20°C were 5.08, 4.63, 4.16, 3.79 and 3.45, respectively; data from eight other film types (not specified) showed that, with one exception, the ratios increased as the temperatures decreased toward 0°C (Tolle, 1971). As many authors have noted, there is a dearth of actual film permeability values at the temperatures and humidities likely to be encountered during storage of MAP horticultural produce.

Another important variable can be the free or headspace volume of the package. In converting concentration measurements into volume of gases, it is usually assumed that the total pressure in the enclosed system is constant over time. However, this is true only when the *RQ* of the produce is unity. As was discussed earlier, this is certainly not always the case in MAP of fresh produce.

For models such as that described earlier to be widely applicable, a great deal of data is required, including the permeances of potentially useful films at likely storage temperatures and the relationship between the rate of respiration and O_2 concentration. It is also necessary to have similar data for CO_2 so that the potentially damaging effects of high CO_2 concentrations on produce quality can be avoided. Even with all this data, the reality is that few polymeric films are capable of maintaining the desired MAs. That is why perforated films and, more recently, films with an adjustable selectivity for CO_2 and O_2 and permeability that increases dramatically as temperature increases (Clarke, 2011), have been developed.

18.4 PACKAGING OF HORTICULTURAL PRODUCTS

18.4.1 Fresh and Minimally Processed Horticultural Produce

18.4.1.1 Introduction

The quality of fruits and vegetables comprises several parameters including flavor, aroma, texture, appearance, nutrition and safety, and the relative importance of each parameter depends on the particular commodity and its intended use. The quality of the produce is compromised whenever one of these parameters falls below a certain desirable level. The most important aspect of produce quality is freshness, typified by the quality of a fruit or vegetable when it is freshly harvested (Cardello and Schutz, 2003). Fresh fruits and vegetables are expected to be crisp, not tough, sweet (where appropriate), juicy, nutritious and free from defects (Zagory, 1995). The challenge is to maintain these properties of freshness during long transportation and marketing periods and packaging has a key role to play here.

In addition to maintaining freshness, modern retail packaging of fresh horticultural produce is expected to meet a wide range of requirements including prevention of mechanical damage resulting from handling, compression and impact; minimization of weight loss and shrinkage and, if the produce is at ambient temperature at the time of packing, the ability to cool the produce rapidly after packing.

Minimally processed fruits and vegetables (MPFVs) are products that have the attributes of convenience and fresh-like quality, and their forms vary widely depending on the nature of the unprocessed commodity and how it is normally consumed. They are increasingly referred to as *fresh-cut* produce, defined as any fresh fruit or vegetable or any combination thereof that has been physically altered from its original form but remains in a fresh state (Lamkanra, 2002). MPFVs have gained a significant proportion of the fresh produce market since their introduction to the U.S. market in the 1970s and to European markets in the 1980s. The purpose of minimal processing is to deliver to the consumer a like-fresh product with an extended shelf life, while simultaneously maintaining the nutritional and sensory quality and ensuring food safety.

MPFVs remain biologically and physiologically active and this results in increased metabolic activity including increased respiration rates. In some cases, C_2H_4 production may also increase. The physiology of minimally processed products is essentially that of wounded tissues as a result of mechanical injury resulting from processes such as cutting, trimming and peeling. Wounding of tissues induces a number of physiological disorders that need to be minimized to get fresh-like quality products. The intensity of the wound response is affected by a great number of factors, the most significant being species and variety, O_2 and CO_2 concentrations, water vapor pressure and the presence of inhibitors.

Of key importance with MPFVs is the control of enzymes, either endogenous from the produce itself or exogenous from invading microorganisms, to maintain the firm, crisp texture and bright, light color. The enzymes can be controlled by inactivation or chemical or physical means. Methods that are currently used include temperature, MAs, very high pressures and chemicals such as ascorbic acid, vanillin (which inhibits polygalacturonase), mannose (which reduces C_2H_4 production, respiration and softening in pears) and gases such as SO_2, CO and ethylene oxide. However, it is unlikely that the widespread use of the latter three gases would ever gain regulatory approval or meet with consumer acceptance given the current trend toward additive-free food.

Enzymic browning caused by polyphenoloxidase (PPO) is often the major concern related to shelf life extension of fresh-cut fruit and strongly affects the consumer's purchase decision. Although sulfites were traditionally used for browning prevention, their use on fresh-cut fruit and vegetables was banned in 1986 by the FDA owing to their potential health hazards. Various alternative approaches have been investigated including reducing agents such as citric acid, ascorbic acid, isoascorbic acid and sodium erythorbate, and thiol-containing amino acids such as *N*-acetylcysteine and glutathione, oxalic acid and 4-hexylresorcinol. Calcium treatments can maintain or improve tissue firmness and crispness of fresh-cut fruit, and $CaCl_2$ has been one of the most frequently used salts although it is reported to impart residual taste to the product. Thus, other calcium salts such as calcium lactate, calcium propionate or calcium ascorbate have been investigated as alternative sources of calcium (Oms-Oliu et al., 2010). The application of edible coatings to deliver active substances is one of the recent major advances made in order to increase the shelf life of fresh-cut produce. Edible coatings also decrease WVTR by forming a barrier on the fruit surface, preventing loss of water and turgor.

Microbial deterioration of MPFV can be controlled by several methods including the use of chill temperatures, reduction of the total microbial population by the use of heat or irradiation and the use of antagonistic organisms that control growth of undesirable microorganisms (Novak, 2010). Antimicrobial agents such as plant essential oils have been introduced as a novel way to improve microbiological stability of fresh-cut fruit (Oms-Oliu et al., 2010). The use of sanitizing chemicals such as chlorine, ozone, chlorine dioxide and peroxyacetic acid in chilled wash water are approved for use on fresh produce.

18.4.1.2 Packaging Materials

At the outset, it must be recognized that fresh produce is not a single commodity since there are hundreds of different fruits and vegetables, each with their own particular requirements for package performance. There have been some publications on the packaging of MPFVs, and generally the same packaging processes are used as for fresh produce. However, allowance has to be made for differences in the respiration rate of produce which has been processed in some way. There is an increasing trend away from heavily processed toward MPFVs, and although some research has been undertaken to develop the most effective packaging systems, more is required.

Normally, a shelf life for packaged fresh produce and MPFVs of at least 7 days at refrigerated conditions (≤5°C) is required, and to achieve this, MAP is usually necessary. The primary spoilage mechanisms are the metabolism of the tissue and microbial growth; both will cause deterioration of the tissue and must be controlled to maintain tissue viability. Generally, the shelf life of MPFVs is inversely proportional to respiration rate. Microbial spoilage has become a major reason for sensory quality shelf life failure for most packaged MPFVs, followed by surface discoloration (e.g., pinking of cut lettuce, browning of cut potato, greying and browning of processed pineapple and grey discoloration of cabbage), water-soaked appearance or translucency (e.g., cut watermelon, papaya, honeydew and tomatoes), moisture loss (e.g., "baby" carrots and celery sticks), off-aroma (e.g., broccoli florets and diced cabbage in low O_2 and high CO_2 atmospheres), flavor changes (e.g., cut kiwifruit) and texture changes (e.g., processed strawberry, grated celery, kiwifruit and papaya). Microbial spoilage including formation of off-flavors (e.g., fermented aroma with cut lettuce, sour taste with cantaloupe and bell pepper), slimy surface (e.g., "baby" carrots), wetness and soft rot (e.g., cut bell pepper), discoloration (e.g., apple wedges) and visual microbial growth/colonies (such as apple wedges, cantaloupe chunks and cored pineapple) has been used as a main or exclusive objective criterion to determine shelf life of fresh-cut products (Barth et al., 2009).

Chill temperatures during storage, dipping in anti-browning solutions and MAP are the most common approaches used to preserve the initial color of MPFVs (Zhuang et al., 2011). Ascorbic acid (AA) and its derivatives have been used in numerous studies in fruits in concentrations ranging from 0.5% to 4%. Recently, Mastromatteo et al. (2011) reported on the effectiveness of different strategies to prolong the shelf life of minimally processed kiwifruit. The use of active MAP (10% O_2 and 10% CO_2) together with a sodium alginate coating to control dehydration and respiration gave a shelf life of up to 13 days at 5°C. The OPP bags of 20 μm thickness used had an OTR at 5°C of 1015 mL m^{-2} day^{-1} and CDTR of 2700 mL m^{-2} day^{-1} (i.e., $\beta \approx 2.7$).

The beneficial effects of MAP for MPFVs have been reviewed (Solomos, 1997; Ahvenainen, 2000). Depleted O_2 or enriched CO_2 levels reduce respiration and decrease C_2H_4 production, inhibit or delay enzymic reactions, alleviate physiological disorders and preserve the product from quality losses. However, exposure to O_2 or CO_2 levels outside the limits of tolerance may lead to anaerobic respiration with the production of undesirable metabolites and other physiological disorders. Nevertheless, the levels of O_2 and CO_2 required to avoid tissue damage or quality loss are unknown for most fruits and vegetables. Low O_2 atmospheres act synergistically with elevated CO_2 levels to reduce C_2H_4 production and respiration rates but do not completely stop senescence and tissue breakdown.

In what at first seems counterintuitive, high O_2 MAP (>60 kPa) has been found to be effective at inhibiting enzymic browning, preventing anaerobic fermentation and inhibiting aerobic and anaerobic microbial growth, possibly as a result of the generation of reactive oxygen species (O_2^-, H_2O_2, $OH^\bullet$) in plant cells that damage vital cell components and thereby reduce cell viability (Jacxsens et al., 2001; Day, 2003). Target gas concentrations immediately after packaging are 80%–95% O_2 and 5%–20% N_2, the aim being to achieve O_2 levels >40% and CO_2 levels 10%–25% throughout chilled storage. A concern with this technology is potential worker safety implications during packaging in the production environment as O_2 concentrations higher than 25% are explosive (Barth et al., 2009). High O_2 barrier films are not suitable; the recommended film is 30 μm OPP.

Oms-Oliu et al. (2008) compared high O_2 (70 kPa) and low O_2 (2.5 kPa) active MAP to traditional passive MAP for fresh-cut pears at 4°C. High O_2 did not prevent the production of acetaldehyde and ethanol during storage but their accumulation was promoted under anoxic conditions. Although low O_2 reduced CO_2 production and inhibited C_2H_4 production, moderate CO_2 concentrations in combination with excessively low O_2 levels inside packages accelerated the accumulation of fermentative metabolites. Both low and high O_2 significantly reduced the growth of microorganisms during storage. Recently, Liu et al. (2010) reported on changes in the quality of mushrooms stored at 2°C for 12 days under 100% and 80% O_2 atmospheres and air. The respiration rate was suppressed in the O_2 atmospheres, and no significant differences were found between 80% and 100% O_2. Weight loss and firmness of mushrooms held in high O_2 were significantly higher than in air, and high O_2, especially 100% O_2, was effective at inhibiting discoloration.

Polymeric films are the most common materials used for the packaging of horticultural products including MPFVs (Toivonen et al., 2009). Early work in the area stressed the primary role of packaging to reduce transpiration, with many studies encouraging film perforation to avoid the development of injurious atmospheres inside the packages. In addition to enabling the creation of MA conditions, polymeric films provide other benefits including maintenance of high RH and reduction of water loss; improved sanitation by reducing contamination during handling; minimal surface abrasions by avoiding contact between the commodity and the shipping container; reduced spread of decay from one produce item to another; use of the film as a carrier of fungicides, scald inhibitors, C_2H_4 absorbers or other chemicals; facilitation of brand identification and providing relevant information to consumers (Kader and Watkins, 2000).

In packages where it is not intended to create a MA, the main concern is to avoid anoxic conditions and condensation of water vapor inside the package. This is most easily achieved either by incomplete sealing or perforation of the plastic packaging.

The relative effect of diffusive flow through holes on package atmosphere can be appreciated by comparing the permeability of gases in air with permeability of the gases in polymers as shown in Table 18.6. Air is much more permeable than polymeric films, so that even a very small hole in a polymeric package can affect the package atmosphere very significantly. This phenomenon is used to advantage with perforated films where the gas permeation can be adjusted by changing the dimensions of the perforations (see Table 4.1). In addition, perforated MAP can effectively reduce the humidity inside the package.

Rennie and Tavoularis (2009) demonstrated the feasibility of modeling perforation-mediated MAP based primarily on fundamental laws that accounted for all the major transport phenomena during storage of fresh commodities. The model can be used for steady-state as well as transient analysis of MAP in a wide variety of circumstances and could prove to be useful in risk analysis studies. Transpiration and condensation, which are often disregarded in models of MAP, were modeled to gain insight into a process that is very hard to investigate experimentally. The results indicated that the majority of the water vapor that is transpired eventually condenses on the package walls or on the commodity. They also showed that the assumption that the product temperature and the storage room temperature are equivalent, a common assumption in many models, could lead to errors in the prediction of the gas concentrations. Their results demonstrated the importance of obtaining accurate respiration rate data for the given variety and the actual conditions of the stored commodity. The sensitivity of the model to variations in the respiration rate for a given respiration rate model were tested by increasing or decreasing the respiration rate by 10%. These changes were found to have a significant effect on the steady-state gas concentrations. Because such variations in respiration rate occur regularly for most commodities, it indicates that, in practical situations, one should not expect to predict precise steady-state gas concentrations for MAP.

González-Buesa et al. (2009) proposed a model for describing the change in gas composition in packages of constant volume with microperforations of varying number and size, taking into account the dependency of the RR on gas composition and hydrodynamic flow through the microperforations. The change in gas composition inside the package predicted by the model was compared with the results of experiments conducted at 4°C with minimally processed peaches, fresh-cut cauliflower and whole black truffle, using seven packages with different numbers (0–14) and sizes (from $90 \times 50\,\mu m$ to $300 \times 100\,\mu m$) of microperforations. The experimental data and those predicted by the model showed a satisfactory agreement for O_2, but the CO_2 was underestimated for products with $RQ < 1$ but in agreement when $RQ > 1$.

The effect of thin layers and droplets of water on the inside surface of films can also be appreciated by reference to Table 18.6, which shows that the permeability of gases is much higher in water than in polymers. As a result, thin layers and droplets of water forming inside polymeric packages do not significantly affect the gas atmosphere in the package (Kader et al., 1998).

TABLE 18.7
Packaging Materials for Vegetables

Vegetable	Packaging Material and Thickness
Peeled potato, both whole and sliced	LDPE, 50 μm (also PA-LDPE, 70–100 μm or comparable)
Grated carrot	OPP, 40 μm, microperforated LDPE-EVA-OPP, 30–40 μm
Sliced swede	LDPE, 50 μm
Grated swede	LDPE-EVA-OPP, 40 μm
Sliced beetroot	LDPE, 50 μm (also PA-LDPE, 70–100 μm or comparable)
Grated beetroot	OPP, 40 μm, microperforated OPP, PE EVA-OPP, 30–40 μm
Shredded Chinese cabbage	OPP, 40 μm, LDPE-EVA-OPP, 30–40 μm
Shredded white cabbage	OPP, 40 μm, LDPE/EVA/OPP, 30–40 μm
Shredded onion	OPP, 40 μm (also PA-LDPE, 70–100 μm or comparable)
Shredded leek	LDPE, 50 μm, OPP 40 μm (also PA-LDPE, 70–100 μm or comparable)

Source: From Laurile, E. and Ahvenainen, R., Minimal processing in practice; fresh fruits and vegetables, in: *Minimal Processing Technologies in the Food Industry*, Ohlsson, T. and Bengtsson, N. (Eds), CRC Press, Boca Raton, FL, pp. 219–244, 2002.

Flexible packaging is the most common format for fresh-cut produce MAP and is available as preformed bags, roll stock and standup pouches. Rigid packaging formats consist of a rigid tray or container that may be designed as a clamshell, have a snap-on lid or a sealable, easy-peel lidding film (Toivonen et al., 2009). Many polymeric films are available for packaging purposes, and those most likely to be suitable include laminated or coextruded materials consisting of blends of LLDPE, LDPE or OPP with EVA copolymer. The polyolefin resins provide excellent strength and are good moisture barriers, while the EVA copolymer provides sealability and a higher O_2 permeability than the pure polyolefin resins. Table 18.7 gives details of packaging materials that have been suggested for MPVs. The O_2 and CO_2 permeabilities of the aforementioned films are required at actual conditions of use, but regrettably such data are scant, making the development of suitable packages a trial-and-error exercise in many cases. The use of such information was illustrated in Section 18.3.4.

As illustrated in Figures 18.1 and 18.2, there are some fruits and vegetables for which LDPE film will never be suitable if the optimum MAP is required. Thus, there is a need for modification of the permeability properties of the common polymeric films to make them more suitable for MAP and developments in this area have already been referred to in Section 5.9. Approaches adopted have included inorganic fillers, perforations and porous patches with a breathable membrane that has an adjustable selectivity for CO_2 and O_2 and permeability that increases dramatically as temperature increases (Clarke, 2011); they were described in Section 15.3.4.

The use of Ar in MAP was discussed in Chapter 16. Recommended MAP of salads using Ar is 70%–90% Ar, 0%–20% CO_2 and 1%–15% O_2 (Spencer and Humphreys, 2003). Over an average 5-day shelf life, O_2 levels declined from 10% to 15% toward 0%, while CO_2 levels rose from an initial 5%–15% to 20%–30% at the end of shelf life. Although increasing concentrations of CO_2 can extend the shelf life, there are undesirable side effects including bleaching of color, generation of off-tastes and deliquescence (dissolving of CO_2 in water), particularly in colored produce such as carrots and red cabbage. The use of Ar rather than N_2 slowed degradation by inhibition of oxidases from both product and microbial sources, with the total viable count being 40% less (Spencer and Humphreys, 2003).

18.4.1.3 Safety of MAP Produce

The general safety aspects of MAP were discussed in Chapter 16. In this section, specific comments relating to MAP of fruits and vegetables are discussed. For a more detailed discussion the reader is referred to Farber et al. (2003), Hui and Nip (2004), Raybaudi-Massilia et al. (2009), Barth et al. (2009) and Ragaert et al. (2011).

It is generally believed that with the use of permeable films, spoilage will occur before toxin production is an issue. However, MAP of produce should always incorporate packaging materials that will not lead to an anoxic package environment when the product is stored at the intended temperature; that is, high O_2 barrier films should not be used. The microorganisms that exist on the surfaces of raw, whole produce appear to be the major source of microbial contamination and consequent spoilage of fresh-cut fruits and vegetables. Fresh-cut products can also be contaminated by spoilage microorganisms through contact with people or equipment during processing and possibly by air during processing and packaging steps, especially in facilities that have been used for produce processing over an extended period of time (Barth et al., 2009). The elimination or significant inhibition of spoilage microorganisms should not be practiced, as their interaction with pathogens may play an integral role in product safety (Farber et al., 2003).

The commonly encountered spoilage bacteria of fruits and vegetables include *Pseudomonas* spp., *Erwinia herbicola*, *Flavobacterium*, *Xanthomonas*, *Enterobacter agglomerans*, lactic acid bacteria such as *Leuconostoc mesenteroides* and *Lactobacillus* spp. (Nguyen-the and Carlin, 1994). Certain common molds such as *Penicillium* spp., *Aspergillus* spp., *Eurotium* spp., *Alternaria* spp., *Cladosporium* spp., *Paecilomyces* spp. and *Botrytis* spp. have been shown to be involved in the spoilage of fresh fruits, as well as yeasts such as *Saccharomyces* spp., *Cryptococcus* spp. and *Rhodotorula* spp. Although this microflora is largely responsible for the spoilage of fresh produce, it can vary greatly for each product and storage conditions. Temperature can play a large role in determining the outcome of the final microflora found on refrigerated fruits and vegetables, leading to a selection for psychrotrophs and a decrease in the number of mesophilic microorganisms.

The effect of MAP on lactic acid bacteria can vary depending on the type of produce packaged. The increased CO_2 and decreased O_2 concentrations used in MAP generally favor the growth of lactic acid bacteria. This can expedite the spoilage of produce sensitive to lactic acid bacteria, such as lettuce, chicory leaves and carrots (Nguyen-the and Carlin, 1994). The effect of MAP on yeasts is negligible, but because molds are aerobic microorganisms, CO_2 can cause growth inhibition at concentrations as low as 10% (Molin, 2000). The antimicrobial properties of high CO_2 concentrations are mostly due to a reduction of pH and interference with the cellular metabolism.

The concern when using MAP for fruits and vegetables arises from the potential for foodborne pathogens, which may be resistant to moderate to high levels of CO_2 ($\leq 50\%$), to outgrow spoilage microorganisms, which may be sensitive to the MA. High levels of O_2 can inhibit the growth of both anaerobic and aerobic microorganisms because the optimal O_2 level for growth (21% for aerobes, 0%–2% for anaerobes) is surpassed. However, there have also been reports of high O_2 (i.e., 80%–90%) stimulating the growth of foodborne pathogens such as *Escherichia coli* and *Listeria monocytogenes* (Amanatidou et al., 1999).

Atmospheres with low O_2 levels inhibit the growth of most aerobic spoilage microorganisms which usually warn consumers of spoilage, while the growth of pathogens, especially the anaerobic psychrotrophic, nonproteolytic Clostridia, may be allowed or even stimulated. However, there have been few studies on the effect of MAP conditions on the microbial safety and stability of fresh-cut fruits.

At extremely low O_2 levels (<1%), anaerobic respiration can occur, resulting in tissue destruction and the production of substances that contribute to off-flavors and off-odors, as well as the potential for growth of foodborne pathogens such as *Clostridium botulinum* (Austin et al., 1998). The absence of outbreaks of botulism linked to MAP produce indicates that *C. botulinum* may be competitively inhibited under the packaging and resident flora conditions of these products. However, more research needs to be done to examine the potential for growth of *C. botulinum* in a wide variety of MAP produce stored at mildly abusive temperatures such as 7°C–12°C. In addition, it has been suggested that other hurdles besides temperature need to be examined to prevent botulinum toxin production (Farber et al., 2003).

Concerns about possible pathogen contamination in MAP produce have focused on *L. monocytogenes* owing to its ability to grow at refrigeration temperatures and remain largely unaffected by MAP while the normal microflora is inhibited (Amanatidou et al., 1999). Thus, although MAP produce can remain organoleptically acceptable, *L. monocytogenes* with a reduced microflora can grow at low temperatures (especially if low levels of lactic acid bacteria are present) to reach potentially harmful levels during the extended storage life of MAP produce (Farber et al., 2003).

Although edible biodegradable coatings are gaining in popularity, a number of problems have been associated with their use. For example, modification of the internal gas composition of the product due to high CO_2 and low O_2 can cause problems such as anaerobic fermentation of apples and bananas, rapid weight loss of tomatoes, elevated levels of core flush for apples, rapid decay in cucumbers and so on. Edible films can create very low O_2 environments where anaerobic pathogens such as *C. botulinum* may thrive, although antimicrobial compounds can be incorporated into the coating in this scenario if legislation permits. Because the antimicrobial or antioxidant can be incorporated and applied directly to the surface of the product, only small quantities are required.

Increasing food safety concerns of losing the biological structure that normally prevents harmful microorganisms from colonizing on food have been raised (Chuang, 2011). Because of the exposed tissue, MPFVs may be more susceptible to colonization by pathogenic bacteria than intact produce, owing to higher availability of nutrients on cut surfaces and greater potential for contamination because of increased handling. The efficacy of MAP to control the physiological decay of fresh-cut fruits warrants further investigation, and knowledge about the influence of MAP on the microbiological safety of these foods is still judged as inadequate by experts (Farber et al., 2003). The emergence of psychrotrophic pathogens such as *L. monocytogenes*, *Aeromonas hydrophila* and *Yersinia enterocolitica*, mesophiles such as *Salmonella* spp., *Staphylococcus* spp. and the microaerophilic *Campylobacter jejuni* is of greatest concern and further investigation is warranted. Despite these concerns, MAP of horticultural produce is now widespread with extremely few food poisoning outbreaks (Hui and Nip, 2004).

Ready-to-eat (RTE) packaged lettuce salads have been implicated in several salmonellosis outbreaks. The survival and growth of *Salmonella* spp., *E. coli* O157:H7 and *L. monocytogenes* inoculated onto shredded lettuce was determined under passive MAP and in air by Oliveira et al. (2010). After pathogen inoculation, the lettuce was packaged into two OPP films of different permeability and stored at 5°C and 25°C. After 10 days at 5°C, populations of *E. coli* O157:H7 and *Salmonella* decreased by ~1 log unit while *L. monocytogenes* increased by about 1 log unit in both package films. At 25°C, the level of pathogens increased between 2.4 and 4.2 log units after 3 days. Psychrotrophic and mesophilic bacteria had similar growth at both temperatures with higher populations in air than in the MAs. The composition of the MAs had no significant effect on the survival and growth of the pathogens at refrigeration temperatures. *L. monocytogenes* inoculated at low dose reached populations >100 cfu g^{-1} at 5°C. These results reinforce the necessity to avoid contamination of vegetables during packing, storage and handling, because if minimally processed vegetables become contaminated with these pathogens, they will be able to grow and survive if the product is not kept at refrigerated conditions.

Recently, Horev et al. (2012) reported on the effects of MAP on indigenous microbial populations and the survival of *Salmonella enterica* on the surface of romaine lettuce. Chlorine-washed lettuce leaves were inoculated with *S. enterica* serotype Typhimurium and packaged in one of three systems: (1) passive MAP in LDPE bags, (2) active MAP in the same bags with a gas mixture of 10% O_2, 10% CO_2 and 80% N_2 and (3) control without MAP. The active MAP had an antimicrobial effect on indigenous lettuce microflora, but not on *Salmonella* and even favored the survival of the pathogen, possibly due to the elimination of its natural antagonists. The effects of the passive MAP were less pronounced. The results obtained draw attention to potential safety risks of ready-to-eat fresh produce kept in active MAP and require further investigation.

In some countries, temperature abuse is a widespread problem in the distribution chain and can occur at any of the stages from storage through transportation to retail display and consumer handling.

In these situations, it is advisable to restrict the shelf life so that psychrotrophic pathogens have insufficient time to multiply and produce toxin. Where the shelf life is greater than 10 days and the storage temperature is likely to exceed 3°C, it has been suggested (Laurile and Ahvenainen, 2002) that the products should meet one or more of the following controlling factors:

- A minimum heat treatment such as 90°C for 10 min
- A pH of 5 or less throughout the food
- A salt level of 3.5% (aqueous) throughout the food
- a_w of 0.97 or less throughout the food
- Any combination of heat and preservative factors which has been shown to prevent growth of toxin production by *C. botulinum*

However, given that the aim is to maintain the freshness of MPFVs, the aforementioned treatments are not practicable and limiting the shelf life is the best solution.

Barth et al. (2009) identified the need for investigation of spoilage patterns and microflora of fresh-cut products packaged with new, emerging MAP technologies, including antimicrobial packaging, microperforated packaging, Breatheway® membrane packaging and high O_2 backflush, in commercial practice. With the continuing development of packaging technologies and changes in marketing fresh and fresh-cut produce, the spoilage microflora of packaged produce in the future may be completely different from today. For example, the headspace gas concentrations of fresh-cut produce in microperforated packages are significantly different from those packaged with conventional films. There is very limited information regarding how changes in atmospheric composition affect the spoilage microflora profile during refrigerated storage.

Fresh-cut produce has an extraordinary record of safety when the number of portions sold and consumed worldwide is considered. Nevertheless, there have been many outbreaks associated with bagged, fresh-cut produce, especially salads and leafy greens. It is unclear if there is a higher incidence of foodborne illness associated with bagged cut produce than with whole commodity produce, or if outbreaks are merely larger, more often detected and more prominent (O'Beirne and Zagory, 2009). When outbreaks do occur, suspicion and regulatory attention typically focuses first, and often exclusively, on the processor, although evidence from outbreak investigations suggests that the field is often the source of the original contamination. Once produce is contaminated, fresh-cut processors cannot completely decontaminate the raw products with currently available processing technologies. Thus, food safety must be based on prevention programs such as HACCP (U.S. FDA, 2008).

18.4.2 Frozen

Packaging materials for frozen fruits and vegetables must protect the product from moisture loss, light and O_2, of which the former is the most important. Freezer burn or sublimation of water vapor from the surface of frozen foods results in their becoming dehydrated with a concomitant loss in weight, and their visual appearance deteriorates. All the common polymeric films have satisfactory water vapor transmission rates at freezer temperatures.

The earliest form of packaging material for frozen fruits and vegetables was waxed cartonboard, often with a moisture-proof RCF overwrap. These were then replaced with folding cartons having a hot melt coating of PVdC copolymer and the ability for the flaps to be heat sealed. Although still used to a small extent for low production volumes, the majority of frozen fruits and vegetables today are packaged in polymeric films based on blends of polyolefins, the major component of which is LLDPE. It is also common for the film to contain a white pigment to protect the contents from light, which could oxidize the pigments. The film is usually supplied in roll form from which it is converted into a tube, then filled and sealed continuously in a FFS type of machine. Premade bags are used for low volume packaging operations.

18.4.3 CANNED

The thermal processes used for canned fruits and vegetables differ markedly depending on the pH of the product: low acid products, that is, products with a pH greater than 4.5 (which includes most vegetables) require a full 12D process, typically 60–90 min at 121°C. In contrast, those products with a pH less than 4.5 need only a mild heat treatment, typically 20 min in boiling water. Some products are acidified to lower the pH below 4.5 and thus avoid the more severe heat treatment.

The majority of "canned" fruits and vegetables are packaged either in tinplate or ECCS cans or glass jars. The cans must have the correct internal enamel applied to avoid corrosion of the tinplate. It is important that all the air is removed from the product prior to packaging to minimize corrosion of the tinplate. For acid fruits such as raspberries, which contain red/blue anthocyanin pigments, the enamel coating must be particularly rigorous since the pigments act as depolarizers, accelerating the rate of corrosion. With some fruits, only the ends of the can are enameled, and for pineapple, a plain can is used so that as the tin dissolves from the tinplate, it reacts with certain constituents of the pineapple and a yellow color develops. White aluminum-pigmented epoxy resin enamels are used with fruits in some countries.

Many vegetables contain sulfur compounds which can break down during heat processing to release H_2S. This can react with the tin and iron of the metal can to form black metallic sulfides which cause an unsightly staining of the can and also of the contents. While this process is encouraged and, indeed, is essential for the production of the desired flavor and color in canned asparagus, it is avoided with other vegetables by the use of special enamels which contain zinc oxide. This reacts with the H_2S to produce barely detectable white zinc sulfide on the inner surface of the can. White aluminum oxide-pigmented enamels based on epoxy resins are also used for cans containing vegetables.

Glass containers are still used for packaging some commercially processed fruits and vegetables, generally for products at the premium end of the market. This is largely because the production rates for glass containers are much lower than those possible for metal cans. Cylindrical, widemouth glass jars are commonly used with either a twist-off or pry-off cap coated with a suitable lining material. Considerably greater operator skills are required to retort glass jars compared to metal cans, because failure to control the overpressure correctly can result in either shattered containers or the loss of pry-off caps.

Retortable pouches made from laminates of plastic film generally with an aluminum central layer can also be used for the packaging of fruits and vegetables which are preserved by the use of heat.

18.4.4 DEHYDRATED

The packaging of dehydrated fruits and vegetables requires the use of a package that will prevent or, at the very least, minimize the ingress of moisture and, in certain instances, O_2. For example, products that contain carotenoid pigments (e.g., carrots and apricots) can undergo oxidative deterioration, and dehydrated potatoes are liable to develop stale rancid flavors unless O_2 is excluded. Vacuum or inert gas packaging may be used if the product is particularly sensitive to oxidation, although this is rare.

Many vegetables, for example green beans, peas and cabbage, are treated with sulfur dioxide prior to drying to retard nonenzymic browning (the principal index of failure in dehydrated vegetables) and increase the retention of ascorbic acid. Sulfur dioxide also has a useful antimicrobial effect during the initial stages of drying and, by varying the form in which it is introduced (sodium sulfite or metabisulfite), it can be used to control pH, which in turn influences the color and subsequent handling and drying characteristics of the product. Concentrations of sulfur dioxide in the dried product normally range from between 200 and 500 ppm for potatoes to between 2000 and 2500 ppm for cabbage.

For the packaging of dehydrated fruits and vegetables, the material normally used consists of one or more polymeric films having the desired barrier properties. This implies that the material must be a very good barrier to water vapor and, depending on the particular product, a good barrier to O_2 and maybe SO_2 and certain volatiles. For premium products, it is common to use a laminate where the center layer is aluminum foil coated on both sides with polymeric films.

18.4.5 Vegetable Oils

Vegetable oils are derived from plants and chemically are composed of triglycerides and several other minor components, which may be very important for different aspects such as nutritional properties. Edible vegetable oils are vulnerable to quality deterioration and must be adequately protected by packaging throughout their commercial life. Sources of edible vegetable oils are many and varied, and their quality attributes such as nutritional properties, health benefits, lipid composition, odor and color are very important. Oils are in general microbiologically stable due to very low moisture content, but they are subject to important chemical and physical changes (Piergiovanni and Limbo, 2010).

The most important vegetable oils used mainly or exclusively for direct consumption and cooking or frying are olive, corn and peanut oils. Olive oil has a unique position among edible oils due to its delicate flavor, stability and health benefits. Extra virgin olive oil (EVOO) is the highest grade of olive oil. To be classified as EVOO, the oil must contain less than 0.8% free fatty acid (measured as oleic acid) and the peroxide value (PV) must not exceed 20 meq O_2 kg^{-1}. Among the factors that significantly influence olive oil quality are the extraction methods, packaging materials and storage conditions such as temperature, exposure to light and contact with O_2. Oxidation leading to rancidity is the most important cause of oil spoilage, and many factors influence oxidation including O_2 dissolved in the oil when packaged, O_2 in the package headspace, O_2 diffusion through the package walls, light, temperature, humidity, pro-oxidant trace metals such as copper and iron, and, obviously, the chemical composition of the oil and natural antioxidant content (Cecchi et al., 2009).

Many different kinds of packaging are used for vegetable oils: tinplate cans, glass bottles, PET, PVC or HDPE plastic bottles, and paper-based cartons are most common. The selection of the kind of package to be used is generally done on the basis of marketing and economic criteria; however, proper packaging should provide conditions to assure adequate shelf life for distribution and marketing. Even though oils are quite stable products, the physicochemical characteristics of packaging materials may significantly affect oil quality during their shelf life. Furthermore, as well as the specific properties of the materials, the packaging geometry and the techniques of filling and closing the containers may also be very important (Piergiovanni and Limbo, 2010).

While O_2 permeability is an important property only for plastic packages, light transmission is important for both glass and plastics. PET, like glass, is an effective barrier to light at wavelengths shorter than 340 nm. On the other hand, while glass containers are able to completely prevent O_2 permeation, PET is only able to slow down the O_2 exchange. The barrier properties of PET can be improved by coating with SiO_x or amorphous carbon. Alternatively, O_2 scavengers (OS) can be added to the plastic matrix.

Glass containers are widely used for bottling olive oils, not only due to marketing requirements but also because glass containers prevent O_2 permeation into the bottle, slowing down the autoxidation rate of polyunsaturated fatty acids. Clear glass, however, leads to photooxidation of olive oil and a reduction in shelf life, and therefore colored glass is preferred to prevent or at least slow down the oxidation process.

Kucuk and Caner (2005) studied sunflower oil packaged in 1 L PET and glass bottles, both with and without headspace and stored in conditions of light (intensity unspecified) and darkness for 9 months. Oil stored in glass and PET in the dark showed very little oxidation and maintained its original profile for a long period as shown in Table 18.8.

TABLE 18.8
Effect of Packaging Materials (With or Without Headspace, in Dark/Light Conditions) and Storage Time on Mean Peroxide Values (meq O_2 kg^{-1}) in Sunflower Oil

			Storage Time (Months)				
Package	With–Without Headspace (Air)	Dark/Light	0	3	6	9	Mean
PET	Air	Light	0.230	0.800	3.306	14.85	4.79[c]
		Dark	0.230	0.400	0.800	1.250	0.67[d]
	Without air	Light	0.230	0.800	3.000	13.90	4.48[f]
		Dark	0.230	0.400	0.500	1.100	0.55[ad]
Glass	Air	Light	0.230	0.990	4.740	10.60	4.14[h]
		Dark	0.230	0.310	0.430	1.010	0.49[a]
	Without air	Light	0.230	0.776	3.133	8.670	3.20[c]
		Dark	0.230	0.300	0.530	0.770	0.44[a]

Source: Kucuk, M. and Caner, C., *J. Food Lipids*, 12, 222, 2005.
Means with different letters are significantly different ($P < 0.01$); standard error 0.0764.

As expected, significantly higher PVs were produced in oil exposed to light than in oil stored in the dark. The authors concluded that glass provided better protection from oxidation than PET bottles, although the latter provided adequate protection, especially when stored in the dark.

In order to reduce the diffusion of O_2 into bottled oil, various solutions have been tried; the most popular involve the use of OS which remove O_2 dissolved in the oil and provide a barrier to O_2 diffusion from the atmosphere. Sacchi et al. (2008) studied the oxidation of EVOO and sunflower oil (SO) stored in PET bottles with two different OS concentrations (1% and 5%). The bottles were stored for 6 months at 25°C under a constant illumination of 400 lux. During the first 3 months of storage, the effect of the scavengers was evident: oils bottled in PET loaded with 5% of OS showed a dissolved O_2 (DO) content lower than oils bottled in PET with 1% OS and in standard PET. Between 3 and 6 months, the level of DO remained almost constant in all packages, indicating that the O_2 consumed during storage was nearly limited to the initial content in the oil. However, the different initial levels of DO raise questions about the validity of their conclusions.

Cecchi et al. (2010) compared 300 mL PET bottles with and without OS on the quality of EVOO over 13 months. The bottles had 2 mL headspace and were stored in the dark or diffuse light at 20°C–22°C. The fatty acid concentration remained constant at 0.3% oleic acid in all bottles over 13 months. For all treatments, peroxides first decreased and subsequently increased over time but always remained below the threshold limit (20 meq O_2 kg^{-1}). This indicates that in the first stage of oxidation, the rate at which hydroperoxides are consumed is higher than the rate at which they are produced through the oxidation of unsaturated fatty acids, leading to a decrease in PV. This highlights a possible role of the PET material in consuming the peroxides. Moreover, PVs of samples stored in the dark were higher than those stored in diffuse light, probably because light increases the rate at which hydroperoxides break down.

Pristouri et al. (2010) studied the effect of packaging parameters (transmission to light and O_2, headspace volume) and storage temperature (13°C, 22°C and 35°C) on quality characteristics of EVOO as a function of storage time (0–12 months). Packaging materials tested included clear glass, clear PET, clear PET + UV blocker, clear PET covered with aluminum foil and clear PP bottles. Changes in the acidity and PV of EVOO stored in the dark at 22°C as a function of packaging material and storage time are summarized in Table 18.9. The best packaging material for EVOO was glass followed by PET; PP proved to be unsuitable for such an application.

TABLE 18.9
Changes in Acidity and PV of Olive Oil Stored in the Dark at 22°C as a Function of Packaging Material and Storage Time

	Acidity (% Oleic Acid)			Peroxide Value (meq O_2 kg^{-1})		
Time (Month)	Glass	PET	PP	Glass	PET	PP
0	0.63	0.63	0.63	12.92	12.92	12.92
3	0.68	0.68	0.70	13.07	14.24	15.93
6	0.68	0.71	0.74	16.57	17.95	19.00
9	0.70	0.79	0.79	17.53	19.75	21.57
12	0.75	0.79	0.83	18.86	20.61	22.54
Limits	≤0.8%			≤20		

Source: Pristouri, G. et al., *Food Control*, 21, 412, 2010.

Exposure of EVOO to light, high storage temperatures (35°C) and large headspace volumes caused substantial deterioration in product quality parameters. The most pronounced effect was that of temperature and light, while the smallest effect was that of headspace volume and packaging material permeability to O_2. Olive oil color was not substantially affected by storage conditions with the exception of storage of olive oil at 35°C exposed to light for 12 months. Shelf life of EVOO was 6 months packaged in clear glass in the dark at temperatures up to 22°C; 3 months in clear PET in the dark at 22°C and less than 3 months in clear PP in the dark at 22°C. When exposed to light, shelf life of EVOO was 9 months when packaged in PET + aluminum foil; 3 months in PET + UV blocker and less than 3 months in clear PET at 22°C. Product shelf life was less than 3 months at 35°C. Finally, O_2 in the headspace resulted in deterioration of product quality. The relative contribution of parameters studied to the retention of EVOO quality was temperature ≈ light > container headspace > packaging material O_2 permeability.

Recently, Samaniego-Sánchez et al. (2012) reported changes in the chemical composition and sensory characteristics of EVOO resulting from storage for up to 9 months in the dark at 4°C and 20°C in glass and PET bottles and LDPE-coated paperboard/alufoil laminate cartons. All container types had the same surface area and no headspace. Losses in both qualitative properties and minor components, as well as antioxidant capacity and sensory features, were detected in all oil samples, especially for oils stored in PET and glass, but less so for those stored in cartons. As far as sensory characteristics were concerned, the EVOOs packed in PET and glass containers exceeded the European limits after 3 month of storage, while the samples stored in cartons maintained acceptable sensory characteristics for at least 9 months.

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19 Packaging of Dairy Products

19.1 INTRODUCTION

Particularly in the Western world, milk from cattle (*Bos taurus*) accounts for nearly all the milk produced for human consumption. The composition of milk reflects the fact that it is the sole source of food for the very young mammal. Hence, it is composed of a complex mixture of lipids, proteins, carbohydrates, vitamins and minerals. The approximate composition of milk and the range of average compositions for milks of lowland breeds of cattle are given in Table 19.1. The water phase carries some of the constituents in suspension, while others are in solution. The fat is suspended in very small droplets as an oil in water emulsion and rises slowly to the surface on standing, a process often termed *creaming.*

Milk is processed into a variety of products, all having different and varying packaging requirements. The simplest product is pasteurized milk where, after a mild heat treatment, the milk is filled into a variety of packaging media and distributed. The shelf life of such a product varies from 2 to 15 days, depending largely on storage temperature and type of packaging. Ultra-high temperature (UHT) milk is subjected to a more complex process and the packaging is also more sophisticated; its shelf life can be up to 9 months. Cream is typically processed and packaged in a similar way to fluid milk and has a similar shelf life. Fermented dairy products, although being subjected to more complex processing operations, are also typically packaged in an analogous manner to fluid milk.

The other dairy products (butter, cheese and powders) are quite different in nature to fluid milk and their packaging requirements are, therefore, also quite different. Each of these groups of dairy products will be discussed in turn.

19.2 FLUID MILK

19.2.1 PASTEURIZED MILK

Milk for liquid consumption is often standardized with respect to fat content and homogenized to retard the natural tendency for the fat globules to coalesce and rise to the surface. In response to consumer needs, a range of nonstandard fluid milk products has been developed in recent years. These products have varying (reduced) fat levels and additives such as calcium or other nutrients (e.g., the fat-soluble vitamins). From a packaging point of view, these nonstandard milks can be treated analogously to standard milks.

19.2.1.1 Effect of Microorganisms

In virtually all countries, liquid milk for consumption must be pasteurized and cooled before it is packed. The primary purpose of the pasteurization is to destroy any pathogenic microorganisms present in the raw milk to make it safe for human consumption, while simultaneously prolonging the shelf life of the milk by destroying other microorganisms and enzymes that might ruin the flavor.

In general, only 90%–99% of all microorganisms present in raw milk are destroyed by pasteurization and pasteurized milk producers depend on refrigerated storage to achieve the required shelf life. Postheat treatment contamination (PHTC) with cold-tolerant Gram-negative spoilage bacteria is the limiting factor affecting the shelf life of commercial pasteurized milks at refrigerated storage temperatures. Although these bacteria are completely inactivated by pasteurization, they are

TABLE 19.1
Approximate Composition of Bovine Milk from Lowland Breeds

Component	Average Content (% w/w)	Range (% w/w)
Water	87.1	85.3–88.7
Solids-not-fat	8.9	7.9–10.0
Fat in dry matter	31	22–38
Fat	4.0	2.5–5.5
Protein	3.25	2.3–4.4
Casein	2.6	1.7–3.5
Lactose	5.0	4.9–5.0
Mineral substances	0.7	0.57–0.83
Organic acids	0.17	0.12–0.21
Miscellaneous	0.15	

Source: Walstra, P. et al., *Dairy Technology: Principles of Milk Properties and Processes*, Marcel Dekker, New York, 1999.

regularly found in pasteurized products. Inefficient sanitation of milk contact surfaces and contamination from the dairy plant atmosphere are the major causes of PHTC, with most problems arising in the filling line where open containers permit ingress of contaminants (Muir and Banks, 2003). Upgrading of pasteurized milk handling and packaging systems to ultraclean standard is an effective method for extending shelf life at refrigeration temperatures. It is also essential to control the number of stoppages on high-speed lines.

In the absence of PHTC, the shelf life of pasteurized milk products depends on the activity of heat-resistant organisms, which survive pasteurization, and their level of activity depends on the storage temperature. A shelf life of at least 8–10 days at 6°C–8°C is typical, while at 5°C, a shelf life of 18–20 days is realistic for pasteurized milk products processed using an ultraclean packaging system.

19.2.1.2 Effect of Temperature

19.2.1.2.1 Thermization

Thermization is a heat treatment of lower intensity than low-temperature-long-time (LTLT) pasteurization (see following sections), typically 62°C–65°C for 10–20 s. The purpose is to delay spoilage of milk during storage in the factory before pasteurization, usually for manufacture into cheese or other products. Thermization is generally insufficient to destroy bacterial pathogens in raw milk with a reasonable margin of safety (Touch and Deeth, 2009) but it will destroy bacteria, especially psychrotrophs, because several of these produce heat-resistant lipases and proteases that may later cause deterioration of milk products (Walstra et al., 1999).

19.2.1.2.2 Pasteurization

All fluid milk, except for a small quantity of "certified" raw milk, is pasteurized at either 63°C for 30 min (referred to as the LTLT method or sometimes the Holder process) or at 72°C for 15 s (referred to as the high-temperature-short-time [HTST] method). The milk is then immediately cooled to 4°C or less. These heat treatments are designed to destroy microorganisms that produce disease and to reduce the number of spoilage microorganisms present. They do not sterilize the product.

Ultrapasteurization involves heating the milk at or above 138°C for at least 2 s to destroy all pathogenic organisms. Ultrapasteurized products are also known as extended shelf life (ESL) or superpasteurized. There is no single definition for ESL milk but Rysstad and Kolstad (2006) defined ESL products as “products that have been treated in a manner to reduce the microbial count beyond normal pasteurization, packaged under extreme hygienic conditions, and which have a defined prolonged shelf life under refrigeration conditions.” If packaged using aseptic filling machines into presterilized containers and kept refrigerated, ESL milk has a shelf life of up to 90 days with little effect on its nutritive value (Henyon, 1999). ESL milk generally has superior sensory properties compared with UHT milk as a result of a milder heat treatment and chill storage. However, limited data are available in the scientific literature on the safety, sensory qualities and shelf life of ESL milk (Rankin et al., 2011).

The disease-producing organisms of chief concern in milk are *Mycobacterium tuberculosis*, a non-spore-forming bacterium that causes tuberculosis and is frequently found in the milk of infected animals; Brucella species that cause brucellosis in animals and humans; and *Coxiella burnetii* that causes a febrile disease in humans known as Q fever. The most resistant of these three organisms is *C. burnetii*, which is characterized by a $D_{65.6}$ of 30–36 s and a z of 4°C–5°C. *M. tuberculosis* is characterized by a $D_{65.6}$ of 12–15 s and a z of 4°C–5°C, with the Brucella species characterized by a $D_{65.6}$ of 6–12 s and a z of 4°C–5°C. It is left as an exercise for the interested reader to calculate the number of decimal reductions achieved for each of the above-mentioned microorganisms by the LTLT and HTST pasteurization processes.

19.2.1.2.3 Shelf Life

One of the most critical factors affecting the shelf life of pasteurized dairy products is the temperature of storage. Attention has been focused on ways of predicting the effect of temperature on the growth of bacteria in foods. The shelf life of pasteurized milk is determined mainly by the level of contamination with Gram-negative psychrotrophic bacteria, although the microflora of pasteurized milk varies significantly with storage temperature. Thus, while spoilage at refrigeration temperatures is mainly due to the growth of *Pseudomonas* spp., Enterobacteriaceae and Gram-positive bacteria assume greater importance in the spoilage of milks stored at temperatures above 10°C. Recently, in order to increase the shelf life of pasteurized milk, processes such as bactofugation and microfiltration have been introduced in the dairy industry and are used to complement HTST pasteurization. Bactofuged pasteurized milk has a shelf life in excess of 10 days under refrigeration packaged in either PET bottles with a UV blocker or LDPE-coated paperboard cartons stored at 4°C ± 2°C (Kontominas, 2010).

In a study seeking to determine the maximum shelf life of fat-free pasteurized milk, Duyvesteyn et al. (2001) found no correlation between the microbial count at the end of shelf life and the sensory quality of the milk. The sensory shelf life of the milk stored in paperboard cartons at 2°C, 5°C, 7°C, 12°C and 14°C was 15.8, 13.7, 12.3, 4.6 and 3.9 days, respectively.

Ultrapasteurized ESL milk keeps longer (up to 90 days under refrigerated [<4°C] conditions but typically 45–60 days) but poses greater challenges than ordinary pasteurized milk (Rysstad and Kolstad, 2006). In pasteurized milk, spoilage organisms limit the shelf life and, as a result, pasteurized milk spoils before becoming unsafe. With ESL milk, the thermal process of ultrapasteurization destroys spoilage organisms along with pathogens. If the milk is contaminated after ultrapasteurization, then the product could potentially develop high levels of pathogens without the usual signs of spoilage.

19.2.1.3 Effect of Light

During processing, distribution, storage and marketing, milk may be exposed to natural and artificial light. Flavor changes as well as loss of vitamins and other nutritional components are attributed to chemical reactions induced in milk by light, particularly in wavelengths ranging from 420 to 550 nm (Skibsted, 2000). Taste panels have indicated that in the early stages of oxidation, milk loses its naturally fresh flavor and becomes quite flat in taste without being objectionable as in the more advanced stages of oxidation.

Riboflavin (vitamin B_2) plays a central role as it is not only destroyed itself by light but, in addition, catalyzes the development of oxidized flavor and ascorbic acid oxidation by generating excited state (singlet) oxygen. Because of its absorption by riboflavin, light of wavelengths of 350–550 nm is the most damaging, the maximum damage occurring at about 450 nm. These wavelengths are contained in the emission spectra of white fluorescent tubes (Bossett et al., 1999). Although riboflavin has been assumed to be a prominent photosensitizer in dairy products, recent results indicate that porphyrins and chlorophyllic molecules might play an even more important role in the photochemical reactions in dairy products (Wold et al., 2009).

Riboflavin destruction by light is greater in low/nonfat milk than whole milk, because light of 400–500 nm wavelengths can penetrate 40–50% deeper into low/nonfat milk than whole milk (Allen and Parks, 1979). Destruction of nutrients by light could present legal problems in connection with nutrient standards and/or labels, because after storage in supermarket cabinets, the milk may not meet regulatory requirements. U.S. federal regulations require low fat and nonfat milk to be fortified with vitamin A, which may degrade from light exposure in a retail dairy case.

A study was conducted on the relative destruction of vitamin A and riboflavin in low-fat milk when exposed to fluorescent light at an intensity of 2000 lm m^{-2} for 24 h (Senyk and Shipe, 1981). It was found that more than 75% of the added vitamin A was destroyed in glass, clear polycarbonate and HDPE containers. Paperboard containers provided the most protection, while gold-tinted polycarbonate, which blocks light of 400–480 nm, provided the second best protection. The presence of milk fat appears to protect against vitamin A degradation in fluid milk products, but adversely affects the flavor quality of milk after exposure to light. Even a brief, moderate light exposure (2 h at 2000 lx) can reduce the nutritional value and flavor quality of fluid milk products (Whited et al., 2002).

Pasteurized milk in LDPE bags without a light barrier suffered vitamin C losses in excess of 50% after 12 h exposure to cool white light, whereas no loss was observed in milk packaged in paperboard cartons (Bossett et al., 1999).

The extent of nutrient loss in a supermarket depends on the proximity of the containers to the light source, the number and wattage of light bulbs in the display case, the exposed surface area of the package and the length of exposure. The detrimental effects of fluorescent light on milk can be alleviated by the following: (1) selecting packaging materials to minimize transmission of light, (2) reducing light intensities in display cases to 500 lm m^{-2}, (3) use of yellow or yellow-green lamps or filters in display cases and (4) rotating packages at retail outlets to limit prolonged detrimental exposure to light (Senyk and Shipe, 1981).

Intawiwat et al. (2010) evaluated the effect of eight different colored filters based on PET on the photooxidation and quality of pasteurized milk (3.9% fat). Samples were stored in different atmospheres (air and N_2) and exposed to light for 20 h at 4°C. The level of photooxidation was used to explain the results by studying degradation of the photosensitizers in the milk. For samples with high O_2 concentration (packed with air in headspace), the red and green filters induced the least adverse effects, probably because of lower light transmission in these filters compared with the others. For samples with low O_2 concentration (packed with N_2) an unexpected, opposite trend was observed: red and orange filters induced the highest oxidation levels. The authors could not explain this phenomenon: why, with regard to photooxidation in milk, there apparently is an interaction between color of the light and the O_2 concentration in the samples. A clear conclusion of the study was that complete blocking of light in the UV and the entire visible region is needed to avoid photooxidation and maximize shelf life for pasteurized milk.

Because it is clear that exposure of milk to light in the 400–550 nm wavelength region can result in the development of off-flavors and destruction of nutrients, packaging materials used for milk should ideally not transmit more than 8% of incident light at 500 nm wavelength and not more than 2% at 400 nm. Figure 19.1 shows the spectral transmission curves of six milk packaging materials and three of them (clear glass and clear and pigmented PET) exceed these guidelines by a

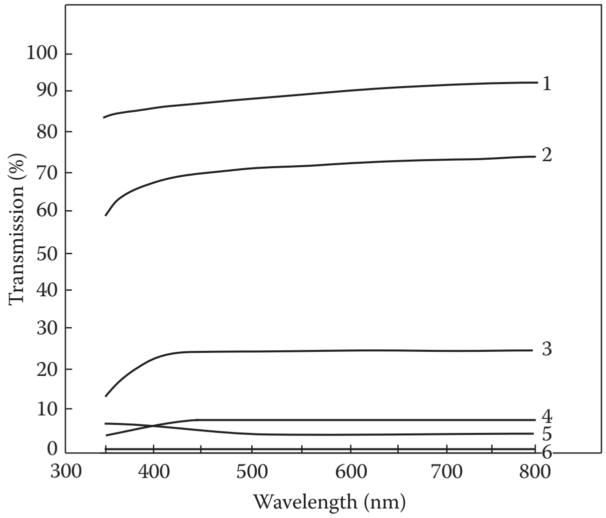

FIGURE 19.1 Spectral transmission curves of milk packaging materials: (1) clear glass, (2) clear PET, (3) pigmented PET, (4) monolayer pigmented HDPE, (5) coated paperboard carton and (6) three-layer pigmented HDPE. (From Karatapanis, A.E. et al., *Int. Dairy J.*, 16, 750, 2006.)

considerable margin. Exposure to direct sunlight should be avoided under all circumstances as this also tends to increase the temperature of the milk, which accelerates microbial spoilage.

19.2.1.4 Effect of Gases

Oxygen plays an important role in the light-induced development of off-flavors in milk. Pasteurized milk at filling is generally saturated with O_2 (about 8 ppm), but if no additional O_2 can gain access, its content falls and the rate of adverse reactions slows or stops. However, additional O_2 from the headspace or entering through a permeable container will maintain the O_2 content and keep the rate of oxidative reactions high. The OTR at 4°C and 50% RH of a commercial 600 mL PET bottle is 19 μL day^{-1} compared to 390–460 μL day^{-1} for a commercial 600 mL HDPE bottle (van Aardt et al., 2001).

It has been known for many years that addition of CO_2 to milk up to ~30 mM (mM is equivalent to mmol L^{-1}) inhibits the growth of bacteria and extends the shelf life under refrigeration of both raw and pasteurized milk (Loss and Hotchkiss, 2003). Gram-negative bacteria are inhibited more than Gram-positives. The shelf life (defined as the time to reach 10^6 cfu mL^{-1}) of low fat milk packaged in high barrier plastic pouches and held at 6.1°C increased from 9.6 days with no added CO_2 to 19.1 days when CO_2 was present at 21.5 mM (Hotchkiss et al., 2006). Higher concentrations of CO_2 enhance inhibition but also decrease the stability of the milk. In milk intended for consumption as a pasteurized fluid product, the CO_2 must be reduced to a level similar to that found in untreated raw milk. Removal of CO_2 can be achieved under vacuum, or the CO_2 can be left to dissipate naturally. It is removed for sensory purposes, as it has a reported flavor threshold of 10 mM, and prior to pasteurization to minimize fouling of heat exchanger surfaces.

CO_2 is being used for extending the shelf life of raw milk, particularly when it is necessary to transport milk in bulk over long distances. In such situations, extensions of shelf life of up to 14 days are possible if the milk is chilled to ~2°C before being transported in insulated but nonrefrigerated containers. CO_2-treated raw milk had lower microbial counts prior to pasteurization and exhibited a lower growth rate and a longer lag phase after pasteurization than non-CO_2-treated milk. It is also used, at ~10 mM, for the shelf-life extension of fresh cheeses such as Cottage cheese and Quark (Deeth and Datta, 2011a). The quality of CO_2-containing Cottage cheese packaged in PS tubs overwrapped with a high barrier heat-shrinkable film can be maintained for 63 and 42 days at 4°C and 7°C, respectively. The use of CO_2 in a range of dairy products has recently been reviewed (Singh et al., 2012).

19.2.1.5 Packaging Materials

Milk for retail sale was traditionally packaged in refillable glass bottles. However, today, single-serve paperboard cartons and plastic containers of various compositions and constructions dominate the market. The packaging material is central to the protection of the flavor and nutritional qualities of fluid market milk. The total amount of light passing through the container wall depends on the material from which the container is made, and also on the pigment either incorporated into the material or used in printing it. The nature of the pigment also determines the wavelength of the light reaching the milk.

Unpigmented HDPE milk bottles in the 350–800 nm spectral region have been found to transmit 58%–79% of the incident light. Light transmission was reduced by pigmenting with TiO_2 (1.6%), with the bottle being opaque below 390 nm. The use of a colorant with the TiO_2 pigment further reduced transmission of light with wavelengths less than 600 nm. The unprinted area of a paperboard carton had less than 1.5% transmission below 550 nm and was opaque to wavelengths below 430 nm (Nelson and Cathcart, 1984).

The effect of prolonged light exposure on the chemical changes in whole and 2% fat pasteurized milk stored at 4°C in clear PET bottles was compared with milk stored in green PET bottles, PET bottles incorporating a UV blocker, PET bottles with exterior labels, HDPE jugs and LDPE pouches (Cladman et al., 1998; van Aardt et al., 2001). The milk stored in the green PET bottles experienced less lipid oxidation and vitamin A loss than milk stored in clear PET bottles, HDPE jugs or LDPE pouches. The PET bottles with UV blockers slowed vitamin A degradation but had little effect on lipid oxidation. Blocking visible light with translucent labels helped to inhibit lipid oxidation and vitamin A degradation.

Vassila et al. (2002) studied changes in chemical and microbial quality parameters of whole pasteurized milk stored under fluorescent light at 4°C in 20 × 15 cm pouches made of (1) LDPE (clear and pigmented with TiO_2) 60 μm thick; (2) coextruded LDPE-PA-LDPE (clear and pigmented with TiO_2) 60 μm thick; and (3) coextruded LDPE + 2% TiO_2-LDPE + 2% TiO_2-LDPE + 4% carbon black-LDPE + 2%TiO_2-LDPE + 2% TiO_2) 60 and 110 μm thick, with varying O_2 (see Table 19.2) and light transmittance for a period of 7 days. Results showed good protection of milk packaged

TABLE 19.2
Oxygen Transmission Rate at 22°C and 60% Relative Humidity of Pouches and Carton for Milk Packaging[a]

Packaging Material	O_2 Transmission Rate (mL Package^{-1} day^{-1})
Clear LDPE pouch, 60 μm	38.3
Pigmented (2% TiO_2) LDPE, 60 μm	38.8
Clear LDPE-PA-LDPE, 60 μm	0.9
Pigmented (2% TiO_2) LDPE-PA-LDPE, 60 μm	0.9
LDPE + 2% TiO_2-LDPE + 2% TiO_2-LDPE + 4% carbon black-LDPE + 2% TiO_2-LDPE + 2% TiO_2, 60 μm	39.5
LDPE + 2% TiO_2-LDPE + 2% TiO_2-LDPE + 4% carbon black-LDPE + 2% TiO_2-LDPE + 2% TiO_2, 110 μm	22.2
LDPE-paperboard-LDPE carton, 450 μm	7.2

Source: Vassila, E. et al., *Int. Dairy J.*, 12, 715, 2002.

[a] Pouch dimensions were 20 × 50 cm; all packages had a capacity of 500 mL.

in all pouches with regard to microbial and chemical parameters with the exception of vitamin retention. In both clear and TiO_2-pigmented LDPE and LDPE-PA-LDPE pouches, vitamin degradation ranged from 50.9% to 73.6% for vitamin A and from 34.4% to 45.3% for riboflavin. In the coextruded pouches containing an inner layer of carbon black, the respective losses were 15.1% and 18.9%. No sensory evaluation was included in the study.

The shelf life of whole and low fat (1.5%) pasteurized milk stored at 4°C for 7 days in a variety of packages has been reported (Moyssiadi et al., 2004; Zygoura et al., 2004). The five packages evaluated were as follows: (1) 0.5 L multilayer pigmented (HDPE + 2% TiO_2-HDPE + 4% carbon black-HDPE + 2% TiO_2) 550–600 μm thick; (2) 0.5 L monolayer pigmented (HDPE + 2% TiO_2) 550–600 μm thick; (3) 0.5 L clear PET 300–350 μm thick; (4) pigmented (PET + 2% TiO_2) 300–350 μm thick; and (5) 0.5 L LDPE-paperboard-LDPE cartons 20–395–35 μm thick, which served as the control. Chemical and microbiological parameters showed satisfactory protection of whole milk in all five packages. For the whole milk, vitamin A losses were 8.8%, 10.5%, 50.9%, 29.8% and 14.0% and riboflavin losses were 18.4%, 20.6%, 47.1%, 30.9% and 19.8%. For the low-fat milk, vitamin A losses were 11%, 11%, 31%, 11% and 16% and riboflavin losses were 28%, 30%, 40%, 33% and 28%. The best overall protection was provided by the multilayer HDPE followed by the monolayer TiO_2-pigmented HDPE bottles.

Karatapanis et al. (2006) investigated changes over 7 days in the volatile profiles of whole pasteurized milk stored under fluorescent light at 4°C and packaged in different containers in a study designed to differentiate between light-induced oxidative and purely autoxidative effects related to packaging material. Packaging materials tested were the same as those detailed in the preceding paragraph. Two distinct patterns of milk flavor deterioration were observed. In light-exposed samples, a light-induced oxidation mechanism prevailed, whereas in light-protected samples, an autoxidation mechanism was apparent. Microbiological data correlated poorly with both sensory and GC/MS data. Sensory data correlated well with selected volatile compounds, pointing to dimethyl disulfide, pentanal, hexanal and heptanal as potential markers of fresh milk quality. Based on sensory analysis, the optimal shelf life of the whole pasteurized milk used in this study was ~5 days.

Mariani et al. (2006) monitored sensory changes in pasteurized milk stored under fluorescent light in a supermarket refrigerator case for a period of 9 days in different packages (1) clear PET bottles, (2) cobalt blue PET bottles and (3) multilayer pigmented gable-top paperboard cartons. Milk packaged in both clear and cobalt blue PET bottles was affected by off-flavor between the first and second day of storage. Milk packaged in paperboard cartons did not develop any off-flavor during the entire storage period.

Clear PET bottles completely transmit light at wavelengths above 320 nm and thus offer no protection against light in the critical range for vitamin degradation. For this reason, pigmented PET bottles are required to protect pasteurized milk against vitamin A and vitamin B_2 degradation. Saffert et al. (2006) stored pasteurized whole milk (3% fat) for 10 days under fluorescent light at 8°C in clear 1 L PET bottles and three variants of pigmented PET bottles with different light transmittance. In clear PET bottles, vitamin A was reduced by 22% and vitamin B_2 by 33%, while vitamin B_{12} remained almost constant. In all pigmented PET bottles, vitamin retention was significantly higher, with losses of 0%–6% for vitamin A and 11%–20% for vitamin B_2, depending on the pigmentation level. No impact of package light transmittance on the vitamin B_{12} content was observed. The use of highly pigmented PET bottles to reduce the light transmittance to below 10% at a wavelength of 450 nm appeared to protect vitamin B_2 sufficiently within the normal shelf life period for pasteurized milk. However, light-induced sensory changes in pasteurized milk cannot be excluded under commercial storage conditions in packages with light transmission rates of 10% or even less at a wavelength of 450 nm.

The influence of storage temperatures from 2°C to 16°C on the microbial stability of homogenized whole pasteurized milk (75°C/15 s) packed in 1 L HDPE bottles and 1 L LDPE pouches pigmented with TiO_2 was evaluated by Petrus et al. (2009). The microbiological shelf life for milk in HDPE bottles stored at 2°C, 4°C, 9°C, 14°C and 16°C was 43, 36, 8, 5 and 3 days, respectively, and for milk in LDPE pouches, 37, 35, 7, 3 and 2 days, respectively. Although no data was presented, it can be assumed that the HDPE bottle had a lower OTR than the LDPE pouch, which would explain the longer shelf life in the former.

19.2.2 UHT MILK

The International Dairy Federation has suggested that UHT milk should be defined as "milk which has been subjected to a continuous-flow heating process at a high temperature for a short time and which afterward has been aseptically packaged. The heat treatment is to be at least 135°C for one or more seconds."

The development of UHT milk processing methods for sterilizing in a continuous flow has brought about the need for aseptic packaging of the product. It is only through the use of aseptic packaging that the benefits of UHT processing can be fully realized.

The quality of the raw milk used in UHT processing is of utmost importance. It is arguably more important than for pasteurized products because of the long periods of storage of UHT products at ambient temperature when even very slow development of defects may lead to end of shelf life. In practice, some manufacturers select milk of the highest quality to use in UHT processes in order to minimize processing difficulties and the incidence of storage-related defects (Datta and Deeth, 2007).

19.2.2.1 Process Description

19.2.2.1.1 Sterilization

UHT processes can be classified as either directly or indirectly heated according to the kind of heat exchangers used (see Deeth and Datta [2011b] for details). Most European regulations rely on spoilage data as a measure of how well an aseptic system works. The U.S. FDA, however, requires microbiological (challenge) and chemical tests to document whether an aseptic system provides an adequate margin of safety.

19.2.2.1.2 Packaging

The various aseptic packaging systems available commercially have been described in Chapter 13 and Robertson (2011). Although all the different systems can be used for UHT milk, the most widely used are the paperboard/alufoil/plastic laminate carton and the plastic container.

19.2.2.2 Microbiology

Destruction of microorganisms during UHT processing has been well documented. The spores capable of surviving the UHT process are mainly *Geobacillus stearothermophilus*, *Bacillus subtilis*, *Bacillus megaterium*, *Bacillus sporothermodurans* and *Paenibacillus lactis*. *G. stearothermophilus* has a high survival potential, but is unable to grow below ~30°C and is a major problem only in tropical climates. In temperate climates, *Bacillus coagulans*, *B. subtilis* and *Bacillus licheniformis* are the most important spoilage species, although some heat-resistant strains of *Bacillus cereus* have also been implicated (Touch and Deeth, 2009).

The quality of raw milk selected for manufacture of UHT milk is critical. UHT milk prepared from raw milk containing more than 5×10^6 cfu mL^{-1} psychrotrophs is at risk of spoilage due to heat-resistant enzymes. For UHT milk to have a shelf life of 1 year, the raw milk must contain less than 0.1 unit of protease mL^{-1} and some high protease-producing bacteria can easily synthesize this amount within a day (Touch and Deeth, 2009).

Massive contaminations of entire commercial lots of UHT and sterilized milk with a then unknown mesophilic aerobic spore former (subsequently identified as *B. sporothermodurans*) were first reported in Italy and Austria in 1985 and in 1990 in Germany. This organism was provisionally called a *highly heat-resistant spore former* (termed HHRS or HRS), as the causative organism survived the UHT process; it occurred more frequently in indirect UHT than in direct UHT processing.

The problem subsequently spread to other countries in and outside Europe. Affected milk products included whole, skimmed, evaporated and reconstituted UHT milk, UHT cream and chocolate milk in different kinds of containers and also milk powders (Scheldman et al., 2006).

B. sporothermodurans does not appear to cause spoilage other than a slight discoloration of the milk and may reach a maximum of 10^5 vegetative cells and 10^3 spores mL^{-1} milk after 15 days' incubation at 30°C of unopened packages of consumer milk. These levels do not affect the pH of the milk and usually do not alter its stability or sensory quality. However, this contamination level far exceeds the sterility criterion of 10 cfu $(0.1\,mL)^{-1}$ specified in EU regulations. Several HRS strains have been tested and none showed pathogenic potential. Despite its poor growth characteristics in milk, UHT milk can be regarded as a new ecological niche for *B. sporothermodurans* because of the lack of competition from other organisms in this product (Scheldman et al., 2006).

The current hypothesis is that highly heat-resistant spores are adapted by sublethal stress conditions (e.g., the H_2O_2 used to sterilize packaging material) in the industrial process and selected for by the heating step. As a result, considerable problems may occur through recirculation (reprocessing) of UHT milk that has passed its use-by date, leading to contaminated lots of milk and milk products. It is extremely difficult to remove from contaminated equipment and has caused the closure of some UHT plants. Reprocessing of UHT milk should not be permitted.

19.2.2.3 Nutrition

The nutritive value of UHT milk can be reduced at two stages: during the UHT treatment and during storage after packaging. The nutritive values of milk components such as fat, fat-soluble vitamins, carbohydrates and minerals are essentially unaffected, whereas values of other components such as the water-soluble vitamins and proteins are adversely affected. Nutrient loss during storage is a function of the temperature of storage, the initial O_2 content of the milk and the nature of the packaging material (in particular, its opacity and permeability to O_2).

19.2.2.3.1 Vitamins

In general, it appears that vitamins are more stable under UHT processing conditions than under pasteurization or other low temperature heat treatments. Fat-soluble vitamins (A, D and E) as well as some water-soluble vitamins (riboflavin, nicotinic acid and biotin) are heat stable and are not adversely affected by UHT processing. Vitamins such as folic acid, C and B_{12} are lost to different extents (Rosenberg, 2011). Considerable variation (from 0% to 100%) has been observed in the losses of water-soluble vitamins during UHT processing and subsequent storage. If the amount of O_2 dissolved in milk is limited, then ascorbic acid losses are minimal. The nutritional value of UHT milk can deteriorate during storage to an extent that is highly dependent on the O_2 level in the product, the temperature and exposure to light. A high nutritional value of UHT milk can be attained by achieving low O_2 levels, selecting packaging materials with effective O_2 barriers and preventing exposure to light by using opaque containers. Low O_2 levels can be achieved either by the use of a deaerator before heating or evaporative cooling after processing, the latter being an essential part of the direct heating process.

19.2.2.3.2 Proteins

The milk constituents that undergo the greatest change during UHT processing and storage are the proteins. Alterations in proteins are related to many technological problems with UHT products such as flavor, gelation, sediment formation, fouling of heat transfer surfaces, loss of nutritional value and browning.

Severe heat treatment causes considerable denaturation (up to 80%) of the serum proteins of milk, especially β-lactoglobulin. Direct heated UHT milk has less serum protein denaturation than indirect heated milk. Although available lysine levels in milk are reduced due to the Maillard reaction, the decrease is small and does not represent a significant loss in nutritional value. No significant changes in other amino acids occur, either during processing or storage.

19.2.2.4 Biochemical and Physical Aspects

Extensive research has reported the presence and characteristics of heat-resistant enzymes in milk and their effects on UHT products during storage (Burton, 1988). Proteases and lipases are of greatest concern. Although phosphatase activity is always zero after milk has been sterilized, it may be reactivated after prolonged storage, where the extent of reactivation increases with storage time and temperature.

The shelf life of UHT milk is sometimes limited by age gelation, an irreversible phenomenon, which is characterized by an increase in viscosity during storage and ultimately formation of a gel, similar to that of custard. It is considered the most important quality problem associated with this type of product, because once the milk has gelled, it has reached the end of its shelf life. The gel is a three-dimensional network of whey proteins and caseins that binds water and engulfs casein micelles and fat globules. The skeleton of the matrix is a protein complex formed between heat-denatured β-lactoglobulin and κ-casein (Datta and Deeth, 2007).

Many factors affect the rate at which gelation occurs, but the major ones are proteolysis, severity of heat treatment, storage temperature, bacteriological quality of the milk and the milk solids content. A widely held view is that gelation is caused by proteolysis of casein caused by the natural milk proteinase, plasmin and/or heat-stable proteinases produced by psychrotrophic bacterial contaminants in the raw milk before processing. The more severe the heat treatment, the longer age gelation is delayed. Thus milks sterilized by indirect heating methods are less susceptible to gelation than milks treated by the direct steam injection and infusion methods. The rate of gelation of UHT milk is markedly influenced by the temperature of storage. Storage at refrigeration temperatures (~4°C) and "high" temperatures (35°C–40°C) delays gelation, while gelation occurs at a maximum rate at ~25°C–28°C. Milk of poor bacteriological quality at the time of processing is much more susceptible to gelling than good quality milk. UHT skim milks are more susceptible to gelation than whole milks. This is attributable to the reduced rate of proteolysis in whole milk caused by partial masking of the protein by fat, which prevents access to the caseins by the proteases (Datta and Deeth, 2007). Recently, a method for detecting very low levels of protease activity and predicting progress of proteolysis in stored UHT whole milk was developed (Button et al., 2011). Although the assays require up to 14 days to complete, this is not an excessive time, compared with the time required for microbiological clearance and total shelf life of the product.

The two main practical ways of preventing gelation or reducing its incidence are to use high quality raw milk and an indirect heating system for the high heat treatment. Addition of sodium hexametaphosphate (SHMP; 0.05% and 0.1%) to milk before heat treatment is effective in retarding gelation. SHMP does not inhibit proteolysis but prevents proteolyzed milks from gelling and is used where food regulations permit.

19.2.2.5 Flavor

The flavor of UHT milk is different from pasteurized milk, with the former generally having a flatter or "purer" taste due to the removal of most of the feedy or barny odors. Fresh UHT milk is characterized by a poor flavor, described as a noticeable "heated" flavor, and by a sulfurous odor note. The initial sensory characteristics of UHT milk disappear within a few days of storage, and a characteristic UHT milk flavor develops with storage time (Rosenberg, 2011).

A U.S. committee on flavor nomenclature (Shipe et al., 1978) has hypothesized that there are four kinds of heat-induced flavors: cooked or sulfurous; heated or rich; caramelized; and scorched. Milk that has been heated to 135–150°C for several seconds exhibits a strong sulfurous or cooked flavor. After several days of storage, this flavor disappears to leave a rich or heated note. Volatile sulfides are believed to contribute to the cooked flavor and it has been suggested that the Maillard nonenzymic browning reaction causes the caramelized flavors. The compounds responsible for the rich or heated note have not been clearly elucidated, and it is possible that what many researchers describe as "stale" is a combination of "rich or heated" and "caramelized" (Mehta, 1980).

Oxidized or rancid off-flavors can also develop in UHT milk, with the extent depending on the level of O_2 and the storage temperature. There is a direct relationship between the level of dissolved O_2 in a product and the headspace volume of a sealed container.

19.2.2.6 Packaging Materials

The most common packaging material used for UHT milk is the paperboard laminate carton, although increasing quantities of plastic-based packages are now being used. The various types of packaging systems suitable for UHT milk were described in Chapter 13 and will not be repeated here.

The sorption of dairy flavor compounds (aldehydes and methyl ketones) by LDPE and PP films has been investigated quantitatively in an attempt to assist aseptic processors select appropriate packaging materials for maximum flavor stability. PP sorbed these compounds to a greater extent than LDPE. Headspace analysis of UHT-processed milk packaged in aseptic paperboard cartons revealed a loss of higher MW flavor compounds after 12 weeks storage, owing to interaction between the LDPE packaging material and the milk (Hansen and Arora, 1990).

Saffert et al. (2008) evaluated changes in the vitamin content of UHT whole milk stored for 12 weeks at 23°C and three different light intensities in PET bottles with a range of light transmittance. Losses of vitamins A and B_2 were more pronounced in transparent PET bottles exposed to the highest light intensity. In these bottles, a reduction in light intensity reduced vitamin A loss from 88% to 66%, whereas in the case of vitamin B_2 its complete decomposition was delayed from 4 to 8 weeks. Vitamin D_3 losses in clear PET bottles were almost independent of light intensity. For the pigmented PET bottles, an increase in package light transmittance and light intensity was found to critically affect vitamin B_2 stability. For vitamin D_3 only, the increase in light intensity was found to be of relevance, whereas for vitamin A stability, no clear effect of light transmittance and light intensity was observed. No sensory evaluation was carried out in the study.

In a similar study, Saffert et al. (2009) stored UHT low fat (1.5%) milk for 12 weeks at 23°C under light of 700 lx in four PET bottle variants representative of those used for milk on the European market in terms of their light transmittance. In clear PET bottles, vitamin A declined by 93% and vitamin D_3 by 66%, whereas vitamin B_2 was completely degraded. In all pigmented PET bottles, the vitamin retention was only slightly higher, with the losses ranging between 70% and 90% for vitamin A, 63% and 95% for vitamin B_2 and 35% and 65% for vitamin D_3 depending on the pigmentation level. In the dark-stored "control" sample, a 16% loss was observed for vitamin A, but the levels of vitamins B_2 and D_3 remained almost stable. On the basis of these findings, the authors concluded that light barrier properties comparable with the high-pigmented PET bottle seemed to be sufficient to protect the light-sensitive vitamins A, B_2 and D_3 in milk for realistic periods on the retailer's shelf. However, they considered that light-induced sensory changes in UHT milk under commercially relevant storage conditions can only be excluded in light-tight packages.

Despite their widespread use, there are virtually no peer-reviewed papers on the shelf life of UHT milk in aseptic cartons. Recently, de Longhi et al. (2012) analyzed five brands of UHT milk sold in Brazil for up to 120 days, which is considered the end of shelf life in that country. None complied with all the physicochemical standards and regulations in Brazil although two brands met all applicable microbiological requirements. Gelation was noticed in all brands after 90 days.

19.3 FERMENTED PRODUCTS

Fermented milks are products prepared from milks (whole, partially or fully skimmed milk, concentrated milk or milk reconstituted from partially or fully skimmed dried milk) homogenized or not, pasteurized or sterilized and fermented by means of specific microorganisms.

Yogurt, the most important of the fermented milk products, is a coagulated milk product obtained by lactic acid fermentation through the action of typically *Lactobacillus bulgaricus* and *Streptococcus thermophilus*. It may contain added fruit or fruit flavors as well as carbohydrate sweetening matter. Kefir has an alcohol content of 0.5%–2% and koumiss of 2%–3%, and both contain considerable quantities of CO_2, which is formed by the heterofermentative, aroma-forming lactic acid bacteria.

The shelf life of yogurt products is determined by the time the product remains safe to eat, the time its functional claims remain true to label or to regulatory requirements and the time its sensory properties remain acceptable to consumers. Fresh yogurt is at its best in the first few weeks of shelf life, after which there is a discernible reduction in sensory characteristics. For example, Salvador and Fiszman (2004) compared storage at 20°C for 21 days with storage at 30°C for 3 days (accelerated) during a study of refrigerated storage (10°C for 91 days) on whole milk and skim milk flavored, set yogurts. They found a gradual deterioration in sensory properties over a 91-day period such that the probability of consumer acceptance was around 40% for the whole milk yogurt and only 15% for the skim milk yogurt after 91 days' storage at 10°C.

A wide range of packaging materials is used for yogurt products (MacBean, 2010). The most popular material by far in current use for spoonable yogurt (either set or stirred) is thermoformed HIPS in the form of small cups or larger tubs, with either an aluminum foil/plastic laminate or a paper/plastic laminate heat seal lid or closure. For example, 6–8 gsm of EVA is applied to foil intended for heat sealing to PS or PP (Özer, 2010). These containers may be produced in form-fill-seal packaging machines or be delivered preformed from packaging material suppliers. It is normal to add pigments such as TiO_2 to the HIPS in order to improve the appearance of the package and to provide some barrier to light (Table 19.3). This also helps in heating and softening the HIPS sheet for thermoforming when radiant heating is used. Rectangular paperboard cartons or cups (with or without an aluminum foil layer), glass containers, PP and blow molded HDPE containers are also used, and for some specialty products in some markets, ceramic containers have been used. A study of the effect of light-induced changes in plain yogurt concluded that PLA provided better protection against photodegradation processes than PS (Frederiksen et al., 2003).

For pasteurized, spoonable yogurt products, laminated materials are desirable if a long shelf life is needed, with some having shelf lives of 4–6 months at ambient temperatures. For these products, a low WVTR is required to stop the yogurt losing water during shelf life. A good O_2 barrier will help to protect the product from oxidation, and a good light barrier will help to delay fading of light-sensitive colors and avoid light-induced oxidation (MacBean, 2010).

TABLE 19.3
Summary of Protective Effects of Different Packaging Materials for Yoghurt

	Protection Against		**Rank in Order of Decreasing Total Protection**
Materials	**Light**	**Oxygen**	
Transparent brown glass	Good	Perfect	1
Unpigmented glass	Moderate	Perfect	4
Transparent brown PS	Good	Moderate	3
Unpigmented PS	Bad	Moderate	5
Paperboard and PS	Excellent	Bad	2

Source: Bossett, J.O. et al., Influence of light transmittance of packaging materials on the shelf life of milk and dairy products—A review, in: *Food Packaging and Preservation*, Mathlouthi, M. (Ed.), Aspen Publishers, Gaithersburg, MD, pp. 222–268, 1999.

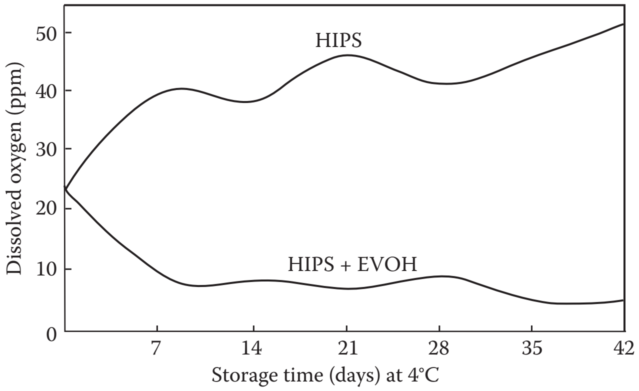

FIGURE 19.2 Dissolved O_2 levels in yogurt stored for 42 days at 4°C in HIPS (upper curve) and HIPS with an EVOH barrier layer (lower curve). (From Miller, C.R. et al., *Packag. Technol. Sci.*, 16, 61, 2003.)

A recent study into the effect of some packaging materials on the flavor of strawberry-flavored, stirred yogurts of 0% and 4% fat content during shelf life showed interesting differences between glass packaging as a reference, PP and 50:50 PS-HIPS (Saint-Eve et al., 2008). In common with an earlier study by Salvador and Fiszman (2004), 0% fat yogurt was found to deteriorate faster than 4% fat yogurt regardless of the packaging type. It was also concluded that PS-HIPS seemed to be preferable to PP for avoiding the loss of fruity notes and for hindering the development of odor and aroma defects, particularly for 4% fat yogurts.

Today, it is common to add probiotic bacteria such as *Lactobacillus acidophilus* and *Bifidobacterium* spp. to yoghurt to impart health benefits to consumers. These bacteria require a low O_2 environment for maximum viability, because dissolved O_2 has a negative effect on their viability. A study by Miller et al. (2003) found that HIPS was ineffective as an O_2 barrier because, during the normal shelf life of commercial yoghurt, the mean dissolved O_2 content increased from 20 to 50 ppm. The use of a packaging material with an added O_2 barrier layer (HIPS-tie-EVOH-tie-LDPE) had a lowering effect on the dissolved O_2 content in the commercial yoghurt, with an initial O_2 content of 20 ppm decreasing to 8 ppm over 42 days (Figure 19.2).

Photooxidation of sour cream packaged in PS cups with different light barrier properties was investigated by Larsen et al. (2009). Three types of cups were evaluated (1) standard PS cups with TiO_2, (2) PS cups with TiO_2 and a barrier layer of Al_2O_3 and (3) PS cups with TiO_2 and a barrier layer of carbon black and Al_2O_3. An area 5 × 7 cm on one side of each cup was exposed to light at 5610 lx for 36 h. Based on sensory evaluation, it was concluded that only cups incorporating a layer of carbon black protected the sour cream from degradation when exposed to light.

19.4 BUTTER AND SPREADS

19.4.1 COMPOSITION

Butter is a fat product obtained from milk and has the following main characteristics: a minimum milk fat content of 80%–82%, total fat-free dry milk solids of 2% and a maximum moisture content of 16%. Approved additives include food colorants (annatto, β-carotene and curcumin), NaCl and cultures of harmless lactic acid-forming bacteria. The pH can be adjusted, if required, by the addition up to a maximum level of 2 mg kg^{-1} of approved neutralizing salts (Fearon, 2011).

During the production process, the milk fat is concentrated by two successive physical steps: separation of the milk and churning of the cream, which is subject to phase inversion by physical disruption of the natural milk fat globule membrane. After washing with clean water to remove milk solids, the granules are physically worked into a uniform mass that is called *butter*. Thus, butter is basically a high fat-content product in which the fat phase is the continuous one. However, the water phase (consisting mainly of small droplets) can migrate slowly. Butter is normally classified into the following four groups:

1. Unsalted butter (i.e., butter not flavored with salt) prepared from sweet cream
2. Salted butter prepared from sweet cream (salt content in the range of 0.2%–2.0%)
3. Unsalted butter prepared from sour cream
4. Salted butter prepared from sour cream

The most common type of butter in the United States is salted butter prepared from sweet cream. It typically has a moisture content of 15.8% w/w and a fat content of 82% w/w.

The shelf life of butter is influenced by microbial, enzymic and chemical reactions. In addition, the susceptibility of butter to readily absorb odors from the surrounding environment can also limit its shelf life. Therefore, the choice of packaging material is usually made with the intention of delaying or preventing the undesirable reactions.

The chemical composition of butterfat plays an important role in oxidation. Heavy metals or their salts (particularly copper) have a very strong catalytic effect, with low pH promoting oxidation. Free fatty acids, fat-soluble amino acids and carotene also promote oxidation, although under the influence of light, carotene acts as an antioxidant. A natural antioxidant in butter is tocopherol (vitamin E). Butter is best stored at −25°C, and sweet cream, salted butter keeps satisfactorily for several years at this temperature. Although slightly oxidized flavors are expected by many consumers and are disguised by salt addition, the shelf life of butter can be usefully prolonged by exclusion of O_2 during packaging and subsequent storage (Muir and Banks, 2003).

The chemical composition of the water phase varies depending on the type of butter in respect of pH and salt, protein and lactose content. Consequently, different microfloras can develop in, or are inhibited by, the various butters. For example, salted butter made from sour cream inhibits the development of certain microorganisms.

Dairy-based spreads are manufactured using similar technology to that used to produce margarine and may have fat contents of 37.5%–76.3%. In contrast to butter, the amount of fat present is low but high levels of milk protein may be incorporated to stabilize the product. Because of the high water content, the water in oil emulsion may have limited stability and this limits shelf life, especially when the product is subject to temperature cycling. A further problem is the potential for bacterial growth and spoilage as a result of the higher water content, limiting the shelf life of spreads especially when stored above 4°C (Muir and Banks, 2003).

19.4.2 PACKAGING REQUIREMENTS

19.4.2.1 Oxidation

Butter is very susceptible to light-induced flavors, which are mostly accompanied by oxidation defects. Light-induced oxidation of butter may occur when it is inadequately protected under illumination. The degree of deterioration depends on factors such as light source, wavelength of light, exposure time, distance of the butter from the light source and β-carotene content of the butter (Hansen and Skibsted, 2000). Butter is generally exposed to fluorescent light during storage in retail display cabinets.

The effect of varying headspace O_2 concentration and color of light on photooxidation and degradation of photosensitizers in butter was reported by Wold et al. (2009). In butter, at least six different photosensitizers are present: riboflavin, protoporphyrin IX, hematoporphyrin, a chlorophyll *a*-like substance and two unidentified tetrapyrroles.

Butter samples were stored at 4°C under 0%, 0.4%, 0.8%, 1.6%, 3.0%, 5.0% and 21% O_2 and exposed to violet, green or red light for 36 h. The higher the O_2 concentration, the more sensory degradation of the samples. Violet light resulted in slightly higher degrees of photooxidation than green and red light for low O_2 concentrations.

In light of the aforementioned points, it is no surprise that the packaging material has a marked effect on the intensity of the oxidized flavor that develops, depending largely on the amount of light transmitted. Butter packaged in various types of conventional parchment papers develops objectionable levels of oxidized off-flavor after a few hours exposure in a supermarket display cabinet. However, aluminum foil laminates are satisfactory even after 48 days of continuous exposure. In a study (Emmons et al., 1986a) that investigated the influence of light on butter packaged with various materials (five mica-filled HDPE-based plastics, some containing yellow pigments; two parchment papers; two aluminum metallized papers; and aluminum foil glue laminated to bleached sulfite paper), oxidation occurred on the light-exposed butter surface with all the materials except the aluminum foil laminate when exposed to the three strongest light intensities.

Various packaging materials differ markedly in their transmission of light as shown in Figure 19.3. The transmission of parchment (A) ranges from 46% to 64%, while the presence of yellow pigments in (B) markedly reduces transmission to 1%–17% in the 300–500 nm range and to less than 50% in the higher range. However, the reduced transmission below 500 nm does not appreciably reduce oxidation, indicating that longer wavelengths are important. Metallized papers transmit less than 10% of light and the foil paper laminate transmits no measurable light. Oxidation is greater at lower intensities of light and at shorter times of exposure than expected from that observed at higher intensities and longer exposure times.

Metallic contamination of butter from dairy processing equipment is now minimal due to the widespread use of stainless steel. In light of the fact that surface oxidation has been documented as the major flavor defect in butter at the retail level (Emmons et al., 1986b), butter should be packaged in laminates containing aluminum foil, which effectively block out all the light.

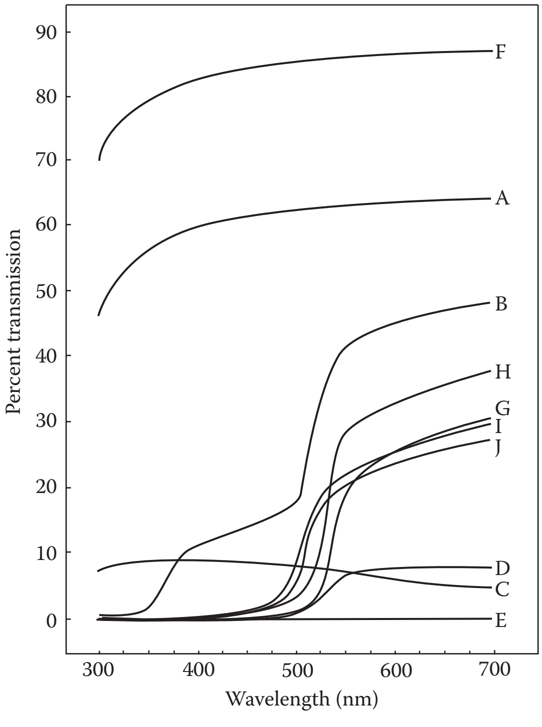

FIGURE 19.3 Spectra of light transmission by paper-based (A, B, C and D); foil laminate (E); and polyethylene-based packaging materials (F, G, H, I and J). (From Emmons, D.B. et al., *J. Dairy Sci.*, 69, 2248, 1986b.)

19.4.2.2 Water Vapor Permeability

The surface desiccation of butter results in discoloration, a defect known as *primrosing*. However, if the packaging material is completely impermeable to water vapor, then there might be an increased risk of surface mold growth in areas where pockets of moisture have developed. The surface drying, which occurs in butter packaged in parchment would thus be an advantage if the butter were susceptible to mold growth.

The WVTR requirements of a satisfactory packaging material for butter vary from country to country but a maximum of 3 g m^{-2} day^{-1} is generally agreed upon.

19.4.2.3 Odor Permeability

The susceptibility of fats to absorb odor compounds means that a satisfactory packaging material for butter should protect the butter from such odors. One simple but common test is to store the packaged butter for 24 h at 18°C over clove oil, after which time the butter should have no odor or taste of clove oil.

19.4.2.4 Packaging in Current Use

Retail packaging of butter is commonly in aluminum foil (0.009 mm thick) laminated either to 40 gsm greaseproof paper or vegetable parchment, or sometimes just the paper or parchment alone. Other types of packaging for butter and dairy spreads include plastic tubs thermoformed from white-pigmented HIPS or PVC with a tight-fitting lid of the same material. To fill tubs with butter, it must be packed directly from the churn or reworked immediately prior to packing so that it will flow into the package and fill it efficiently.

19.5 CHEESE

19.5.1 CLASSIFICATION

Cheese is the generic name for a group of fermented milk-based foods produced in at least 500 varieties around the world. Although some soft cheese varieties are consumed fresh (i.e., without a ripening period), production of the vast majority of cheese varieties can be subdivided into two well-defined phases: manufacture and ripening. Despite differences in detail in the manufacturing processes used for individual varieties, the conversion of milk into cheese generally comprises four stages:

1. *Coagulation*: physicochemical changes in the casein micelles due to the action of proteolytic enzymes and/or lactic acid lead to the formation of a protein network called coagulum or gel
2. *Drainage*: separation of the whey, after mechanical rupture of the coagulum, by molding and, in certain cases, by pressure, to obtain a curd
3. *Salting*: incorporation of salt by deposition on the surface or within the body of the cheese, or by immersion in brine
4. *Ripening*: biochemical changes in the constituents of the curd brought about by the action of enzymes, mostly of microbial origin

Cheese manufacture can be viewed as essentially a dehydration process in which the fat and casein in milk are concentrated between 6- and 12-fold, depending on the variety. The degree of hydration is regulated by the extent and combination of the three steps listed earlier in addition to the chemical composition of the milk. In turn, the level of moisture in the cheese, the salt content and the cheese microflora regulate the biochemical changes that occur during ripening and thus determine the flavor, aroma and texture of the finished cheese. Although the nature and quality of the finished cheese are determined in very large measure by the manufacturing steps, it is during the ripening phase that the characteristic flavor and texture of the individual cheese varieties develop.

With the exception of some soft cheeses, most cheese varieties are not ready for consumption at the end of manufacture but undergo a period of ripening (also referred to as *curing* or *maturation*), which varies from about 4 weeks to more than 2 years. The duration of ripening is generally inversely related to the moisture content of the cheese, although many varieties may be consumed at any of several stages of maturity depending on the flavor preferences of consumers.

19.5.2 MICROBIOLOGY

The microflora in cheese can be divided into two main groups: starter and secondary flora. The starter flora, added at the beginning of manufacture or naturally present in the milk, is responsible for acid development during cheese production. Mesophilic and thermophilic starters, with optimal growth temperatures of ~30°C and 45°C, respectively, are used. The secondary flora is composed of complex mixtures of bacteria, yeasts and molds and contributes significantly to the specific characteristics of a particular cheese variety (Poças and Pintado, 2010).

A great variety of microbial species are involved in the ripening of cheese, the total population generally exceeding 10^9 organisms per gram. The principal bacterial groups involved in ripening are the lactic acid *Streptococci*, *Leuconostoc*, *Lactobacilli* and *Propionibacteria* species. *Micrococci* and *Corynebacteria* species may also be involved; they are aerobic and salt tolerant and thus grow especially on the surface of cheeses.

Yeasts are widely distributed in nature and are found in raw milk and some cheeses, with the basic flora in the majority of cheeses being species of the genus *Kluyveromyces*. Yeasts produce enzymes capable of degrading the constituents of the curd and so can contribute to modifying the texture of the cheese and to the development of flavor and aroma. They are capable of converting lactose into CO_2 and may also take part in lipid degradation.

Among the fungal flora found in or on mold-ripened cheeses, species of the genus *Penicillium* are of particular importance. *Penicillium camemberti* is the original mold of Camembert and Brie and has a single habitat—the surface of a few cheeses and the environment of cheese factories. By contrast, *Penicillium roqueforti*, a microaerophilic mold, is widely distributed and is the mold of mold-ripened cheese; it grows very well at quite low O_2 levels (5%). *Geotrichum candidum* is present on certain soft cheeses where it forms a characteristic grayish-white crust on the surface. The role played by molds in ripening is a major one for soft and mold-ripened cheeses.

Fermentation of lactose to lactic acid during manufacture and the metabolism of residual lactose during the initial stages of ripening reduce the pH of cheese to around 5 depending on variety; at this pH, the growth of many pathogenic bacteria is inhibited. During ripening, the pH of the cheese rises due to the formation of alkaline N-containing compounds and/or the catabolism of lactic acid (Fox, 2011).

The influence of pH on microbial growth and enzyme activity is particularly decisive. Only lactic acid bacteria, yeasts and molds can grow at pH values below 5. Enzymes are also very sensitive to variations in pH, with most microbial proteases having greatest activity in the pH range of 5.0–7.5, and lipases in the range of 7.5–9.0. Curd at the end of drainage has a pH of less than 5.5 and is the site of active lactic acid fermentation. This acidic character of the curd is a necessity in that it slows down enzyme action and impedes the development of a harmful bacterial flora.

Soft cheese curd has a pH below 5, with the pH of Camembert increasing from 4.5 to over 6.0 in the interior and over 7.0 on the surface by the end of ripening (about 30 days). Hard cheeses have pH values around 5.2–5.3, and neutralization of the cheese is undesirable. The pH tends to remain at about this level during ripening, partly because of the high degree of mineralization of the cheese, which gives it a high buffering capacity.

19.5.3 PACKAGING REQUIREMENTS

The two key parameters contributing to the stability of cheeses are pH and a_w. However, neither of these parameters is low enough to ensure complete stabilization of the product, with the result that cheeses as a class lie between perishable foods on the one side and intermediate moisture foods on the other. While the packaging will have no influence on the pH of the cheese, the a_w of the surface (and ultimately the interior) of the cheese will be affected by the WVTR of the packaging material.

Two other key environmental factors that must be considered in the packaging of cheese (and indeed in the packaging of all dairy products) are light and O_2. As discussed earlier in this chapter, light initiates the oxidation of fats, even at temperatures found in refrigerated display cabinets. In unripened cheeses, this gives rise to off-flavors, which have been described as "cardboardy" or "metallic." Although lipid oxidation has been the main focus due to its high impact on flavor and off-flavor formation, the increasing production and sale of low fat dairy products, including low fat cheeses, makes the oxidation of amino acids and proteins of interest due to their higher impact on off-flavor formation in products with limited fat content. Sulfur compounds have been suggested to be of major importance in protein oxidation in dairy products and dimethyl disulfide (DMDS) has been identified as a major protein oxidation product in milk, including low fat cheeses (Dalsgaard et al., 2010). The generation of DMDS is reduced in vacuum-packed cheese when compared with cheeses packed in air.

Photooxidation of cheeses may be reduced by (1) minimizing light exposure, (2) optimizing the package barrier to light and (3) minimizing both the headspace volume and its residual O_2 levels (Mortensen et al., 2004). A review of light-induced changes in packaged cheeses concluded that integrating results and conclusions on the effects of light on the sensory characteristics of packaged cheeses is very complicated because published reports contain various levels of detail about the experimental setups and methodologies. It was suggested that there is an urgent need for a more systematic approach to shelf life testing with respect to time, temperature, light sources and their intensity (Mortensen et al., 2004).

The oxidation reactions initiated by light may continue even if the cheese is subsequently protected from light (Hong et al., 1995) and any metallic ions contained in the packaging material will catalyze the reactions. In addition, the ingress of O_2 through the packaging film is undesirable as it will contribute to the oxidation of fats and the growth of undesirable microorganisms.

For the purposes of providing a framework to discuss packaging requirements, the following classification scheme for cheeses will be used: very hard and hard, semisoft and soft, fresh, and processed.

19.5.3.1 Very Hard and Hard

The very hard class of cheese (sometimes referred to as *grating grade*) is ripened by bacteria and is characterized by a moisture content (on a fat-free basis) of <51%, (e.g., Parmesan 42%; Romano 31%; and Mozzarella 45%). The hard class of cheese is also ripened by bacteria and is characterized by a moisture content of 49%–63%, where the range 49%–56% is categorized as hard, and the range of 54%–63% is categorized as semihard. Cheeses in this class include Cheddar (still the cheese produced in the greatest quantities worldwide), Edam, Gouda, Cheshire, Gloucester, Derby and Leicester, as well as those with eyes such as Emmental and Gruyere. Also included in this class are Provolone, Mozzarella and Kasseri.

19.5.3.1.1 Rindless Ripening

Rindless cheese may be defined as cheese that has been ripened under a plastic film that allows little or no evaporation into the atmosphere to occur. Cheeses to which the technique of rindless ripening can be applied are obviously those in which the rind does not play an essential role in ripening. Such cheeses include the cooked, hard cheeses such as Emmental, as well as the uncooked hard cheeses such as Cheddar, Edam, Gouda and Saint Paulin. A feature of all these cheeses is that they do not have surfaces covered with molds, bacteria or yeasts producing enzymes responsible for ripening.

The development of the technique of ripening under film (also known as *rindless ripening*) was motivated by various factors. One was the need to produce blocks better suited to a high degree of mechanization. Another was to increase cost-effectiveness by replacing earlier techniques of coating, thus reducing handling during ripening and losses due to drying-out. The first techniques (which appeared around 1930 and were used for cheddar) involved coating the blocks with mineral oil. In 1950, J.B. Stine of Kraft Foods filed two patents concerning the use of a plastic packaging material for blocks of Swiss cheese; these patents have since passed into the public domain. A further factor was the development of prepacked, self-service, consumer portions of cheese for or by supermarkets, where the losses resulting from removal of the rind were considered unacceptable. This led to the idea of rindless cheese (Fradin, 1987).

There are three variables which may be used to adjust the process of ripening rindless cheese: the permeability of the packaging material; the ripening temperature; and the ripening time. Discussion will be limited to the first of these variables.

Mineral waxes used for coatings on cheeses consist of refined hard paraffin, petroleum jelly and microcrystalline waxes with various additives. Paraffin wax comprises mostly saturated aliphatic unbranched alkanes, and a range of different colored waxes are used to differentiate cheeses. For example, Gouda cheeses are typically coated with yellow or white waxes, whereas Edam cheeses are coated with red wax. Wax protects the cheese from mold growth and weight loss through moisture evaporation and prevents aerobic ripening because of its barrier to O_2. Mineral waxes present a higher barrier to O_2 than acetoglyceride-based waxes, which are also used for cheese. Water-based dispersions are typically copolymers of ethylene and vinyl acetate. These coatings may be uncolored or pigmented with different colors and are used as carriers for antifungal agents such as natamycin (E235), calcium sorbate (E203) and potassium sorbate (E202). These coatings are applied in one or several layers before the wax layer (Poças and Pintado, 2010).

Plastic films are widely used for packaging rindless cheese, and the specifications of some retail packages used for rindless cheeses are presented in Table 19.4. Unfortunately, the package dimensions and test conditions for the transmission rates were not specified, making the data of limited applicability.

One of the major problems faced by consumers of packaged cheeses is mold growth once the package has been opened. The incorporation of zip-lock press-to-close resealable technologies featuring flanged interlocking zipper profiles on plastic pouches for cheese has solved this problem. Resealable packages can also be made using a slider that features an ergonomically designed "clip" to enable consumers to easily open and close a package. Both technologies are ideal for premade pouches and form-fill-seal applications, and can run on virtually all packaging formats and machinery configurations.

Analysis of the gas found in the holes of, for example, an Emmental cheese revealed that it was composed of 95% CO_2 and 5% N_2. This atmosphere protects the entire cheese against the development of molds (Stehle, 1987).

19.5.3.1.2 Role of Oxygen

The fate of O_2 in cheese is still not completely understood. What is certain is that the gas present in the space between the packaging material and the cheese (either produced as a product of enzymic action in the cheese, left in the package after sealing or diffusing through the packaging material) determines whether or not microbial growth will occur on the surface of the cheese.

The extent to which oxidation occurs largely depends on the storage temperature and time; also important are the surface area:volume ratio of the cheese and the O_2 permeability of the packaging material. The latter will vary with temperature and may vary with RH, depending on the chemical nature of the material.

Packaging films for Cheddar cheese must be sufficiently impermeable to O_2 to prevent fat oxidation and mold growth. Data on the minimum partial pressure of O_2 necessary for the development of molds are scarce. In the absence of CO_2, molds will grow at O_2 partial pressures below 0.133 kPa. In the presence of CO_2 at partial pressures of 8.7–15 kPa, microbial growth is inhibited up to an O_2 partial pressure of 2.0–2.7 kPa.

TABLE 19.4
Specifications of Some Retail Packaging Materials Used to Package Rindless Cheese

Laminate Composition	Thickness (μm)	Transmission Rate (mL m^{-2} day^{-1} atm^{-1})			
		O_2	CO_2	N_2	H_2O
Sliced cheeses (with no gas production, e.g., Cheddar):					
Lower films PET-LDPE or	300/50	12	60	7	1.5
PET-LDPE	250/50	14	42	9	1.0
Upper films PET-LDPE	36/70	35	128	21	2.0
or PET-PET-LDPE	12/23/54	40	160	20	8.0
Sliced cheese (with slight gas production, e.g., Gouda) using hard box pack (RC[a]):					
Cover film (OPET-LDPE)	23/75	85	340	43	2.0
Trough film (PET-HM[b]-LDPE) with migration barrier	200/25/25	5	20	2.5	1.5
Tubular bag (OPA-LDPE)	15/40	60	240	30	4.0
Sliced cheeses (with high gas production, e.g., Emmental) using hard box pack (RC[a]):					
Cover film (OPET-LDPE)	40/60	550	2200	275	1.5
Trough film (PET-HM-LDPE) with migration barrier	200/25/25	5	20	2.5	1.5
Tubular bag (OPA-LDPE)	10/50	90	360	45	4.0
Cheese portions without gas production:					
Tubular bag (OPA-LDPE)	15/40	4	16	2	4.0
Cheese portions with low gas production:					
Cover film (OPA-LDPE)	15/40	60	240	30	5.0
Bottom film (PA-LDPE)	15/120	40	160	20	1.5
Tubular bag (OPA-LDPE)	15/40	60	240	30	5.0
Grated cheese (e.g., Emmental):					
Tubular bag (OPA-LDPE)	15/40	60	240	30	5.0

Source: Schneider, Y. et al., Packaging materials and equipment, in: *Technology of Cheesemaking*, 2nd edn., Law, B.A. and Tamine, A.Y. (Eds), Blackwell, Malden, MA, pp. 413–439, 2010.

[a] RC is reclosable.

[b] HM is not melt.

It is likely that problems of mold growth on hard cheeses packaged in the films in common use today are a function of hygienic conditions in the packing room, the degree of vacuum inside the package and the integrity of the heat seal, rather than the O_2 permeability of the packaging material used.

19.5.3.1.3 Modified Atmosphere Packaging

Modified atmosphere packaging (MAP) is used particularly for portioned and sliced hard cheeses as they are more prone to deteriorative changes because of a larger surface area exposed to light and O_2, and, therefore, high barrier packaging must be used. Vacuum packaging may have a negative impact on the appearance of some cheeses, particularly those with eyes, such as Emmental, Edam and Gouda, which may collapse under reduced pressure. For more resistant cheeses, vacuum skin packaging is very common. In MAP, the gas mixture should be optimized for each cheese; a recent review (Khoshgozaran et al., 2012) helpfully summarizes the reported optimal MAs for a range of cheeses. Some cheeses withstand mixtures with compositions richer in CO_2; others suffer from sensory problems and package collapse and, therefore, MAs with a lower percentage of CO_2 and more N_2 are used. Multilayer films composed of combinations of PA or EVOH as gas barriers and polyolefin-based materials such as LLDPE, EVA copolymer and ionomers as moisture barriers and sealing layers are used (Poças and Pintado, 2010).

In a study evaluating various gas mixtures (Favati et al., 2007), CO_2 and N_2 (30:70) best preserved portioned Provolone cheese by slowing down the proteolytic and lipolytic phenomena typical of cheese ripening. This packaging system extended the shelf life to more than 9 months at 8°C, an increase of 50% compared with that obtained under vacuum packaging. The packaging film was 20 μm PA-80 μm LDPE with an O_2 permeability at 23°C of 7.7 *barrer.* Although the study indicated that 400 g portions of cheese were packaged, unfortunately, the surface area of the packs was not specified making the findings nontransferable. In commercial applications, pillow pouches of portions of Provolone are given a 6 month shelf life when refrigerated at 4°C–8°C.

Graviera hard cheese had a shelf life of 9 weeks when stored in the dark at 4°C under atmospheres of 100% N_2 or 50:50 CO_2:N_2, compared with 2–3 weeks for unpackaged cheese. The packaging material consisted of 75 μm LDPE-PA-LDPE with an OTR of 11 mL m^{-2} day^{-1} and WVTR of 1.29 g m^{-2} day^{-1} (temperature and humidity test conditions unspecified). Samples packaged under 100% CO_2 developed a bitter score after 5 weeks of storage (Trobetas et al., 2008). Arvanitoyannis et al. (2011) investigated the shelf life of Graviera cheese stored at 4°C for up to 90 days in 90 μm PA-LDPE pouches under three different MAs: MA1 40% CO_2:55% N_2:5% O_2; MA2 60% CO_2:40% N_2; MA3 50% CO_2:50% N_2. Control cheeses were packaged in air. Pouch barrier properties were given as OTR 40–50 mL m^{-2}, CDTR 150 mL m^{-2} and N_2TR 10 mL m^{-2}, but temperature and humidity test conditions were not specified, and neither were the pouch dimensions. The microbiological analysis revealed that there were no colonies of *Staphylococcus aureus* and *Listeria monocytogenes*, whereas both *Escherichia coli* and total viable counts increased strongly in control samples but were inhibited under all MAP compositions. After 10 days of storage, the sensory characteristics of the control cheeses were found to be unacceptable. The most effective mixtures for inhibiting the growth of *E. coli* were MA2 and MA3. Both MA1 and control samples had a very negative effect on sensory quality.

The effect of an oxygen scavenger combined with an ethanol emitter (EE) and a MA of 100% N_2 in combination with a high barrier experimental SiO_x-coated PET-LDPE film on shelf life extension of grated Graviera cheese stored for 10 weeks at 4°C and 12°C was investigated by Mexis et al. (2011). Sensory shelf life was ~1, 1.5, 4.5, 6, 9 and at least 10 weeks for control samples (12°C and 4°C), for N_2 packaged samples (12°C and 4°C) and samples packaged with the OA + EE (12°C and 4°C), respectively.

The introduction of pure CO_2 into the package often produces the appearance of vacuum packaging after a certain period of storage. This is the result of absorption of CO_2 by the cheese as well as some loss by diffusion through the packaging material. Because the permeability of polymer films to CO_2 is approximately four times that of O_2 or N_2, the rate of loss of CO_2 is greater than the rate at which these other gases can permeate in from the surrounding atmosphere. As a result, there is a decrease in volume of the package and the packaging material collapses around the cheese. A similar phenomenon was described in Chapter 18 in connection with MAP of fruits and vegetables. The more CO_2 which the cheese has “lost” at the time of cutting/slicing and packaging, the greater the absorption of CO_2 from gas flushing and the greater the contraction of the package volume. Thus, in the gas flush packaging of cheese slices it is recommended that a mixture of gases (CO_2 and N_2 in the ratio 80:20 or 70:30) be used to avoid the slices being pressed against each other by atmospheric pressure (Alves et al., 1996).

Unattractive calcium lactate crystals (CLC) on Cheddar cheese have been documented since the 1930s. Agarwal et al. (2005) reported heavy CLCs on the surfaces of all gas-flushed but not on vacuum packaged cubes (1 × 1 × 4 cm) after 12 weeks storage at 7°C, regardless of the gas composition. Although milk composition and the presence of nonstarter lactic acid bacteria can contribute to the development of CLC on cheese surfaces, gas flushing is the most important factor.

19.5.3.2 Semisoft and Soft

This class of cheese is also ripened by bacteria and is characterized by a moisture content of 61%–69% on a fat-free basis and 43%–55% on a total basis. Soft cheeses are cheeses which, independently of lactic acid fermentation, have undergone other ripening processes. The body is neither cooked nor pressed and may contain internal mold.

Examples of semisoft and soft cheeses include those that have been ripened by bacteria such as Brick and Munster, those ripened by bacteria and surface microorganisms such as Limburger and Trappist, those ripened by surface mold such as Brie and Camembert and those ripened by internal (blue) mold such as Roquefort, Gorgonzola and Stilton. Other semihard cheeses include Havarti, Samsø and Edam.

19.5.3.2.1 Light

Sliced, rindless Havarti cheese packaged in an atmosphere of 25% CO_2 and 75% N_2 and stored under light for up to 21 days at 5°C showed a decrease in yellowness, an increase in redness and no significant changes in lightness (Kristensen et al., 2000; Mortensen et al., 2002). Sliced, rindless Samsø cheese packaged in atmospheres of CO_2 and N_2 (0:100; 20:80 and 100:0 with residual O_2 at time of packing <0.24%) and stored under varying light conditions for up to 21 days at 5°C also showed significantly decreased yellowness and increased redness (Juric et al., 2003). Cheese stored in 100% CO_2 had significantly lower lightness and was described by the sensory panel as having a rancid taste and odor, as well as a dry/crumbly texture.

In contrast to fresh cheeses, semisoft and soft cheeses require limited protection against light to maintain quality. When the cheese is ripe enough to be packaged, the influence of light on soft cheeses with a surface mold is of little importance. Although light can slow down or hinder the germination of conidia, there is no such hindering effect with thick layers of mycelia at an advanced stage of ripening. The same applies to red smear, and light does not even reach the internal mold of blue-veined cheeses unless they are sliced. Mold mycelia, as well as the rind, which forms during ripening, also provide protection against light.

19.5.3.2.2 Gases

The consumption of O_2 and the production of CO_2 are closely connected with the total bacterial count and the ripening conditions of temperature, humidity, pH, a_w and so on. In the case of Camembert, for example, there is an increase in the starter bacterial count to about $10^{10}\,g^{-1}$ after the first turning, declining more or less rapidly until ripe for packaging to stabilize at about 10^7–$10^9\,g^{-1}$. For a Camembert weighing 100 g, the peak O_2 requirement is about 15 mL h^{-1} with a CO_2 release of 10 mL h^{-1}. On further ripening prior to packaging, this drops to about 4.5 mL h^{-1} for O_2 and about 3.6 mL h^{-1} for CO_2.

Measurements taken of unpackaged and packaged Camembert have shown that the unpackaged cheese loses about 0.04% of its weight per hour during ripening, whereas packaged cheese loses about 0.006% h^{-1} as water vapor (International Dairy Federation, 1987). These figures were obtained at 10°C, and temperature clearly has an important influence. Thus, at 20°C, the O_2 requirement is 11 mL h^{-1} and at 30°C it is 17.5 mL h^{-1}. The surface area:volume ratio is also important in determining the level of CO_2 release, and the greater the surface area for a given cheese weight, the higher the CO_2 release.

The effects of MAP on the growth of *L. monocytogenes* in mold-ripened Stilton cheese during refrigerated storage over a 6 week period have been studied (Whitley et al., 2000). When samples were inoculated with *L. monocytogenes* and stored under MAP at N_2:CO_2:O_2 ratios of 80:10:10, 100:0:0 and 80:20:0, a significant decrease in count was found in samples stored in the 80:10:10 atmosphere. A greater inhibitory effect was achieved when CO_2 concentration was increased to 20% than by reducing the O_2 content. Results indicated that an 80:10:10 ratio is not suitable for use with blue Stilton cheese when *L. monocytogenes* may be present.

19.5.3.2.3 Humidity

The growth of microorganisms in and on soft cheese is dependent on the a_w of the cheese, which is clearly influenced by the water vapor permeability of the packaging material. If the humidity of the air under the package becomes too high, then the fungus mycelia begin to turn yellow and exude liquid in the form of droplets, finally showing autolytic symptoms. This results in a clear shift of the flora composition toward hydrotrophic bacteria such as *Brevibacterium linens*. Conversely, if the permeability of the packaging material is too low, the growth of mold or surface smear may be stopped, resulting in the appearance of facultative anaerobic bacteria with strong proteolytic activity.

Most polymeric packaging materials are too impermeable to be used for soft cheeses and must, therefore, be perforated before use. No definite rules can be laid down with regard to the number and size of the perforations as these must be found experimentally for the particular type of cheese. It should also be borne in mind that soft cheeses of the same type (e.g., Camembert) may behave differently depending on the method of production.

In some countries, it is permissible to treat the packaging materials with fungicide to prevent subsequent mold growth on the surface after packing. Typically, the packaging material is impregnated with sorbic acid or its salts, where the concentration needs to be sufficiently high (and the packaging material sufficiently close to the cheese surface) in order to prove successful.

19.5.3.2.4 Ripened by Internal Mold

The packaging material for internal molded cheese should allow for the passage of O_2 to promote mold development in the curing channels of the cheese. The package should also allow for a certain permeability to CO_2 and water vapor (Odet and Zachrison, 1982). However, blue-veined cheeses seem to be less dependent on the gas permeability of the packaging material than other soft and semisoft cheeses. For example, *P. roqueforti* grows in O_2 concentrations as low as 5%, as found in the curd holes of the cheese. The presence of CO_2 seems to stimulate growth, and therefore more impermeable packaging materials such as aluminum foil, PP film or thermoformed packages made from rigid PVC or PS with a transparent multilayer film lid for portions have proved effective (International Dairy Federation, 1987).

19.5.3.2.5 Ripened by Surface Mold

In surface mold-ripened cheeses such as Camembert and Brie, lactate is metabolized to CO_2 and H_2O by the activity of *P. camemberti*. For these cheeses, it is important that packaging does not take place until the mold has grown to a certain extent. The packaging material must have a limited permeability to O_2 to minimize the risk of development of anaerobic proteolytic bacteria, which can also develop if the permeability to water vapor is too low resulting in condensation inside the package. The material should not adhere to the surface mold of the cheese (Odet and Zachrison, 1982).

A suitable material for the packaging of these cheeses is perforated OPP, where the perforations are necessary to allow the passage of controlled quantities of water vapor. Paper is also used for packaging but, if it is in direct contact with the surface of the cheese, it must be coated with wax or laminated to perforated film to avoid decomposition of the paper by cellulase enzymes produced by certain molds. Aluminum foil is also used at a thickness of 7–9 µm if laminated to other materials and 12 µm if used alone. It must be given a protective coating of lacquer otherwise NH_3 (a metabolite in the cheese ripening process) many corrode the metal, turning it black. It is preferable not to perforate the inner layer in direct contact with the surface of the cheese in order to avoid mycelia growing through the perforation and becoming apparent on the outside of the package.

Thermoformed packages made from PS and PVC are used, sometimes extrusion coated with LDPE to reduce WVTRs. Special packages for the sterilization of Camembert are made from combinations, which consist of OPP-PVdC copolymer-PP, PET-PVdC copolymer-PP or OPA-PP-PVdC copolymer for deeper containers with higher puncture resistance (Stehle, 1987).

With few exceptions, soft cheeses are placed in an additional outer package prior to marketing. Traditionally, these consisted of wood, but the use of paperboard or a combination of a plastic base and a paperboard cover has become the norm. The plastic bases (PVC or HIPS) are designed in such a way that corrugation and air channels in the base ensure that sufficient gas and water vapor exchange occur.

Soft-mold (Camembert-type) cheeses are packaged early in the ripening process as soon as *P. camemberti* mycelium covers the cheese surface. The effect on cheese-ripening dynamics of four films with different WVTRs (ranging from 1.6 to 500 g m^{-2} day^{-1} at 38°C and 90% RH) was compared to unwrapped cheeses by Picque et al. (2010). The packaged cheeses were stored at 6°C and 75% RH. Water loss ranged from 0.5% to 12% on day 23, compared with 15% for unwrapped cheeses, and this appeared to be a key factor in controlling cheese-ripening progress. Low water losses (from 0.5% to 1% on day 23) led to over-ripening in the cheese underrind, which became runny as a result. Water losses of around 3%–6% on day 23 led to good ripening dynamics and the best cheese quality. This level of water loss appeared to be ideal in terms of cheese film design.

The shelf life of Stracciatella cheese (similar to Mozzarella) packaged in various MAs of CO_2:N_2:O_2 gas mixtures (50:50:0 [M1], 95:5:0 [M2], 75:25:0 [M3] and 30:65:5 [M4]) and stored at 8°C was investigated by Gammariello et al. (2009). Cheeses in traditional tubs and under vacuum were used as the controls. Results showed that MAP, in particular M2 and M3, delayed microbial growth of spoilage bacteria, which determined end of shelf life; the sensory quality did not limit shelf life.

Recently, Rodriguez-Aguilera et al. (2011) compared MAP of a soft surface mold ripened full fat (45%) cheese (St. Killian) under two atmospheres: A (0% O_2: 27% CO_2) and B (2% O_2:19% CO_2) at 12°C with an existing commercial packaging system (a wax layer in contact with the cheese surface, a paper layer and an outer layer of varnish, and inserted in an open cardboard box). The predicted shelf life was found to be 14, 6 and 17 days for control, MAP-A and MAP-B, respectively. It was concluded that MAP of surface-mold-ripened cheese with low levels of O_2 (1%–3%) and relatively high levels of CO_2 (17%–21%) can be used to extend the shelf life of soft cheese by 20%. However, the package has to be suitably designed, as total loss of O_2 (as in MAP-A) would shorten the shelf life; a high barrier plastic container was suggested but not tested. The shelf life of the control is ~4 weeks when stored at 4°C.

19.5.3.2.6 Ripened by Smear Coat

The quality of smear-coated cheeses, such as Havarti, Limburger and Munster, is strongly dependent on the vitality of the surface culture (often *B. linens*), which is related to the RH inside the package. These cheeses are sometimes wrapped in clear or orange pigmented OPP combined with greaseproof paper. Vegetable parchment is also recommended in view of its mechanical strength when wet, and its consequent moistening function for the surface flora of the cheese, which require a high a_w for their growth. Although vegetable parchment is sometimes used alone, it is more often used in a combination laminated to aluminum foil or an aluminum/tissue paper laminate to give a shelf life of 6–10 weeks.

19.5.3.3 Fresh

Fresh cheeses are slow drainage cheeses, which have been subjected to lactic acid fermentation; they are characterized by a moisture content of >80%. The three major types of fresh cheeses are Cottage, Quark and Petit Suisse.

19.5.3.3.1 Manufacturing Processes

19.5.3.3.1.1 Cottage Cottage cheese is normally prepared from pasteurized skim milk by the in situ production of lactic acid by starters consisting of *Streptococcus lactis*, *Streptococcus cremoris* and *Leuconostoc citrovorum* (for flavor). The desired pH is ≈4.6, which may be reached in 5–16 h depending on the level (0.5%–5%) of starter addition and the set temperature (22°C–32°C). The coagulum is cut and cooked to 50°C–55°C over a 1.5 h period during which time considerable syneresis occurs and the curd assumes a firm, meaty texture. After removable of the whey and washing of the curd, salt (≈1% NaCl) is added, and the curd mixed with a creaming mix to give a level of ≈4% fat in the finished cheese. A good quality product has a shelf life of 1–2 weeks at chill temperatures, which may be extended by packaging in an atmosphere of CO_2 (Fox, 2011).

19.5.3.3.1.2 Quark Quark is produced in a very similar manner to Cottage cheese, with *Streptococcus diacetylactis* replacing *L. citrovorum* for flavor development. After setting, the coagulum is broken and the whey removed from the uncooked curd/whey mixture by filtration or centrifugation. Compared to Cottage cheese, Quark has a smooth consistency and a significant lactose content since it is not washed. Quark typically has a moisture content of 82% (Fox, 2011).

19.5.3.3.1.3 Cream and Petit Suisse These are produced by in situ production of acid in cream and typically have a moisture content of 54%. After coagulation, the curds are separated from the whey by filtration or centrifugation. Gums may be added to cream cheeses to improve texture and consistency, and they may also be heat treated and homogenized to produce a product with a longer shelf life (Fox, 2011). Cream cheese has a shelf life of 3–6 months, while Petit Suisse has a shelf life of 3–4 weeks (International Dairy Federation, 1987).

19.5.3.3.2 Packaging Requirements

The packaging requirements for fresh and cream cheeses are basically similar to those for the other types of cheeses, namely protection against light, O_2 and loss of moisture.

Due to their high moisture content, low salt concentration and high pH, fresh cheeses are susceptible to microbial spoilage and consequently have a limited shelf life. They are also very sensitive to dehydration, and most fresh cheeses keep draining slowly. Because of their high a_ws, the adsorption of moisture from the atmosphere is of little importance but loss of water through evaporation, particularly from the surface, must be avoided. Although fresh cheeses do not seem to be as sensitive to the influence of light as milk, cream or butter, the cream cheeses with their greater fat content (≈34%) are. For all the cheeses in this class, the packaging must provide protection against light transmission. The O_2 in fresh cheeses may either be present in the cheese as a result of the processing techniques used (e.g., centrifugation), in the headspace inside the package, or permeate through the package over time. Some of these cheeses are packed under a low O_2 MA.

19.5.3.3.3 Packaging Materials

While a number of plastics have been used over the years, the standard material is HIPS, which is thermoformed on form-fill-seal machines. It is also coextruded or extrusion coated with PVdC copolymer to improve its barrier properties, and pigmented with TiO_2 to provide a better barrier to light. Injection molded containers made of HDPE or PP with slits in the side to allow drainage of whey are also used, with the fresh cheese being ladled directly into the containers. Outer packaging of PA-LDPE laminates make these containers gas tight.

The shelf life of Cottage cheese, without chemical preservatives, stored at 3–4°C is 14–21 days. Flushing the headspace (25%) of commercial packages of Cottage cheese with pure CO_2 extended the shelf life at 8°C by about 150% without altering the sensory properties or causing any other negative effects (Poças and Pintado, 2010).

Genuine vegetable parchment or greaseproof paper was frequently used in the past to package fresh cheese and is still used in some markets for Petit Suisse. It is usual for the paper to have a basis weight of 40–60 gsm. Paper coated with paraffin or PVdC copolymer is still sometimes used in the form of a banderole; for example, for packaging an unripened cheese intended for consumption within a short time (Stehle, 1987).

Aluminum foil with a thickness of 7–20 μm can be used, with the thicker foils (15–20 μm) formed into containers of either rectangular shape with straight walls, or cylindrical section with corrugated or pleated sides. In all cases, the aluminum must be protected against corrosion, either by applying a suitable enamel or by laminating with LDPE or PP. If this is not done, then the whey coming into contact with the aluminum will cause the formation of aluminum lactate and attack the walls of the container, sometimes perforating them (Stehle, 1987). MAP has been suggested to maintain the quality of Cottage cheese (Maniar et al., 1994).

19.5.3.4 Processed Cheese and Analogues

19.5.3.4.1 Manufacture

Attempts at the end of the nineteenth century to export hard cheeses from Europe to tropical countries were largely unsuccessful. This led to the development by the Swiss company Gerber in 1911 of "processed" cheese that was made by removing the rind from Gruyère or Emmental cheese and heating it to about 80°C while stirring in a solution of sodium citrate as an emulsifying salt. The cheese formed a "sol," which could be packaged in a metal foil while hot. On cooling, this gave a gel, which was pleasant to eat, had a taste reminiscent of the original cheese and (if the acidity was properly controlled) had good keeping qualities. In 1916, processed cheese was manufactured in the United States by J.L. Kraft from Cheddar cheese using a mixture of citrates and orthophosphates as emulsifying salts (Kapoor and Metzger, 2008).

Processed cheese is produced by blending natural cheese of different ages and degrees of maturity in the presence of emulsifying salts and other dairy and nondairy ingredients, followed by heating and continuous mixing to form a homogeneous product with an extended shelf life. Today, a wide range of processed cheeses is available containing a variety of flavoring compounds and sometimes fruits, vegetables and/or nuts. Preservatives such as sorbic and propionic acids and their salts may be added to prevent mold growth. Nisin may be added to prevent the growth of anaerobic spore-formers such as *Clostridia* spp. The addition of antioxidants is also permitted in many countries. Generally, the hot processed cheese is filled into packages such as pouches or polymer-coated aluminum foils, after which the packages are sealed and the product is cooled.

19.5.3.4.2 Packaging

A detailed discussion of packaging materials and equipment has been presented by Buys and Mostert (2011). Traditional packaging of processed cheese consisted of triangular portions (usually weighing 20–30 g) packaged in tinfoil (97% tin, 3% antimony and traces of lead, copper and iron) because of its resistance to corrosion by processing salts. For economic and technical reasons, tinfoil was replaced by heat sealable, lacquered aluminum. The thickness of the aluminum varies from 12 to 15 μm. An opening device consisting of narrow strips of PET film sealed onto the inner side of the aluminum foil is provided to facilitate opening a portion of the cheese. The strips extend several millimeters beyond the packaging material so that they can be grasped between two fingers. Their point of exit from the packaging must itself be sealed to avoid any possibility of leakage or contamination. The strips are normally colored red to attract the consumer's attention (Stehle, 1987). The triangular portions are often assembled into a circular paperboard carton or plastic container complete with lid.

Typical packaging systems used for spreadable processed cheese are (Poças and Pintado, 2010):

1. Squeezable nonbarrier tubes made of LDPE, high barrier tubes made of multilayer materials containing EVOH as a barrier layer, or metal tubes
2. Cups made of PP, PET-LDPE or PS-EVOH-LDPE heat sealed with alufoil or plastic laminate
3. Glass cups heat sealed with an alufoil plastic laminate or with an easy-open tinplate cap

Slices of processed cheese were first marketed in the United States in 1950, and were manufactured either by forming strips of cheese, which were then cut up and packaged, or by molding the cheese in the form of a tube around which a web of plastic was wrapped, with the whole assembly then being flattened and cooled. The films most often used are laminates of PET-LDPE, or if a more impermeable package is required, PET-PVdC copolymer-LDPE or OPP-EVOH copolymer-LDPE (Stehle, 1987).

A Brazilian processed cheese (Requeijão cremoso) was stored for 60 days at 10°C in five different packages: (1) glass cup with an easy-open tinplate cap, (2) glass heat sealed with aluminum foil-based laminate and plastic cover, (3) PP cup heat sealed with aluminum foil-based laminate and plastic cover, (4) LDPE-HDPE squeeze tube and (5) coextruded LDPE-HDPE squeeze tube with an EVOH copolymer O_2 barrier (Alves et al., 2007). When all the packages were stored under light (1000 lx), the shelf life in terms of overall sensory quality was only 17 days for the nonbarrier tube (4). Because of their shape, the squeeze tubes presented the largest surface area exposed to light, followed by the glass containers; the PP cups had the smallest surface area exposed to light. The stability of the product was similar for the coextruded tubes (5), PP cups (3) and non-vacuum-sealed glass cups (1) due to the combined effect of the initial O_2 available and the package barrier to O_2 and light. Among the types of packages studied, the vacuum-closed glass (2) preserved the initial quality of Requeijão cremoso for the longest period (32 days) as a result of the minimal amount of available O_2 contained in its headspace. The results confirmed that it is not enough that a package has good gas barrier properties; it is also necessary to reduce the amount of headspace O_2 and use materials that offer a barrier to light.

Some processed cheese is packaged in either tinplate or aluminum cans, both of which must be adequately enameled inside to prevent corrosion occurring. A small quantity of spreadable processed cheese is packaged in tubes, which used to be manufactured from aluminum but are now made of five-layer laminates containing aluminum foil as the central core. The tubes are filled through the unsealed base opening, which is then welded by a high-frequency current (Stehle, 1987).

19.6 MILK POWDERS

19.6.1 Manufacture and Properties

Milk and milk products are dried mainly by spray drying. This involves converting concentrated milk into a fog-like mist (atomizing) where it is given a large surface area and exposing this mist to a flow of hot air in a drying chamber. When the atomized product is in contact with the hot air, the moisture evaporates quickly, and the solids are recovered as a powder consisting of fine, hollow, spherical particles with some occluded air.

An important quality attribute of milk powder is the bulk density. It is obviously of considerable interest from an economic point of view as it influences the cost of storage, packaging and transport. The bulk density is governed chiefly by the total solids of the feed to the atomizer but also by the temperature of the drying air. Agglomeration also has a marked affect on the density, with a heavily agglomerated particle being very light.

Instantization produces milk powder with better rehydration properties (e.g., wettability, sinkability, dispersibility, solubility and rate of dissolution) by using two or three-stage drying. Instantization is based on agglomeration, which enables a larger volume of air to be incorporated between the powder particles, resulting in a characteristic coarse, cluster-like, agglomerated structure (Schuck, 2011a). The instantizing process for skim milk powder (SMP) consists of agglomeration of the particles into porous aggregates of sizes up to 2–3 mm. As a result, the amount of interstitial air (i.e., the air between the particles) is increased; reconstitution commences when the interstitial air is replaced by water. Powder agglomeration may be regarded as intentional caking as a result of forced compaction under controlled conditions.

Instantization results in a reduction of bulk density (e.g., for SMP from 0.64 to 0.55g mL^{-1}, although the bulk density of agglomerated particles can be as low as 0.35–0.40 g mL^{-1}). The free space volume has an important influence on the rate of oxidation of foods. If a food is packaged in air, a large free space volume is undesirable because it constitutes a large O_2 reservoir. Conversely, if the product is packaged in an inert gas, then a large free space volume acts as a large "sink" to minimize the effect of O_2 transferred through the package. It follows that a large package surface area and a low bulk density result in greater O_2 transmission.

The instantizing process for whole milk powder (WMP) is more complicated due to the hydrophobic nature of the fat. Reconstitution of the agglomerates will not take place in water at temperatures below 45°C unless the powder particles have been coated with a surface-active or wetting agent.

The use of lecithin as a surface-active agent is accepted worldwide and it is mixed with butter oil and sprayed at 70°C onto the powder (which should be ~50°C) to give a final concentration of 0.2% in the powder. The best results are obtained when the powder is packaged at this temperature, but because the hot powder is very vulnerable to oxidation of the fat, it must be packaged with inert gas to reduce the O_2 level in the package to a maximum of 2%.

SMP typically has a fat content of 1%, lactose 51%, protein 36%, mineral 8.5% and moisture content 3.5%, while WMP has a fat content of 28%, lactose 37%, protein 28%, mineral 6% and moisture content 3.0%. Buttermilk (the liquid remaining after the manufacture of butter) can be evaporated and spray dried, as can whey, which results from the manufacture of casein, quark and cheese. Infant milk formula contains added lactose and whey powders in order to increase the lactose content to that of human milk, which is significantly higher (7.0%–7.5%) than that of bovine milk (3.5%–4.0%). However, a higher lactose content presents greater challenges when drying such milks.

The physicochemical properties of free and bound water affect the physical state, transition temperatures, sticking temperature, reaction kinetics and stability of milk powders. The quality and shelf life of dairy powders are significantly dependent on the physical state of both lactose and other carbohydrates, which themselves are dependent on T_g and a_w. In fresh spray dried milk powders, lactose exists in a metastable amorphous state, because the rapid rate of concentration and spray drying does not allow sufficient time for it to crystallize. During storage, an increase in temperature or a_w enhances an irreversible transition to stable crystalline forms which will occur if T_g is reduced to below the powder temperature (Fitzpatrick et al., 2007).

Murrieta-Pazosa et al. (2011) studied water diffusion in SMP and WMP and related it to surface composition of the dairy powders. Their results suggested that powder microstructure and the chemical state of the key components could play an important role in determining water diffusivity. Silalai and Roos (2010) showed that T_g can be used to describe time-dependent stickiness and crystallization phenomena in milk powders. The T_gs of lactose and SMP as a function of a_w at 24°C are shown in Figure 19.4. T_g is usually well above the storage temperature for most dry powders but this may not be the case when powders produced in temperate climates are marketed in, or shipped through, tropical climates.

19.6.2 DETERIORATIVE REACTIONS

19.6.2.1 Oxidation

The detrimental effect of O_2 on the flavor of milk products (especially those high in fat) has already been discussed earlier in this chapter. Lipid peroxidation is responsible for changes in the taste and

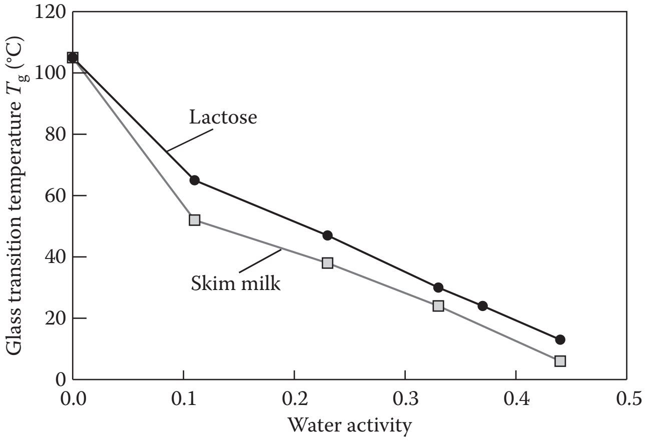

FIGURE 19.4 Glass transition temperatures T_g of lactose ● and skim milk powder □ as a function of water activity a_w at 24°C. (Adapted from Silalai, N. and Roos, Y.H., *J. Food Sci.*, 75, E285, 2010.)

odor of milk powders through the development of off-flavors caused by the formation of secondary reaction products (alkanes, alkenes, aldehydes and ketones) and thus limit the shelf life of milk powders. O_2, light exposure, storage temperature, a_w and concentration of unsaturated fatty acids are the most important factors that affect oxidation.

19.6.2.2 Browning

Maillard or nonenzymic browning of milk powders during prolonged storage at moderate to high temperatures is initiated by condensation of lactose (functioning as a reducing sugar) with the free amino group of lysine in milk proteins (Thomas et al., 2004). In addition to the undesirable change in color, Maillard browning can also give rise to undesirable flavors.

19.6.2.3 Caking

Caking is a problem that arises when a low-moisture, free-flowing powder becomes lumpy, then agglomerates into a solid and finally transforms into a sticky mass. Many methods have been proposed for eliminating, minimizing or controlling caking, e.g., (1) controlling storage conditions below a_w 0.57 if no amorphous lactose is present, and below a_w 0.25 if it is present; (2) avoiding mixing of powders with different initial a_ws and temperatures; (3) cooling the powder immediately to an appropriate temperature (well below T_g) before packaging; and (4) minimizing temperature variation during storage. Although these techniques delay caking, they do not prevent it.

19.6.3 PACKAGING REQUIREMENTS

19.6.3.1 O_2 Permeability

The most effective method of extending the shelf life of milk powder is to package it in a high O_2 barrier package from which air has been removed and replaced by an inert gas such as N_2. This is particularly true for WMP where the shelf life is governed to a large extent by the rate of oxidation of the unsaturated fats and the consequent development of objectionable flavors. The advantage of gas packing SMP is much less but it has been found to be worthwhile in preventing the development of stale flavors, especially where the storage period might be prolonged or the storage temperature is high. An alternative to gas packing is vacuum packaging and this is discussed in Section 19.6.5.2.

19.6.3.2 Water Vapor Permeability

The rate of development of oxidized flavor or oxidative rancidity during the storage of WMP depends on both the O_2 concentration and the a_w. Therefore, if the maximum shelf life possible is to be obtained from milk powders (especially WMPs), it is important that the moisture content corresponds to the a_w at which the rate of lipid oxidation is a minimum. This is usually taken to be the a_w which corresponds to the monolayer value. The a_w of WMPs is mainly controlled by the moisture content of the nonfat solids, because fat has no influence. Thus, differences in a_w of different kinds of dairy powders are mostly the result of the state of the proteins and the physical state of the lactose (Schuck, 2011b).

A generalized MSI for SMP and WMP at 20°C is presented in Figure 19.5 and shows a break for SMP between 0.4 and 0.5 a_w, owing to lactose crystallization (Thomas et al., 2004). In the case of WMP, lactose crystallization does not occur until ≥ 0.66 a_w, due to the role of milk fat, which is believed to act as a hydrophobic barrier and limits the diffusion of hydrophilic molecules and the growth of lactose crystals (Kelly, 2009). If the moisture content is calculated on a nonfat basis, the isotherms for SMP and WMP are almost identical. The a_ws of WMP typically vary from 0.25 to 0.35 and for SMP from 0.32 to 0.43 (Tehrany and Sonneveld, 2010). During crystallization, the amorphous lactose initially absorbs moisture from the surroundings due to its hygroscopic nature, and subsequently releases moisture as it crystallizes. At low a_ws, lactose generally occurs in the anhydrous form, the less hygroscopic α-lactose monohydrate containing about 5% water as water of hydration.

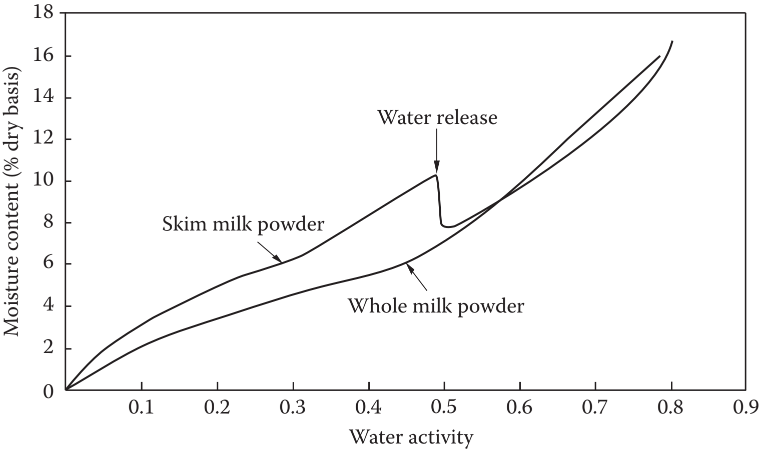

FIGURE 19.5 Generalized moisture sorption isotherms of skim and whole milk powders at 20°C. A break (water release) appears in the skim milk isotherm just below 0.5 a_w because of lactose crystallization. This break is not observed if experimental points are not close enough. (From Thomas, M.E.C. et al., *Crit. Rev. Food Sci. Nutr.*, 44, 297, 2004.)

The change in crystal structure from the anhydrous to the hydrated form can, therefore, only take place when the moisture content exceeds 5%. The proportion of hydrate increases as a_w rises above 0.5.

In selecting a suitable packaging material for milk powders, three factors must be taken into account: the initial moisture content of the powder, the final acceptable (critical) moisture content of the powder and the shelf life required. Assuming that the powder equilibrates rapidly whenever moisture enters the package, the maximum quantity of moisture, which can enter the package can be calculated and the maximum water vapor permeability of the packaging material specified. This will vary depending on the surface area of the package and the weight of dry solids in the package, a point often overlooked when pack sizes are changed without any consideration of the resultant effect on product moisture content. These factors were discussed earlier in Chapter 12.

19.6.3.3 Light

It is necessary to protect milk powders (especially those made from whole milk) from light, otherwise oxidative reactions will be accelerated. The nature of these reactions and the light barrier properties of various packaging materials have been discussed earlier in this chapter.

19.6.4 PACKAGING MATERIALS

19.6.4.1 Metal Cans

The traditional method for packaging milk powders for consumers uses three-piece tinplate cans where the atmospheric air is withdrawn from the powder and replaced with an inert gas such as N_2 prior to seaming the base onto the can. When correctly seamed, the can is essentially impermeable to O_2, water vapor and light, and can be filled at high speeds. Its mechanical strength facilitates transport and handling, and the reuse possibilities of the empty can contribute to its popularity in many parts of the developing world. It is usual for the top of the can to have a lid, which can be levered off and, in order to provide a gas-tight seal under the lid, an aluminum foil diaphragm is sealed to the rim of the can. This is punctured by the consumer immediately prior to use. The use of an easy-open lid incorporating a ring-pull made from scored aluminum is now quite common; a plastic overclosure is supplied to provide a limited degree of protection once the metal end has been removed.

Milk powder has a long shelf life when packed in metal cans due to their excellent barrier properties. The exchange of moisture and O_2 and the influx of light are not possible. Powders with a higher fat content are more susceptible to oxidation, and most powders are susceptible to deteriorative effects such as lumping and caking from moisture ingress. With adequately constructed cans, a shelf life in excess of 5 years is realistic, but national food safety authorities often adopt a conservative approach by reducing the nominated shelf life.

SMP and powdered whey beverages are available at the retail level in many countries packaged in no. 10 cans (157 × 178 mm with a capacity of 3108 mL) in a reduced-O_2 atmosphere to prolong shelf life (up to 54 months). Lloyd et al. (2004) found that in the 10 U.S. brands tested, a wide variation existed in headspace O_2, can seam quality, sensory quality and vitamin A (with 6 of 10 brands entirely lacking the vitamin). The a_ws of the brands ranged from 0.14 to 0.28, corresponding to 3%–5% moisture content. The brand that scored highest in overall acceptability had an average headspace O_2 of 7% and poor can seams, calling into question the ability of the package to maintain product quality over an extended storage time.

19.6.4.2 Laminates

In recent years, aluminum foil-plastic laminates have been introduced as a replacement for the tinplate can. The laminates can be formed, filled, gas flushed and sealed on a single machine from reel stock. Gas flushing is achieved by saturating the powder with inert gas. The main advantages associated with laminates are lower material cost and lighter material weight. The disadvantages are that laminates do not have the mechanical strength and durability of rigid containers, and there can be difficulty in obtaining a satisfactory heat seal because of contamination of the heat seal area by powder during filling at high speed.

A typical construction would be an inner layer of LDPE so that the pouch can be sealed and an outer layer of BOPP or PET with alufoil in the middle. Alternatively, with pouches for which a shorter shelf life is acceptable, the alufoil layer may be replaced with a high-barrier plastic layer such as EVOH or PVdC copolymer, and the PET may be coated with SiO_x.

19.6.4.3 Fiber Cans

Fiber cans or composites manufactured by spiral winding of paperboard strip are available with a wide variety of liners. They can give a similar degree of protection to that obtained from alufoil-LDPE-paper bags and have similar strength to a metal can. They have the added advantages of being lighter than metal cans and not corroding, a problem which can occur with metal cans under high humidity conditions. A typical specification for fiber cans for use with either WMP or SMP is 0.9 mm board and a foil coating of 5 μm with a nitrocellulose lacquer to protect the powder from the aluminum foil. An outer decorative label incorporating a fiber seal material gives increased protection against moisture penetration (Cummins, 1982).

19.6.5 PACKAGING TECHNIQUES

19.6.5.1 Gas Packing

The technique of gas packing is simple and, provided that the package is airtight, the O_2 content can easily be reduced from the 21% present in air to 1% or less immediately after the operation is finished. However, with spray dried powder, this reduction in O_2 content is limited mainly to the atmosphere surrounding the hollow powder particles. Up to 28 days may need to elapse before equilibrium is established between the gases within and around the particles, although most of the change will usually be complete after 7–10 days. During this desorption period, the O_2 content within the can may rise to as much as 5%; this is considerably above the level of 1%–1.5% required to ensure optimal keeping quality. When O_2 levels of the order of 1% are needed, there is no alternative in the usual gas packing technique but to store the powder after the initial gas packing long enough for desorption to take place and then to gas pack the cans a second time. This is costly and time consuming, requires considerable storage space, increases the handling of the cans and is unsuitable for normal factory routine. Thus, any process that will remove the desorbed O_2 as it is liberated is likely to receive close scrutiny.

Occluded air trapped in vacuoles within powder particles is not removed during gas flushing of cans or laminate packs. Depending on the volume of occluded air in the powder, the equilibrium residual O_2 content of the pack could exceed the 0.02–0.03 mL g^{-1} normally tolerated. This problem can be alleviated by conditioning the powder under vacuum for 24–48 h prior to gas flushing to remove occluded air.

The U.S. industry standard for shelf life of whole WMP is 6–9 months at <27°C and <65% RH, although flavor changes have been detected after 3 months at ambient storage. Lloyd et al. (2009) evaluated the shelf life of WMP (initial a_w 0.17 and moisture 2.46%) packaged in PA-EVOH-LDPE laminate pouches (OTR 1.5 mL m^{-2} day^{-1} but temperature and RH unspecified) with air or N_2 and stored at 2°C or 23°C for 1 year. Optimum shelf life from a flavor standpoint was about 3 months, and N_2 flushing greatly enhanced the storage stability of WMP by preventing the development of "painty" flavor. Packaging headspace O_2 levels should be as low as possible to prevent lipid oxidation and off-flavors. Storage at 2°C enhanced storage stability of WMP, but to a lesser extent than N_2 flushing.

19.6.5.2 Vacuum Packaging

An alternative method of reducing the O_2 content of packaged WMP is by compression of the powder. However, although such a procedure reduces the air content, it results in a significant increase in bulk density and (usually) a decrease in performance as measured by ease of solubility. Vacuum packaging is used to reduce the O_2 content and it achieves this by evacuation of the interstitial air and some compression as a consequence of the vacuumization. The main problem associated with vacuum packaging of milk powder is that of removing air from the package without removing powder fines, which could damage the vacuum pump and contaminate the sealing area of the laminate bag. This problem can be avoided by applying the vacuum at a slow rate so that powder particles are not disturbed.

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20 Packaging of Cereals, Snack Foods and Confectionery

20.1 INTRODUCTION

Cereals are the fruits of cultivated grasses, members of the monocotyledonous family *Gramineae*. The principal cereal crops are wheat, barley, oats, rye, rice, maize, sorghum and the millets. Cereals have been important crops for thousands of years and the successful production, storage and use of cereals has contributed in no small measure to the development of modern civilization. Today, cereals and cereal-based products are an important part of the diet in most countries, and each year new products based on cereals are developed and marketed to increasingly sophisticated consumers.

20.2 GRAINS

The cereals of commerce and industry are harvested, transported and stored in the form of grain. The anatomical structure of all cereal grains is basically similar, differing from one cereal to another in detail only.

The mature grain of the common cereals consists of carbohydrates, nitrogenous compounds (mainly proteins), lipids, mineral matter and moisture, together with small quantities of vitamins, enzymes and other substances, some of which are important nutrients in the human diet. Carbohydrates are quantitatively the most important constituents, forming 77%–87% of the total dry matter. The lipids in milled cereal products are liable to undergo two types of deterioration: hydrolysis from endogenous lipases and oxidation from endogenous lipoxygenases or molecular O_2. The products of lipid hydrolysis are glycerol and free fatty acids, which give rise to unpleasant odors. The products of lipid oxidation cause the odor and flavor of rancidity. Damage to the grain and the fragmentation that occurs in milling promote deterioration by bringing the lipid and the enzyme together (Kent and Evers, 1994).

20.2.1 WHEAT

The wheat grain is a living, respiring organism, which usually carries endemic fungi. Respiration is slow at 14% moisture content and 20°C, but rises as moisture content and temperature increase. The process of respiration generates heat (which is difficult to remove because wheat is a poor conductor) as well as CO_2 and water vapor, resulting in a loss in weight. Unless the grain is turned over to allow evaporation of the moisture, it will sweat and become caked in the bin.

Wheat at moisture contents between 16% and 30% can support fungal growth and there is thus the risk of mycotoxin production. Above 30% moisture content, wheat is susceptible to bacterial attack, leading to spoilage, excessive heat production and possibly charring. Insect life also becomes more active as the temperature rises and, because of their respiration, live insects in grain also raise the grain temperature. Deterioration during storage is aggravated by mechanical damage during harvesting because microorganisms attack damaged grains more readily than intact grains (Kent and Evers, 1994).

The shelf life for wheat as a function of moisture content and temperature is presented in Table 20.1. This table shows the importance of drying grain in that a drop of 3% in moisture content

TABLE 20.1
Safe Storage Life (Days) for Grains as a Function of Moisture Content and Temperature

	Grain Moisture (%)		
Grain Temperature (°C)	**14**	**15.5**	**17**
10.0	256	128	64
15.5	128	64	32
21.1	64	32	16
26.7	32	16	8
32.2	16	8	4
37.8	8	4	2

Source: Adapted from Bailey, J.E., Whole grain storage, in: *Storage of Cereal Grains and Their Products*, 4th edn., Sauer D.B. (Ed.), American Association of Cereal Chemists, St. Paul, MN, pp. 141–169, 1992.

increases the shelf life by a factor of four. The major problems at higher moisture contents include accelerated wheat enzyme activities and microbial spoilage.

20.2.2 Flour

Wheat flour is the product prepared from grain by grinding or milling processes in which the bran and germ are partly removed and the remainder is comminuted to a suitable degree of fineness (Cauvain and Young, 2008). It has been recommended that for long storage periods, flour should be stored in a closed atmosphere. Under these conditions, flour acidity increases due to the accumulation of linoleic and linolenic acids.

Flour is stored commercially in bags or bulk bins. The storage hazards for flour are similar to those of wheat in storage, which include mold and bacterial attack, insect infestation, oxidative rancidity and eventual deterioration of baking quality. The expected shelf life of plain white flour packaged in paper bags and stored in cool, dry conditions and protected from infestation is 2–3 years. The rate of increase in acidity increases with storage temperature and decreasing flour grade (i.e., as the ash residue increases). Thus, the shelf life of brown and wholemeal flours is shorter than that of white flour. Freedom from insect infestation during storage can be ensured only if the flour is free from insect life at the time of packing and if the storage area is free from infestation.

The optimum moisture content for the storage of flour is related to the intended shelf life, the barrier properties of the packaging material, as well as the ambient temperature and humidity. For use within a few weeks, flour can be packaged at 14% moisture content, but at moisture contents higher than 13%, mustiness resulting from mold growth may develop over time. At moisture contents lower than 12%, the risk of lipid oxidation and the development of rancidity increases (Kent and Evers, 1994).A moisture content of 12% corresponds to approximately 0.5 a_w.

As with wheat and other grains, the moisture content is an unreliable guide to stability and will vary depending on the type of grain as well as the variety. To determine the moisture content that corresponds to the maximum a_w for stability at a particular storage temperature, moisture sorption isotherms at various temperatures are required. Published data on both the shelf life of flour at various a_ws and values for critical moisture contents are lacking, and it is therefore difficult to specify precisely the type of water vapor barrier required in a package. Notwithstanding the lack of information about critical moisture contents and shelf lives as a function of a_w, bags made from cotton twill or paper have been used successfully for decades for consumer packs of flour. Kraft paper bags with an LDPE liner would provide additional protection and therefore a longer shelf life, but this does not seem to be justified.

20.2.3 RICE

Cultivated on every continent except Antarctica, rice is a crop that feeds half of the world's population and has fed more people over a longer period of time than any other crop. Brown (unmilled) rice is more nutritious than milled rice, but storage stability problems and a traditional consumer preference for whole (milled) rice have limited the quantities of brown rice packaged and sold for direct consumption. A major deterrent to greater user of brown rice is the accumulation of free fatty acids in rice stored under warm and humid conditions. Fatty acids can be released by lipases present in the rice aleurone (bran) layer of damaged grains and by high lipase-containing bacteria and fungi adhering to rice.

20.3 BREAKFAST CEREALS

Breakfast cereal foods can be classified according to the amount of domestic cooking required, the form of the product and the cereal used as raw material. All cereals contain a large proportion of starch, which, in its natural form, is insoluble, tasteless and unsuited for human consumption. It must be cooked to make it digestible and acceptable. In the case of hot cereals, the cooking is carried out in the home, while ready-to-eat cereals are cooked during manufacture (Fast and Calwell, 2000).

If the cereal is cooked with excess moisture and moderate heat as in boiling, then the starch gelatinizes and becomes susceptible to starch-hydrolyzing enzymes in the human digestive system. If the cereal is cooked with a minimum of moisture (or without moisture) but at higher temperatures as in toasting, then nonenzymic browning between protein and reducing sugars may occur and there may be some depolymerization of the starch.

20.3.1 MANUFACTURE

Ready-to-eat cereals probably owe their origin to the Seventh Day Adventist Church whose members, preferring an entirely vegetable diet, experimented with the processing of cereals in the mid-nineteenth century. A granulated product called "Granula," made by J.C. Jackson in 1863, may have been the first commercially available ready-to-eat breakfast cereal. A similar product called "Granola" was made by J.H. Kellogg by grinding biscuits made from wheatmeal, oatmeal and maize meal (Kent and Evers, 1994).

Ready-to-eat cereals comprise flaked, puffed, shredded and granulated products, generally made from wheat, maize or rice, although oats and barley are also used. The basic cereal may be enriched with sugar, honey or malt extract. All types are prepared by processes which tend to cause hydrolysis (dextrinization) rather than gelatinization of the starch.

Flaked products are made from wheat, corn, oats or rice. After cooking (often at elevated pressure) and the addition of flavorings such as malt, sugar and salt, the cereal is dried to 15%–20% moisture content and conditioned for 1–3 days. It is then flaked, toasted, cooled and packaged.

Puffed products are prepared from conditioned whole grain wheat, rice, oats or pearl barley, or dough made from corn meal or oat flour with the addition of sugar, salt and sometimes oil. It is cooked for 20 min under pressure, dried to 14%–16% moisture content and pelleted by extrusion through a die. A batch of the conditioned grain or pelleted dough is fed into a heated pressure chamber which is injected with steam. The starch becomes gelatinized and expansion of water vapor on release of the pressure causes a several-fold increase in volume. The puffed product is dried to 3% moisture content by toasting and then cooled and packaged.

Shredded products are made from whole wheat grains which are cooked to gelatinize the starch. After cooling and conditioning, the grain is fed through shredders. The shreds are baked for 20 min at 260°C, dried to 1% moisture content, cooled and packaged.

Granulated products are made from yeast dough consisting of wheat flour and salt. The dough is baked as large loaves, which are then broken up, dried and ground to a standard degree of fineness.

Flaked or puffed cereals are sometimes coated with sugar or candy to provide a hard, transparent coating that does not become sticky even under humid conditions. The sugar content of cornflakes increases from 7% to 43% as a result of the coating process, and that of puffed wheat from 2% to 51% (Kent and Evers, 1994).

20.3.2 INDICES OF FAILURE

There are five indices of failure to be considered when selecting suitable packaging materials for breakfast cereals. They are as follows:

1. Moisture gain resulting in loss of crispness
2. Lipid oxidation resulting in rancidity and off-flavors
3. Loss of vitamins
4. Breakage, resulting in an aesthetically undesirable product
5. Loss of aroma from flavored product

The shelf life of breakfast cereals depends to a large extent on the content and quality of the oil contained in them. Thus, products made from cereals with a low oil content such as wheat, barley, rice and maize grits (oil content: 1.5%–2.0%) have a longer shelf life than products made from oats (oil content: 4%–11%, average 7%). Although whole corn has high oil content (4.4%), most of the oil is contained in the germ, which is removed in making grits (Kent and Evers, 1994).

20.3.3 PACKAGING

The materials used for the packaging of ready-to-eat breakfast cereals are discussed later in relation to the major indices of failure.

20.3.3.1 Loss of Crispness

Data on the permissible increase in moisture content or a_w before loss of crispness occurs is required so that the water vapor barrier required to achieve the desired shelf life can be calculated. Sauvageot and Blond (1991) reported a slight decrease in crispness intensity of commercial samples of cornflakes (m_i 6.0%) and rice crispies (m_i 6.9%) between 0 and 0.50 a_w or 7% water content, after which there was a very rapid decrease. However, it is important to note that the effect of hydration on crispness of cereal-based products varies with the formulation. For example, Valles-Pamies et al. (2000) reported that extruded waxy maize starch products exhibited a loss of crispness at 0.40 a_w, whereas the critical a_w was 0.75 when the starch contained 20% sucrose (Figure 20.1).

A particular challenge arises with breakfast cereals where dried fruit such as raisins are blended with the cereal prior to packaging. These so-called multidomain foods are dynamic systems in which moisture gain or loss occurs continuously from one domain to another until thermodynamic equilibrium between the food components and the surrounding gaseous environment is reached. Water migration and the resulting changes in moisture content affect the shelf life through undesirable modifications of their physical, sensory and microbial qualities. A simulation of moisture transfer in a cereal-raisin system stored in an impermeable package was developed by Sapru and Labuza (1996). Risbo (2003) included the package permeability properties in his shelf life calculations on a cereal-raisin system. Roca et al. (2008) developed a more general model to predict moisture transfer and shelf life in multidomain foods over the temperature range 5°C–30°C.

Packaging of breakfast cereals has traditionally been in fiberboard boxes with a supercalendered, waxed and glassine liner. As well as providing a barrier to water vapor, the liner must also confine cereal aromas within the packaged product and simultaneously prevent foreign odors entering. It should also be reclosable to protect the cereal remaining in the package (Monahan, 1988). The glassine liner has been largely replaced by various plastic materials, in particular thin gauge HDPE. HDPE coextruded

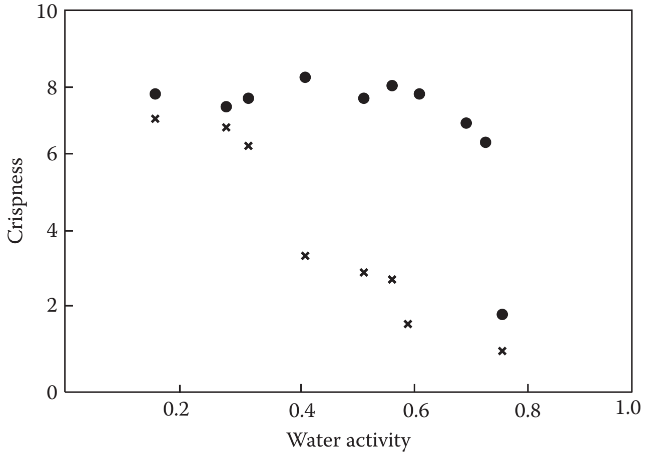

FIGURE 20.1 Sensory crispness of expanded starch-based extrudates versus a_w (● without sucrose; **x** with 20% sucrose). (From Valles-Pamies, B. et al., *J. Sci. Food Agric.*, 80, 1679, 2000.)

with a thin layer of EVA copolymer is also used, where the EVA copolymer permits a lower heat seal temperature while offering the consumer an appealing and peelable seal (Monahan, 1988).

In a few cases where the cereal product is not hygroscopic and/or retains a satisfactory texture when in equilibrium with the ambient atmosphere, a liner may not be needed for moisture protection and may even serve to entrap rancid aromas. Where this is the case, either no liner or one which is vapor permeable may be used (Monahan, 1988). Some shredded wheat products are in this category and are discussed in the following.

20.3.3.2 Lipid Oxidation

The primary mode of chemical deterioration in dry cereals is lipid oxidation and two reasons have been advanced for this (Labuza, 1982). First, the a_w of dry cereals is at or below the monolayer, which essentially stops all other types of deteriorative reactions. Second, unsaturated fats are required in lipid oxidation, and the grains used in breakfast cereals have a high ratio of unsaturated to saturated fats.

To minimize oxidative rancidity, it is important that the package exclude light and most cereals are packed with an outer paperboard carton mainly for this reason. Excluding O_2 may be of limited assistance in extending shelf life although O_2 is almost never rate limiting (Labuza, 1982). For this reason, most companies do not bother to use packaging which is a good O_2 barrier. However, in a study of the storage stability of a flaked oat cereal product packaged in materials of different O_2 barrier properties with and without the addition of an O_2 absorber, Sakamaki et al. (1988) observed that the absorber retarded or delayed lipid oxidation provided that it was used with a packaging material that was a good O_2 barrier such as PVdC copolymer-coated PP-LDPE. Larsen et al. (2003) studied the effect of package OTR (including the use of an O_2 absorber), light and temperature (23°C and 38°C) on the sensory stability of extruded oat pellets packaged in N_2 over a period of 3 months. Oats stored under light developed a high degree of paint odor (rancidity) at both temperatures when in medium and high OTR packages, while those stored in the dark only did so at 38°C. Extruded oat in packages with low OTR, with and without an O_2 absorber, did not develop paint odor during 3 months of storage at either temperature, even when exposed to light; the headspace O_2 concentration in these packages did not exceed 1%.

Although the use of synthetic antioxidants in the package liner has been shown to be successful in extending shelf life, it is not generally permitted in most countries. Paradiso et al. (2008) showed that natural tocopherols limited the development of off-flavors in cornflakes during storage at room temperature for a year.

20.3.3.3 Loss of Vitamins

The vitamin and mineral fortification of cereals is widely practiced in many countries and there are usually associated nutritional labeling requirements. The major factor influencing vitamin loss in packaged cereals is the temperature of storage. In a study on the effects of processing and storage on micronutrients in breakfast cereals, it was concluded that micronutrient loss would not be a major factor in determining the shelf life of dry cereals. There were no substantial losses of added vitamins during normal shelf lives with the possible exception of vitamin A and, to a slight extent, vitamin C. Vitamin A survived six months (the average distribution time) at room temperature with no measurable loss (Labuza, 1982).

20.3.3.4 Mechanical Damage

The rigidity of the carton stock and the compression resistance of the finished carton must together provide the necessary resistance to product breakage throughout production line operations, warehouse storage and distribution from the manufacturer to the retailer and consumer. Rigidity also prevents the bulging of the carton. Protecting breakfast cereals from breakage does not appear to be a problem using currently available carton stock and carton designs.

20.3.3.5 Loss of Flavor

This can be a problem with certain cereal products to which fruit flavors have been added prior to packaging. In these situations, loss of flavor results in the product being considered to be at the end of its shelf life by the consumer. A study (Mohney et al., 1988) evaluating two typical cereal liner materials (HDPE and glassine) found that the permeability coefficients of *d*-limonene (a common flavor component in citrus products) in the HDPE liner were three to four orders of magnitude higher than those in glassine. It was also found that the solubility of *d*-limonene in the glassine liner was substantially lower than in the HDPE liner for the same vapor pressures. Thus, equilibrium distribution of the limonene vapor between a product such as a fruit-flavored cereal and the respective liners will result in a much lower limonene concentration within the glassine liner and "scalping" of the cereal flavor can be assumed to be much more significant in the HDPE liner.

20.4 PASTAS

Although the word "pasta" is traditionally associated with Italy and with durum wheat semolina, Italy cannot claim to have invented this popular food and semolina (the coarsely ground grain of durum wheat with particles mostly between 0.25 and 0.75 mm in diameter) is not the original raw material. The Chinese invented pasta that was produced as noodles from rice and legume flours several thousand years BCE. Today, pasta consumption is increasing in many countries to the extent that pasta can be classed as a truly international food.

Part of the appeal of pasta products (macaroni, spaghetti, vermicelli, noodles) is that they may be prepared from several raw materials according to countless formulations, and cooked and served in numerous ways to various tastes. Durum wheat semolina is considered to be the best raw material for pasta making because of the functional characteristics of its proteins, low lipoxygenase activity and high yellow pigment content. The limited availability and high cost of durum wheat compared with other cereals has lead to the use of flours and starches from rice, maize, barley, soft wheat, cassava and potato in pasta formulations in various parts of the world (Fuad and Prabhasankar, 2010).

The original composition of Italian pasta (water, durum wheat semolina and egg) has altered considerably to include vitamin supplements, iron salts, powdered vegetables, tomato concentrate, milk protein, other cereal flours and meat and cheese in filled pasta in order to satisfy the tastes and food habits of different populations. The introduction of MAP has enabled certain types of pasta (particularly the fresh and filled varieties) to progress from being a small-scale manufacturing operation to an established position in the food industry where, for example, fresh product is distributed across the United States.

Pasta can be subdivided into two categories. The first, macaroni, has come to represent a generic family of over 140 items in the United States and includes spaghetti, macaroni and vermicelli. This class of product is made from semolina, water and, in most cases, added vitamins and minerals, and contains about 1.5% fat.

The second broad category of pasta is noodles, which are discussed in the following.

20.4.1 Dried Pasta

Dried pasta is produced by the reduction of dough moisture content from 30% to about 11% by means of a dehydration process, the length of which is determined by the temperature used. The drying of pasta products at temperatures above 60°C has become widely accepted by pasta manufacturers, with benefits of this approach including control of bacteria in egg products and shorter drying cycles. If the drying stage of pasta manufacture is not properly controlled, then extensive growth of microorganisms such as *Salmonella* spp. and *Staphylococcus aureus* can occur, resulting in a potential hazard to public health (Aureli et al., 1986).

Two modes have been identified for dried pasta product failure: moisture gain or loss and color loss. The major mode is moisture gain, with the optimum moisture content for pasta storage appearing to be 10%–11%. If the pasta moisture content increases to 13%–16%, then mold growth (which makes the pasta unfit for consumption) and starch recrystallization or retrogradation (which makes the pasta unacceptably tough when cooked) occur (Labuza, 1982). As with other dried products, the optimum moisture content for stability is derived from the maximum “safe” a_w; that is, a moisture content that is in equilibrium with 70% relative humidity or an a_w of 0.70.

For macaroni, a moisture content of 12.8% corresponds to an a_w of 0.70 at 25°C, while for egg noodles, the corresponding moisture content is 14.7% at 25°C and 13.3% at 27°C for vermicelli. The a_w corresponding to a moisture content of 10%–11% is about 0.56 at 25°C for macaroni, 0.44 for egg noodles at 25°C and 0.45 at 27°C for vermicelli, thus providing a margin for moisture increase during storage before the critical moisture content m_c is reached. If the moisture content of the pasta is allowed to fall to less than a certain level (9.5% in the case of vermicelli, which corresponds to 0.32 a_w) it becomes too fragile and unacceptable in quality.

A second mode of deterioration is color loss through oxidation of carotene pigments by lipoxidase enzymes found naturally in semolina flour. These enzymes oxidize lipids and the peroxides formed attack the pigments. Light accelerates the oxidation process. An associated mode of deterioration is staling, which results from the oxidation of the lipids in the product. An analysis of published shelf life data suggests that the basic mode of failure in dried pasta is lipid oxidation rather than moisture gain (Labuza, 1982).

Manufacturers of pasta claim shelf lives of macaroni and spaghetti products ranging from 6 months to indefinite, and noodle shelf life claims range from 1 to 6 months. The exact shelf life depends on the storage temperature, RH and packaging material, none of which are well defined. The traditional packaging material for dried pasta was the paperboard carton, which frequently contained a plastic window so that the customer could view the contents. Today, most pasta products are packaged in plastic films such as OPP or LDPE-PET laminate.

20.4.2 Fresh Pasta

The production of fresh pasta involves kneading of the dough, followed by extrusion or lamination and then drawing. In the case of special pasta, this latter stage is accompanied by filling, using a cooked meat or vegetable-cheese mixture, thus resulting in a variety of potential microbiological flora. The moisture content of fresh pasta is >24% and requires refrigerated storage at <4°C (Costa et al., 2010).

Fresh pasta products are refrigerated for retail distribution and may be pasteurized. The microbiological quality of fresh pasta will thus depend on the quality of the raw materials, the cleanliness and hygiene of the processing environment and equipment and the handling of the product during production and packing. In addition, the temperature of the product during storage, distribution and retailing is crucial with respect to microbiological quality. Pasta is typically pasteurized by passing through a chamber on a perforated conveyor belt using injected steam at a temperature of 91°C and for a time of 9 min, followed by cooling to 4°C within 15 min inside a forced circulating air freezer (Sanguinetti et al., 2011).

The use of MAP has become widespread for fresh pasta products and a range of N_2 and CO_2 gas compositions are used. A survey for *Staphylococci* spp. and their enterotoxins in wet pasta packaged in a MA of CO_2:N_2 20:80 from five processors showed that 12% of fresh products were contaminated with *S. aureus* (Park et al., 1988). The pasta had a recommended shelf life of 4 weeks when stored at 4°C. The results showed that proper refrigeration was essential to ensure the safety of MAP wet pastas.

Fresh pasta packaged in a MA of CO_2:N_2 22:78 was compared with a control air package and monitored by Lee et al. (2001) for quality changes during storage at 8°C. The MAP suppressed the microbial growth of total aerobic bacteria, yeasts and molds with a concomitant reduction in the rates of physical and chemical quality changes. The shelf life was successfully extended from 20 days in air packs to 40 days in MAP based on a microbial criterion for end of shelf life of 10^6 cfu g^{-1}. The shelf life extension was greater when the initial microbial quality of the product was better.

Mold growth is a major problem in the shelf life of fresh filled pasta. Pasteurized, fresh cheese-filled pasta was packaged in a MA of CO_2:N_2 50:50 or in air and changes in microbial growth, chemical and physical parameters and sensory attributes were monitored by Sanguinetti et al. (2011) for 42 days at 4°C. MAP allowed a mold-free shelf life of 42 days, whereas air-packaged samples spoilt between 7 and 14 days.

The influence of chitosan (1–3 g kg^{-1} dough), gas headspace and film barrier properties on the microbiological and sensory shelf life of fresh pasta was studied by Costa et al. (2010). Results suggested that the sensory quality, in particular the odor of the packaged product, played a significant role in determining product acceptability. MAP (CO_2:N_2 70:30), chitosan and high barrier packaging acted in a synergistic way to control the quality loss of fresh pasta during refrigerated storage at 4°C from both microbial and sensory points of view, giving a shelf life of almost 18 days compared to 10 days in low barrier packaging.

The actual packaging materials used for fresh pasta products depend on whether or not the product is pasteurized (in which case, the package must be able to withstand the pasteurization process without deforming) and whether or not the product is to be heated in its package in a microwave oven by the consumer (in which case, the package must be able to withstand domestic microwave temperatures). For products which are not pasteurized nor intended to be heated in their package, a rigid tray of PVC-LDPE onto which is sealed a PA-LDPE film is common. However, if microwave heating is used, then the rigid tray is usually made from CPET or PS-EVOH-LDPE, and the film may be based on PVdC copolymer-coated PET, OPET-EVOH-LDPE or PP.

20.4.3 NOODLES

Wheat flour noodles are staple foods in many Asian countries and account for the end use of at least one-eighth of global wheat production. Noodles have now become more widely adopted for everyday use and storage has been facilitated by the introduction of dried noodles and boiled and packaged long shelf life noodles. Consumption of noodles, particularly instant noodles, has been expanding very rapidly during recent decades. The primary ingredient of Asian noodles is refined flour milled from bread wheat (*Triticum aestivum*, also known as common wheat), in contrast to pasta where semolina from durum wheat (*Triticum durum*) is the primary ingredient.

Asian noodles are made in a wide variety of types that are categorized based on formulation (particularly the presence or absence of alkali), cross-sectional dimensions and postcutting processes such as steaming, frying, drying or boiling. For consumers of these products, the quality of the noodles themselves is primarily defined by texture and appearance. Other factors are also important, for example, for instant fried noodles, rehydration rates during final preparation and the absence of rancid taste after extended storage. The first instant noodle, called *chicken ramen*, was produced by Nissin Foods of Japan in 1958 (Fu, 2008). Another milestone was reached in 1971 when Nissin introduced cup noodles: instant noodles in a foam PS cup to which boiling water could be added to rehydrate and heat the noodles.

The three main styles of Asian wheat noodles are white salted, yellow alkaline and instant. The ingredients of Asian noodles include wheat flour, water and either common salt (sodium chloride) or alkaline salts (typically mixtures of sodium and potassium carbonates). It is believed that the original purpose of including alkaline salts in noodles was to extend the shelf life by inhibiting mold growth (Fu, 2008). Generally speaking, a white, soft and elastic noodle texture is characteristic of white salted noodles, while a bright, clear yellow color with a firm, chewy texture and a smooth surface is typical of yellow alkaline noodles. The alkaline salt in yellow alkaline noodles inhibits enzyme activity and changes the flour pigments (flavonoids) to yellow. This results in a product with a desirable bright yellow color, favorable noodle strength and palatability. The processing of instant noodles involves precooking of the fresh noodle strands by steaming and then deep frying which gives a texture distinct from that of white salted and yellow alkaline noodles. Instant noodles are increasingly popular due to their ease of preparation.

Asian noodles may be sold as a fresh product, in the moist form following partial cooking or dried prior to packaging. The moisture content of fresh noodles ranges from 32% to 40%. The main disadvantage of fresh noodles is their relatively short shelf life, ranging from one to several days, depending on the packaging and storage conditions (Fu, 2008). The final moisture content of dried noodles is usually less than 14%.

Starch noodles, produced from purified starch from various plant sources, are a major category of Asian noodles. Starches derived from the mung bean, yellow peas and potato are widely used in the production of these noodles (Tan et al., 2009). Rice noodles (the second principal form of rice product after cooked rice grains) are also widely consumed in Asia. Traditionally, rice noodles are made from long-grain rice with high amylose content (>22% amylose).

For deep fried instant noodles, oxidation leading to rancidity (instant noodles are 15%–22% fat) is the major reason for end of shelf life. Rancidity development is a minimum at $a_w = 0.3$ (corresponding to the monolayer) and shelf life is typically 4–5 months. Addition of antioxidants to the frying oil extends shelf life, for example, 200 ppm of TBHQ and 500 ppm EDTA quintuples shelf life. Other deteriorative reactions in instant noodles are moisture uptake (instant noodles have 3%–6% moisture content) and nutrient degradation (especially B group vitamins such as riboflavin).

Ling (2010) reported the following data for retail Asian noodles presumably purchased in Canada:

1. Dried noodle sticks a_w 0.550–0.614 and fat 0.4%–2.0%
2. Instant noodles in bags a_w 0.140–0.626 and fat 12%–17%
3. Instant noodles in cups a_w 0.481–0.504 and fat 20%–37%

No indication was given as to the age of the samples or how much of their shelf life remained at the time of testing.

Rachtanapun and Tangnonthaphat (2011) evaluated the effects of packaging type and storage temperatures on the sensory and microbial shelf life of fresh rice noodles packed in four different packages: HDPE film (OTR 1372 mL m^{-2} day^{-1} at 25°C and 52.5% RH); HDPE pouch (OTR 1773), PET pouch (OTR 37) and PA-LDPE pouch (OTR 19) under vacuum conditions. Noodles in the PA-LDPE pouch had the longest shelf life (13 days) when stored at 25°C. When stored at 4°C, the shelf life was 29 days with end of shelf life being starch retrogradation; low temperatures inhibited microbial growth and slowed down the decrease in pH.

Li et al. (2011) added humectants to fresh noodles to lower their a_w from 0.94 to 0.85 and combined this with irradiation at 4 kGy to extend the microbial (TPC < 10^6 cfu g^{-1}) and sensory shelf life at 37°C more than sevenfold from 2 to 16 days. A trained panel of 10 evaluated the noodles for odor and color, and samples that scored <5 on a 10 point scale were considered unacceptable. No mention was made of any packaging of the noodles.

20.5 BAKERY PRODUCTS

Bakery products have been an important part of a balanced diet for thousands of years. Flour and its principle baked product, bread, are the cheapest and most important staple foods for many nations of the world. The function of baking is to present cereal flours in an attractive, palatable and digestible form. A wide variety of bakery products can be found on supermarket shelves including breads, unsweetened rolls and buns, doughnuts, sweet and savory pies, pizza, quiche, cakes, pastries, biscuits, crackers and cookies. It is useful to classify bakery products on the basis of their a_w and pH, because these parameters are a good indication of the spoilage problems likely to be encountered. The a_w and pH of a range of bakery products is presented in Table 20.2.

20.5.1 BREAD

20.5.1.1 Manufacture

The production of bread and other fermented products accounts for the greater volume proportion of all manufactured baked products (Cauvain and Young, 2011). Although breads come in a wide variety of forms and apparently different processes, the underlying principles involved in their manufacture are similar. Bread is made by mixing wheat flour, water, yeast and salt. Other ingredients which may be added include flours of other cereals (e.g., malt flour and soy flour), fat, yeast foods, emulsifiers, milk and milk products, fruit and gluten. After mixing, the individual dough pieces are shaped, expanded through fermentation and then heat-set in the baking process.

TABLE 20.2
Water Activity and pH of Typical Bakery Products

Water Activity (a_w)	pH	Products
0.99		Creams, custards
0.97	6.0	Crumpets
0.95–0.99	5.6	Breads, fermented products
0.90–0.95		Moist cakes (e.g., carrot cake)
0.91	6.3	Yeasted pastries (e.g., Danish, croissant)
0.84	4.2	Fruit pies
0.82–0.83	6.3	Chocolate-coated doughnuts
0.80–0.89		Plain cakes (e.g., Madeira, sponge cakes)
0.70–0.79		Fruit cakes
0.65–0.66	5.6	Bread crumbs, biscuit crumbs
0.60–0.69		Some dried fruits or fruit cakes
0.61		Biscuits, chocolate, some dried fruits
0.3		Pastries

Source: Adapted from Cauvain, S.P. and Young L.S., *Bakery Food Manufacture and Quality: Water Control and Effects*, 2nd edn., Wiley-Blackwell, Oxford, England, 2008; Smith, J.P. et al., *Crit. Rev. Food Sci. Nutr.*, 44, 19, 2004.

20.5.1.2 Indices of Failure

Although several indices of failure are possible in bakery products, the four most important are now discussed in turn.

20.5.1.2.1 Microbial Spoilage

Microbial growth, particularly mold growth, is the major factor limiting the shelf life of bakery products. Spoilage types for typical bakery products are shown in Table 20.3. Chemical preservatives are used by the bakery industry in many countries to prevent or retard microbiological spoilage; chemicals used include calcium and sodium propionate, sorbic acid, potassium sorbates, sodium diacetate, methylparaben, propylparaben, sodium benzoate and acetic acid at levels of 0.005%–0.5% w/w (Smith et al., 2004). The extension of shelf life resulting from the use of preservatives is limited by the development of off-odors and flavors or effects on product quality (Seiler, 1998). As well, the trend toward foods free of preservatives is driving the development of alternative methods to overcome the problem. Principal among these is MAP, using mainly CO_2.

It has been mentioned earlier in this book (see, in particular, Chapter 16) that CO_2 has an inhibitory effect on the growth of certain microorganisms, where its effectiveness increases as the product storage temperature is reduced. Microorganisms tend to vary in their tolerance of CO_2, with molds generally being more affected than bacteria or yeasts.

For bakery products with an a_w of 0.86 or above, the *Penicillium* group of molds tend to govern mold-free shelf life, but as the a_w falls below this level, the *Aspergillus glaucus* group of molds predominate. These latter organisms are more susceptible to the effects of CO_2 than *Penicillium* species, although certain of the latter species (in particular *Penicillium roqueforti*, a common contaminant of rye bread) are much more CO_2 resistant than others. The type of molds present, rather than the a_w, is a more important factor affecting the antimold activity of CO_2. Bakery products such as cakes, which have an a_w of 0.85 or below, can be expected to show a large increase in mold-free shelf life by packaging in CO_2 (Smith et al., 2004).

With high a_w bakery products, the shelf life is sometimes limited by the growth of yeasts or lactic acid bacteria rather than molds. These microorganisms are resistant to the effects of CO_2 and cause spoilage either in the form of visible growth or by the generation of quantities of CO_2, which cause the package to expand. Of particular importance is the group of filamentous yeasts known as *chalk molds* (usually *Pichia burtonii*). Chalk molds produce a white powdery spreading growth which tends to be more obvious on the surfaces of dark-colored breads. Lactic acid bacteria (particularly

TABLE 20.3
Spoilage Types for Typical Bakery Products

Water Activity (a_w)	Products	Spoilage Types
0.99	Creams, custards	Bacterial spoilage (e.g., "rope" mold growth and "chalk molds")
0.90–0.97	Breads, crumpets, part-baked yeasted products	Bacterial spoilage (e.g., "rope" mold growth and "chalk molds")
0.90–0.95	Moist cakes (e.g., carrot cake)	Mold and yeast, bacterial spoilage (e.g., "rope")
0.8–0.89	Plain cakes	Molds and yeasts
0.7–0.79	Fruit cakes	Xerophilic molds and osmophilic yeasts
0.6–0.69	Some dried fruits or fruit cakes	Specialized xerophilic molds and osmophilic yeasts, sugar-tolerant yeasts
<0.6	Biscuits, chocolate, some dried fruits	No microbial spoilage

Source: Cauvain, S.P. and Young L.S., *Bakery Food Manufacture and Quality: Water Control and Effects*, 2nd edn., Wiley-Blackwell, Oxford, England, 2008.

Leuconostoc mesenteroides) have been found to be responsible for spoilage of gas-packaged crumpets. Fortunately, post-baking contamination with yeasts and lactic acid bacteria is uncommon and can be controlled by the adoption of appropriate hygienic precautions (Seiler, 1998).

20.5.1.2.2 Staling

Staling is the common description of the decreasing consumer acceptance of bakery products as they age, caused by changes in crumb other than those resulting from the action of spoilage organisms; it is the major mode of deterioration. Bread staling falls into two categories: crust staling and crumb staling. Crust staling is generally caused by moisture transfer from the crumb to the crust, resulting in a soft, leathery texture and is generally less objectionable than crumb staling. Crumb staling is more complex, more important and less well understood (Pateras, 2007). The firmness of bread varies with position within a loaf, with maximum firmness occurring in the central portion of the crumb. The most widely used indicator of staling is measurement of the increase in crumb firmness (Gray and Bemiller, 2003). Most white bread in the United States has a commercial shelf life of 2 days after which it is no longer considered fresh because of the staling process. As a consequence, large quantities of bread are discarded or returned to the manufacturer, posing an economic burden to both the baking industry and consumers.

Bread staling is a complex phenomenon in which multiple mechanisms operate, and neither the bread system nor the staling process is well understood at the molecular level. The most plausible hypothesis is that retrogradation of amylopectin occurs, and because water molecules are incorporated into the crystallites, the distribution of water is shifted from gluten to starch/amylopectin, thereby changing the nature of the gluten network (Gray and Bemiller, 2003). The formation of complexes between starch polymers, lipids and flour proteins is thought to inhibit the aggregation of amylose and amylopectin, so that, for example, cookies and biscuits (which have a higher lipid content than bread) tend to stale more slowly. Staling can be prevented if bread is stored above 55°C or below −18°C (Kent and Evers, 1994). Antistaling enzymes or carbohydrases, which work by hydrolyzing the amylopectin fraction and thereby preventing retrogradation and hence staling, increased shelf life of white pan bread by over two days (Gil et al., 1999).

An interesting aspect of the staling of bread is that the rate has a negative temperature coefficient, so that as the temperature increases up to 55°C, the rate of staling decreases. The staling rate passes through a maximum close to 4°C and decreases as the temperature declines below this point. From a packaging point of view, nothing can generally be done through the selection of different packaging materials to either accelerate or impede the rate of staling, although an exception is pita bread, which is discussed in the next section on gas packaging.

Evidence for the effect of CO_2 on the rate of staling is conflicting. Rasmussen and Hansen (2001) found no significant effects of 100% CO_2 or 50:50 CO_2:N_2 during storage of bread for 7 days at 20°C compared to control bread in air. The development of bread firmness during storage in 100% CO_2 for 49 days was correlated to amylopectin retrogradation and to changes in the freezable water fraction of the breads in a nonlinear manner, suggesting that bread firmness is influenced by both the crystallization behavior of starch and by changes in hydration.

20.5.1.2.3 Moisture Loss/Gain

The cooling of bread can create problems, particularly when the bread is to be sliced and packaged before sale. Bread leaves the oven with the crumb at a temperature of about 98°C and a moisture content at the center of about 45%. The crust is hotter (about 150°C) but much drier (1%–2% moisture content) and cools rapidly. During cooling, water moves outward from the interior toward the crust and then to the atmosphere. Excessive drying during cooling results in weight loss and poor crumb characteristics. If the moisture content of the crust rises considerably during cooling, then the texture of the crust becomes leathery and tough and the attractive crispness of freshly baked bread is lost (Kent and Evers, 1994).

After cooling, the moisture content of white bread is 36% and the a_w is 0.96. Packaging has a major influence over whether or not a bakery product will gain or lose moisture during storage, although clearly the difference between the a_w of the product and the RH of the ambient atmosphere will be the primary driving force. Softness or resistance to deformation and recovery from deformation are important crumb characteristics and are directly affected by the level of water remaining in the product, coupled with a fully developed and resilient crumb structure (Cauvain and Young, 2008).

The loss of crust crispness is an important and beneficial change in sandwich bread types because it adds to the perception of freshness by the consumer. When purchasing bread, consumers can only assess freshness by squeezing the loaf, knowing that fresh bread has little resistance to squeezing and will rapidly spring back to its original shape (Cauvain and Young, 2008).

Although loss of crust crispness as a result of moisture gain is, at least in theory, a possible cause of end of shelf life for bread, such an occurrence is rare and can generally be overcome by selecting a more permeable package. An associated problem with moisture gain is an increase in crust a_w and an increased likelihood of mold growth. Conversely, excessive moisture loss can also be easily controlled by selecting a less permeable packaging material.

20.5.1.2.4 Rancidity

The development of oxidative rancidity in bread is not normally considered to be a problem as bread has relatively high oxidative stability. However, changes in aroma and flavor attributes such as "acidic," "off," "rancid" and "dust" together with the taste attributes "sweet" and "bitter" have been found to increase during storage of whole wheat bread. Jensen et al. (2011) reported small but significant differences in oxidative stability for whole wheat bread crumb and crust stored in plastic bags with 100% N_2 at room temperature. The overall antioxidative capacity was reduced during storage with the accumulation of lipid hydroperoxides peaking after 2–3 weeks of storage. Bread crust was generally found to be more stable to oxidation compared to the crumb. They suggested that the quality of bread with extended shelf life may be improved by minimizing oxidation through the use of antioxidants.

20.5.1.3 Packaging

The objective in packaging bread is to maintain the bread in a fresh condition by preventing too rapid drying out, without providing too good a moisture barrier which would promote mold growth on a soggy crust. The most commonly used material is an LDPE bag in which the end is twisted and sealed with a PS tag. This form of packaging helps retard one mode of deterioration in bread; namely, moisture loss. However, the moisture which tends to migrate from the crumb to the crust is prevented by the package from passing freely into the atmosphere, and results in a crust with a tough, leathery consistency. Some specialty breads such as French and Italian are packaged in OPP or PET bags perforated with small holes which allow moisture to escape and thus retain a crisp crust. Several hole sizes and densities are available, depending on the particular product and its surface area:volume ratio.

An assessment of the risk of physical contamination of bread packaged in perforated OPP films and sold in self-service retail outlets found a correlation between the risk and the geometrical characteristics of the film including the size of the holes and the area of the holes as a percentage of the total surface area (Piergiovanni et al., 2003). Pagani et al. (2006) investigated variations in the moisture content inside the loaf during storage and their influence on changes in crumb softness over 48 h when packaged in perforated OPP films of varying hole diameter and density. Moisture loss varied from 10% to 25% of the initial moisture content. The best performing film had a mean hole diameter of 0.54 mm and hole density of 21.4 holes cm^{-2} (corresponding to an open surface of 5%) and allowed both crust crispness and crumb softness to be maintained, something that cannot be achieved with, for example, paper bags.

Vacuum packaging is not a suitable technology to extend the mold-free shelf life of most soft bakery products because the product is crushed under a vacuum. However, it has been used to prevent mold problems in flat breads such as naan and pita, and pizza crusts. An alternative to vacuum packaging is to modify the atmosphere inside the package and the three approaches that have been investigated are discussed in the following.

20.5.1.3.1 Gas Packaging

The idea of modifying the gas atmosphere inside a package of bread in order to extend the product shelf life is not new. In fact, it was shown as early as 1933 that the storage of bread in atmospheres containing at least 17% CO_2 delayed the appearance of mold (Skovholt and Bailey, 1933). At a concentration of 50% CO_2, the mold-free shelf life of bread was doubled under storage conditions favoring mold development.

Extensive research on the use of CO_2 for extending the shelf life of bakery products was undertaken by Seiler in the United Kingdom in the 1960s (Seiler, 1998). In detailed studies with bread and cake stored at 21°C and 27°C and CO_2 concentrations of 0%–60%, it was shown that the mold-free shelf life increased with increasing CO_2 concentrations, with the effect (not unexpectedly) being greater at lower temperatures. Subsequent studies with mixtures of CO_2 and N_2 and with 100% CO_2 confirmed the need for CO_2 in the package headspace, where simply displacing headspace O_2 with N_2 alone was insufficient to prevent mold growth.

A range of gas mixtures has been used to extend the shelf life of bakery products, from 100% CO_2 to 50:50 CO_2:N_2. The optimum blend of gases for a specific product cannot be determined by trial and error but only through a detailed, systematic study of the variables influencing product shelf life. Extensions of 3 weeks to 3 months at room temperature are achievable using appropriate mixtures of CO_2 and N_2 (Smith et al., 2004).

Degirmencioglu et al. (2011) added potassium sorbate to bread dough at concentrations of 0%, 0.15% and 0.30% and packed the sliced bread in expanded APET-EVOH-LDPE trays sealed with a PA-LDPE film and six different gas concentrations (air, 100% N_2, 70:30 N_2:CO_2, 50:50 N_2:CO_2, 30:70 N_2:CO_2 and 100% CO_2). The packaged bread samples were stored for 21 days at 20°C and 60% RH. None of the samples showed signs of mold growth after 21 days, and 100% CO_2 with 0.30% potassium sorbate was the most effective treatment for the inhibition of bacteria.

Pita bread (also called Arabic, Egyptian baladi, flat or pocket bread) is made from flour, water and yeast and has a shelf life of only a few hours, mainly due to its large surface area:volume ratio. Hardening caused by staling and drying is the main factor limiting shelf life, with the moisture content and a_w of unpackaged pita bread reducing from 55.5% and 0.95 to 40.3% and 0.92, respectively, in 6 h. Using a laminate film containing EVOH as a barrier layer, a gas atmosphere of 99.5% CO_2 or a mixture of 73:27 CO_2:N_2 enabled the shelf life of pita bread to be extended to 14 days at which time yeast growth terminated shelf life. Staling, as determined by means of a penetrometer, was delayed in MAP pita bread (Avital and Mannheim, 1988). Black et al. (1993) prevented microbial spoilage for up to 28 days in packs containing EVOH and flushed with 100% CO_2, but stale flavors developed after 21 days and no clear pattern of firming over time or between treatments was found.

In a review on the use of MAs for the packaging of bakery products, Smith et al. (2004) concluded that MAP may not be suitable for all types of bakery products and that knowledge of a product's physical, chemical and microbiological characteristics are critical to the success of this technology. Furthermore, the importance of combining technologies such as O_2 absorbers and ethanol vapor generators with MAs to increase the shelf life of bakery products was emphasized.

20.5.1.3.2 Alcohol Vapor

It has been known for many years that ethanol is a powerful bactericide. Indeed, ethanol is still used in this application for the sterilization of surgical instruments and working surfaces. Ethanol is also a very effective antifungal agent and, as such, has the potential to extend the shelf life of bakery products. In 1976, a U.S. patent was granted to cover the use of ethanol for retarding mold growth in partially baked pizza crust. The data presented demonstrated that where pizza bases were sprayed on all surfaces with 95% ethanol to give a concentration of 2% based on product weight, the shelf life was increased by up to fivefold. Subsequently, the U.S. FDA affirmed the GRAS status of ethanol as a direct human food ingredient and permitted its use for spraying prebaked pizza bases at concentrations up to 2% by weight (Seiler, 1998).

Extensive tests were carried out in the United Kingdom to determine the effectiveness of treatment with 95% ethanol in increasing the mold-free shelf life of a range of bakery products (Seiler, 1998). At a given level of treatment, the antimold activity of ethanol was greater when the products were tightly packed in film than when loosely packed and when gas impermeable films were used. The ability of ethanol to act as a vapor phase inhibitor was confirmed by the finding that similar increases in mold-free shelf life were obtained when the same amount of ethanol was sprayed over all surfaces of the product prior to packaging and sealing and when ethanol was merely added to the base of the same size bag before adding the product and sealing. Extensions in mold-free shelf life varied according to the type of product, tightness of the package, gas permeability of the packaging material and seal integrity. Treatment with 0.5% by product weight of food grade ethanol (95%) was found, under optimum conditions, to at least double mold-free shelf life, while treatment with 1.0% was found to at least triple shelf life. Ethanol was found to retard the rate of staling of both bread and cake in addition to inhibiting mold growth. The flavor of ethanol could be detected by sensory panels in cake treated with 1.0% but not 0.5% ethanol by product weight (Seiler, 1998).

Another way of adding ethanol (besides the injection or deposition of a small amount into the package immediately prior to sealing) is to use sachets of paper-EVA copolymer containing powdered silica gel (35% w/w) onto which food grade ethanol (55% w/w) has been absorbed. Vanilla can be added to mask the smell of ethanol. These sachets are available commercially and can be placed inside the package prior to sealing. They allow the slow release of alcohol vapor, which exerts the preservative effect. The extension in shelf life has been shown by the supplier of the sachets to depend on the ethanol permeability of the packaging material, the integrity of the seals, the a_w of the food and the type of microorganisms present. Data on the permeability of plastic films to ethanol is scant; the permeability coefficient for ethanol through LDPE has been reported as 2.8×10^{-4} g cm m^{-2} day $^{-1}$ kPa^{-1}.

Ethanol vapor generators have been shown to be effective in controlling at least 10 species of molds, including *Aspergillus* and *Penicillium* species; 15 species of bacteria including *Staphylococcus*, *Salmonella* and *E. coli* spp; and 3 species of spoilage yeast (Smith et al., 2004). For products with a_ws of less than 0.90, long increases in mold-free shelf life can be obtained using 0.34%–0.69% of ethanol by weight of the product. For higher a_w products, up to 4% ethanol by weight may be required.

20.5.1.3.3 Oxygen Absorbers

It is very difficult to reduce the O_2 content to a very low level in packages of bakery products. The porous interiors of these products tend to trap O_2 in such a way that it does not readily interchange with gas which is flowing through the package as occurs in a simple flushing operation carried out as part of MAP. Repeated vacuumizing followed by release of vacuum with an anaerobic gas system would probably solve this problem but would also lead to collapse of products such as bread and rolls. One approach to overcome this problem is to place an O_2-absorbent material inside the package after it has been flushed with N_2 or CO_2. Sachets containing iron powder which rapidly react with O_2 have been evaluated for this purpose.

In tests reported by Seiler (1998), slices of bread and Madeira cake which had been artificially inoculated with molds were placed in bags of O_2 impermeable film with an O_2-absorbent sachet and heat sealed; no mold growth appeared even after prolonged storage at 27°C. In further tests in which films with higher O_2 permeability and leaking seals were used, the extensions in mold-free shelf life were greatly reduced. Permeability of the film was found to be more important than leakage sites in the seals. It was concluded from these tests that the use of O_2-absorbing sachets can result in commercially worthwhile increases in shelf life of baked products, provided that the packaging material used is sufficiently impermeable to O_2 and the packages are well sealed.

The effect of an ethanol emitter (EE) or ethanol emitter combined with an O_2 absorber (EE + OA) on the shelf life extension of sliced bread packaged in high barrier SiO_x-coated PET-LDPE pouches stored for 30 days at 20°C was investigated by Latou et al. (2010). Bread with (WP) and without (WOP) preservatives served as controls. Aroma quality deterioration during storage was due to the loss of volatile compounds and the formation of “off-flavors” from lipid oxidation. Neither the EE nor the EE + OA had an adverse effect on the initial odor, taste and texture of bread. Based on sensory (texture) and microbiological data, shelf life was ~4 days for samples WOP; 6 days for samples WP; 24 days for samples containing the EE and at least 30 days for samples containing the EE + OA.

20.5.2 Biscuits, Cookies and Crackers

20.5.2.1 Manufacture

The three basic ingredients used to manufacture products in this category are wheat flour, fat and sugar which are combined in different combinations, together with salt and other ingredients in lesser quantities, to produce a wide range of products. The mixing process achieves two purposes: intermingling of ingredients, and certain chemical and physical changes which depend on the type of product being produced.

Doughs fall into two categories: hard and short. Hard doughs (crackers and “tea and coffee” biscuits) have low fat, high water and receive a single-stage mix. Short doughs (pastry products, shortbread and American-style cookies) have high fat, low water and usually high sugar levels, and are usually mixed in two stages. Baking is usually carried out in tunnel ovens where the formed dough pieces are conveyed through a series of heated sections. From the oven, the product is taken onto a series of conveyors where it cools and loses the last traces of moisture. After cooling, some products are directly packaged but many types require additional processing to add non-baked enrichments such as cream and chocolate (Manley, 2011).

20.5.2.2 Indices of Failure

Three indices of failure are usually associated with biscuits: loss of crispness, development of rancidity and development of fat bloom. The possible role that packaging may play in controlling the rate of deterioration is now discussed for each index.

20.5.2.2.1 Loss of Crispness

Freshly baked biscuits usually have moisture contents within the range 1%–5% and a_ws from 0.1 to 0.3. If biscuits are completely sealed in a material with a very low WVTR, then the small amount of moisture in the atmosphere inside the package will rapidly come into equilibrium with that in the biscuits and no further change will take place. However, if the packaging material has a medium WVTR or if the package seals are not perfect, moisture from the ambient air will enter the package and ultimately lead to a loss of crispness.

The critical a_w at which biscuits, cookies and crackers lose their crispness depends on their formulation but it is typically ~0.5 ± 0.2. Given the large volume of such products manufactured each year, there are surprisingly few published moisture sorption isotherms (MSIs). Palou et al. (1997) reported the MSIs for three cookies and two corn snacks at 25°C, 35°C and 45°C; McMinn et al. (2007) reported the MSIs for oatmeal biscuits at 5°C, 20°C, 40°C and 60°C; Cervenka et al. (2008) reported the MSIs for gingerbread over the temperature range 20°C–30°C; and Al-Muhtaseb et al. (2010) reported MSIs for Madeira cake over the temperature range 5°C–60°C.

Figure 20.2 presents the MSIs at 20°C for crackers and cookies. At any particular a_w, the cracker had a higher EMC or sorbed water than the cookie, which was not surprising as the latter contained 10 times as much fat as was in the cracker (Kim et al., 1999).

Although it is possible to produce cream fillings that contain no moisture, some products such as Amaretti cookies are multidomain systems characterized by a soft internal almond paste ($a_w \sim 0.74$; moisture content ~13%–14%) and a crunchy external crust ($a_w \approx 0.40$; moisture content ~5%–6%).

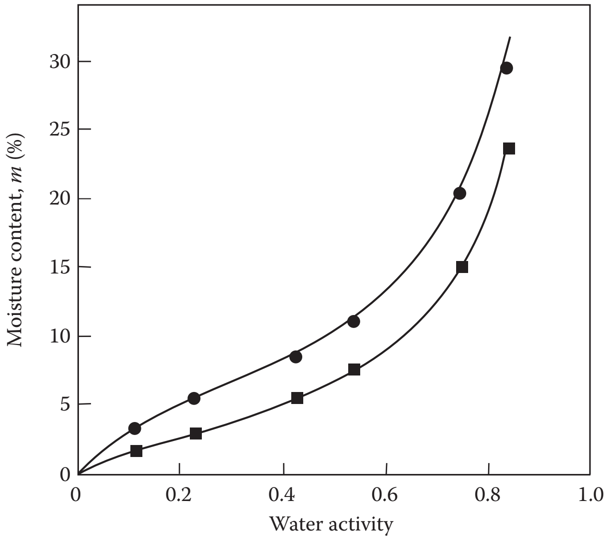

FIGURE 20.2 Moisture sorption isotherm at 20°C for a cracker (●) and cookie (■). (Redrawn from Kim, S.S. et al., *J. Food Sci*., 64, 300, 1999.)

This leads to a severe hardening of the internal almond paste and a softening of the crust due to the redistribution of water, severely limiting the shelf life to only a few days (Farris and Piergiovanni, 2008). Arimi et al. (2010) monitored the loss of crispness in Crackerbread biscuit with increasing a_w; the critical water activity (a_c) at 25°C ranged between 0.51 and 0.59.

Obviously, it is useful to know the initial and critical moisture contents or a_ws of biscuits so that a satisfactory package can be selected that will give the desired shelf life in a particular environment. The following example (Robertson, 2011) demonstrates how this can be done.

Example 20.1

McMinn et al. (2007) reported the moisture sorption data for oatmeal biscuits and the resulting MSI at 40°C is shown in Figure 20.3. For the purposes of this example, it is assumed that the biscuits had an initial moisture content m_i of 1.0% (0.010 g H_2O per g of dry solids) and a critical moisture content m_c of 3.6% due to loss of crispness. The equilibrium moisture content m_e at 40°C corresponding to 90% RH is 11.5% and the pseudo-equilibrium moisture content m_e' obtained by linearizing the straight line portion of the isotherm is 5.0%; the slope of the straight line (b) is 0.055 g H_2O g solids^{-1} unit a_w^{-1}.

Calculate the shelf life of the biscuits if they are packed in either a 26 μm two side acrylic coated OPP film or a 50 μm one side acrylic coated, one side PVdC copolymer coated white opaque OPP. The weight of biscuits in the rectangular package is 250 g and the dimensions of the package are 8 × 16 × 4 cm. The packed product is to be distributed under tropical conditions (38°C and 90% RH).

$$\text{Surface area of the rectangular packs} = 448\ \text{cm}^2 = 0.0448\ \text{m}^2$$

$$\text{Weight of dry solids in the package} = 250 \times 99\% = 247.5\ \text{g}$$

$$\text{Vapor pressure of pure water at 38°C} = 4.969\ \text{cm Hg}$$

Using data from the plastic film supplier, the WVTR of the two films at 38°C and 90% RH are as follows:

$$26\ \mu\text{m OPP} = 5.0\ \text{g m}^{-2}\ \text{day}^{-1}$$

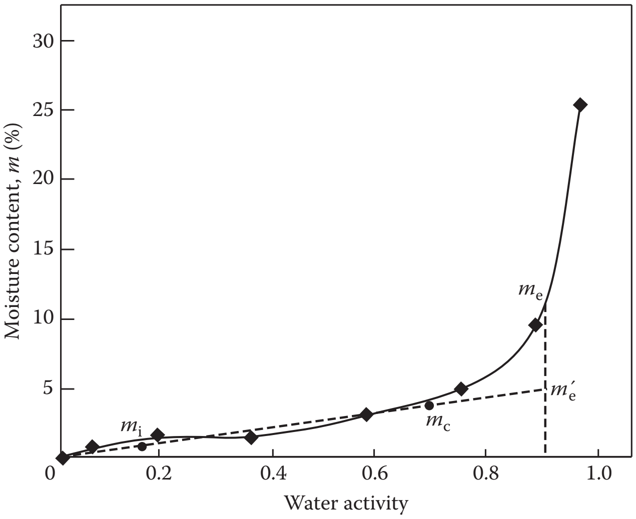

FIGURE 20.3 Moisture sorption isotherm at 40°C for oatmeal biscuits with a superimposed straight line of slope *b*. Initial (m_i), critical (m_c) and equilibrium (m_e) moisture contents are indicated together with the pseudo-equilibrium (m_e') moisture content used for package shelf life calculations. (Plotted using data from McMinn, W.A.M. et al., *J. Food Eng*., 79, 481, 2007.)

$$50\,\mu\text{m OPP} = 3.4\text{ g m}^{-2}\text{ day}^{-1}$$

The WVTRs must be converted into water vapor permeances *P*/*X* by dividing by the driving force for water vapor transfer:

$$\text{Driving force at 38°C and 90\% RH} = 4.969 \times 0.90 = 4.472\text{ cm Hg}$$

For 26 mm OPP film:

$$\frac{P}{X} = \frac{5.0\text{ g}}{\text{m}^2\text{ day}} \times \frac{1}{4.472\text{ (cm Hg)}}$$
$$= 1.118\text{ gm}^{-2}\text{ day}^{-1}\text{(cm Hg)}^{-1}$$

For 50 μm OPP film,

$$\frac{P}{X} = 0.760\text{ gm}^{-2}\text{ day}^{-1}\text{ (cm Hg)}^{-1}$$

Substituting into Equation 12.10 for biscuits packed in 26 μm OPP film:

$$\ln\frac{0.05 - 0.010}{0.05 - 0.036} = 1.118 \cdot \frac{0.0448}{247.5} \cdot \frac{4.969}{0.055} \cdot \theta_s$$

Solving for shelf life θ_s:

$$\theta_s = \frac{[\ln 2.857]}{0.01828} = \frac{1.0498}{0.01828} = 57\text{ days}$$

If the biscuits were packed in the 50 mm OPP film instead:

$$\theta_s = 84\text{ days}$$

> If a longer shelf life were required (say 200 days), then Equation 12.10 could be recalculated for another film with a lower permeance. As noted earlier, the calculated shelf life will be longer than what would actually be achieved in practice because the pseudo-equilibrium moisture content m'_e used in the calculations is significantly less than the real equilibrium moisture content which is the driving force for water vapor transport. Because of the simplifying assumptions made in the previous calculations, the calculated shelf lives should be verified by actual shelf life testing.

20.5.2.2.2 Rancidity

The development of oxidative rancidity in biscuits is not normally a problem, even when the biscuits are stored under light as the packaging material typically contains a white pigment. Lu and Xu (2009) reported on the effect of light-barrier properties of packaging films on the photo-oxidation and shelf life of commercial cookies containing 23.5% fat. Cookies were packed in three different films: 125 mm transparent BON-LDPE, 170 mm semi-transparent PET-BON-LDPE and 45 mm opaque BOPP-metCPP. They were stored at 40°C under UV light with an intensity of 5 lx (the same intensity as from fluorescent lights in supermarkets). The shelf life (determined as the time to reach a critical peroxide value [PV] of 19.7 meq kg^{-1}) was 37 days for BON-LDPE, 52 days for PET-BON-LDPE and 76 days for BOPP-metCPP. However, there were large differences in the OTRs of the three films (the OTR of the best was 25 times that of the poorest) which would have had a significant influence on shelf life, in addition to the effect of the different light transmission properties of the three films which varied by a factor of 12. Where fat oxidation is a problem, antioxidants may be added to the biscuits or they could be packed in a reduced O_2 or MA.

A shelf life prediction model of lipid-containing bakery products (biscuits with 20% fat) was developed by Calligaris et al. (2007). PV was chosen as a representative index of the quality depletion of biscuits during their shelf life, as changes in PV were linearly related to consumer acceptability. The evolution of peroxides was predicted by a modified Arrhenius equation accounting for changes in the physical state of biscuit fat. Knowledge of the relationship between peroxides and sensory acceptability, together with the temperature dependence of peroxide formation, allowed the development of a mathematical model to simply and quickly calculate the shelf life of biscuits. However, as Talbot (2011) has pointed out, peroxides measured by the PV test are, in themselves, generally tasteless and it is only when they are broken down further into aldehydes, ketones, etc., that off-flavors develop.

20.5.2.2.3 Fat Bloom

Fat bloom is a gray discoloration which can occur on the surface of biscuits during storage. Its identity is easily confirmed by gently warming the product when the discoloration will disappear. The formation of bloom is accelerated by cyclic variations in temperature during storage of the products and is associated with the use of certain fats and fat blends. This mode of deterioration is unlikely to be affected by different packaging materials.

20.5.2.3 Packaging

The traditional material used for the packaging of biscuits has been RCF coated with either LDPE or PVdC copolymer and often with a layer of glassine in direct contact with the product if it contained fat. However, this combination of material has been largely replaced by OPP, either as plain or, more commonly, pearlized OPP film, coextruded OPP film or acrylic-coated on both sides. Plain OPP films are economical but generally require a heat seal coating to improve sealability. Coextruded OPP films provide superior seal strength. If a superior O_2 barrier is required, then acrylic-coated OPP is used, and one side is sometimes coated with PVdC copolymer rather than acrylic. In addition, acrylic and PVdC copolymer-coated OPP films provide a superior flavor and aroma barrier compared with that of uncoated OPP.

Mechanical protection is generally provided either by placing the product in a protective rigid container such as a paperboard carton of appropriate caliper or by packing the product tightly together, the choice depending on a number of factors. If the product is particularly moisture sensitive, the carton will need to be overwrapped with a film which can provide a good barrier to water vapor. A further option is to place the biscuits inside a tray (typically made from thermoformed PVC or HIPS but now more commonly PET) and then overwrap the tray with a film that provides suitable protection from water vapor and O_2.

20.6 SNACK FOODS

Dictionary definitions of a snack include "a slight or casual or hurried meal, a small portion of food or drink, or a very light meal" and "a food not meant to be eaten as a main meal of the day, but consumed to get a brief supply of energy for the body or consumed between meals purely for the enjoyment of its taste." Until the 1970s, commercial snack foods were basically potato chips or crisps, nuts, cookies and confectionery. Snack foods now include a very wide range of products, including potato and corn chips, alkali-cooked corn tortilla chips, pretzels, popcorn, extruded puffed and baked/fried products, half-products, meat snacks and rice-based snacks (Lusas and Rooney, 2001).

The snack food industry today relies more and more on extrusion cooking processes. A major distinction can be made between direct expanded snack foods and the expanded pellet forms. The former are usually very light structures, which emerge from the cooker/extruder and require only adjustment to moisture content before enrobing and flavoring, whereas the latter are typically compact and dense and require rather specialized drying before expanding. This is achieved by means of a number of techniques including frying in oil, rotating in sand or salt roasters, microwave heating or fluid bed toasters.

20.6.1 Fried Snack Foods

20.6.1.1 Manufacture

Fried snack foods can consist of many different ingredients. Although the most popular have been based on potatoes and nuts, large quantities are also made from cereal ingredients, with the most widely used cereal being corn. Nuts are consumed on their own, with dried fruits or used as components in various foods such as muesli, snack bars and chocolate confectionery. The most commonly consumed nuts include almonds, Brazil nuts, cashew nuts, chestnuts, coconut, hazelnuts, macadamia, peanuts, pecans, pine nuts, pistachio nuts, sunflower seeds and walnuts. There has been increasing interest in the nutritional components of nuts, particularly phytochemicals including carotenoids, phenolic acids and phytosterols, and polyphenolic compounds such as flavonoids, proanthocyanidins and stilbenes (Bolling et al., 2011).

Common to all these snacks is fat which is used as a processing agent to dehydrate the product (as in the case of potato chips) or puff it (as in the case of some extruded products) and develop characteristic flavors. As a consequence, the end of shelf life of many fried snack foods is closely related to the development of rancidity by the fat.

The manufacture of potato chips (also referred to as crisps in some countries) is quite straightforward. After washing, peeling and trimming, potatoes are thinly sliced, washed to remove adhering starch granules, blanched and then dried before passing on a conveyor through hot oil in which they are rapidly dehydrated and cooked. Excess oil is drained or centrifuged off and the chips cooled, salted, flavored (usually by powder adhesion to the residual fat on the chips) and packaged. During the processing of potatoes to chips, the moisture content of the potato is reduced from about 79%–5%, and of the final 95% of dry matter in chips, 35%–40% is fat.

20.6.1.2 Indices of Failure

There are two major indices of failure of fried snack foods: development of fat rancidity and loss of crispness.

20.6.1.2.1 Rancidity

All fats are subject to deterioration by oxidative and hydrolytic rancidity which leads to the formation of objectionable odors and flavors. Hydrolytic rancidity is responsible for the development of "soapy" flavors and for facilitating deterioration by direct oxidation. Oxidative rancidity results in food spoilage associated with fat deterioration, that is, the presence of pungent or acrid odors, and this is the more important of the two mechanisms with respect to food acceptability (Labuza, 1982).

The susceptibility of fried snack foods to oxidative rancidity depends on the type of fat used and the number of unsaturated bonds in the fatty acid moiety. Oxidation of oils is mainly responsible for volatile compound changes in potato chips during storage. To minimize the development of rancidity, the product must be protected from O_2, light and trace quantities of metal ions. The addition of phenolic-type antioxidants such as BHA, BHT and TBHQ is very helpful but is not always permitted by legislation.

Several approaches for improving the storage stability of potato chips are available. Since the bulk density of chips is typically 0.056 g mL^{-1}, they have a very large headspace volume per unit weight of product. If the product is packed at atmospheric O_2 concentration, then the headspace O_2 is sufficient to cause O_2 uptake in excess of 3 mL O_2 (STP) g^{-1}. Consequently, inert gas packaging results in a very significant increase in the shelf life of potato chips, provided that the headspace O_2 concentrations attained are below 1% and the package permeability to O_2 is very low. The package should be designed to avoid light penetration.

Lee and Pangloli (in press) fried potato chips in mid-oleic sunflower oil and stored them in closed glass jars at ambient temperature (~22°C) either in the dark or under fluorescent light (16.1–18.3 lx) for 6 weeks. Lightness and yellowness of chips decreased with storage time, and PVs were influenced by storage conditions and time. The results indicated that potato chips fried in mid-oleic sunflower oil might retain the desirable fried flavor during 6 weeks storage in a sealed container in the dark, which is not an option for products sold through supermarkets unless the package is a very good light barrier.

Bellomo et al. (2009) packaged pistachio kernels in pouches containing either PA or EVOH as an O_2 barrier layer, with and without O_2 scavengers, and stored them at 10°C, 25°C and 37°C for 14 months. The oil showed a slight increase in acidity and PV, irrespective of storage temperature.

20.6.1.2.2 Loss of Crispness

Crispness is a salient textural characteristic for fried snack foods, and its loss due to absorption of moisture is a major cause of snack food rejection by consumers. Water affects the texture of snack foods by plasticizing and softening the starch/protein matrix, which alters the mechanical strength of the product. Although several investigators have discussed a moisture content limit at which the textural quality of a snack food product becomes organoleptically unacceptable (typically 3%–3.5%), moisture content limits are strongly dependent on the method used for moisture determination. A more reliable approach to establishing moisture conditions for textural acceptance is as a function of a_w. The critical a_w for potato chips and corn is in the range of 0.40–0.50. The initial a_w for potato chips has been reported as 0.076, which corresponds to a moisture content of 0.65 g H_2O per 100 g solids, well below the monolayer value of 2.9 g H_2O per 100 g solids (Katz and Labuza, 1981). The critical a_ws for puffed corn curl and extruded rice snacks have been reported as 0.36 and 0.43, respectively (Min et al., 2010). The influence of different packaging materials and of gas flushing on the O_2 content of potato chip packages is shown in Figure 20.4.

20.6.1.3 Packaging

From the modes of deterioration discussed earlier, it is clear that a satisfactory package for fried snack foods would need to provide a good barrier to O_2, light and moisture.

Fried snacks foods are typically packaged in multilayer structures, although spiral-wound, paperboard cans lined with aluminum foil or a barrier polymer and sealed under vacuum with an LDPE-foil end are used for some specialty products which also require mechanical protection. In addition,

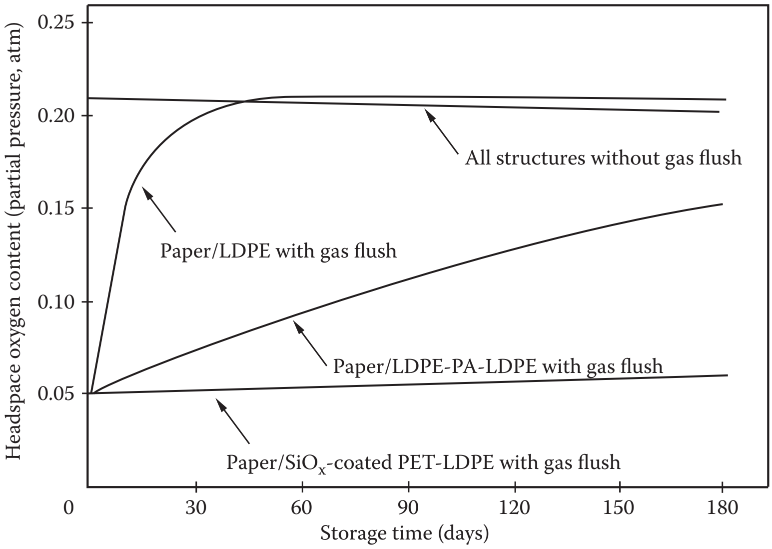

FIGURE 20.4 Influence of different packaging materials and of gas flushing on the O_2 content of potato chip packages at 25°C. (From Pfeiffer, C. et al., *Food Technol.*, 53(6), 52, 1999.)

the use of metal cans for fried nuts is popular for premium products, where the container is usually gas flushed with N_2 immediately prior to seaming.

Limited information is available on the effects of packaging materials on the stability of snack foods during ambient storage. Because these products are frequently displayed for sale under fluorescent lights, flexible packages are usually pigmented or (occasionally) placed inside paperboard cartons. The use of metallized films is widespread, and although they are reasonably efficient light barriers, they do permit some light to penetrate into the package.

Potato chips packaged in OPP-LDPE-PVC, HDPE-EVA copolymer plus a UV light-absorbing compound or HDPE-EVA copolymer plus a TiO_2 light barrier developed distinct oxidized flavors within 7 days when stored at 21°C, 55% RH and under 1100–2500 lx of continuous fluorescent light. Potato chips stored under the same conditions, but packaged in HDPE plus TiO_2 and a brown light-absorbing pigment construction or an aluminum foil-LDPE construction were stable throughout 10 weeks of storage (Kubiack et al., 1982). O_2-barrier film characteristics did not influence the oxidative stability of the air-packaged potato chips. The barrier properties of the various films used are presented in Table 20.4.

TABLE 20.4
Construction and Properties of Flexible Packaging Materials Used for Packaging of Potato Chips

Film Construction	WVTR[a] (mL m^{-2} day^{-1})	OTR[b] (mL m^{-2} day^{-1})
OPP-LDPE-OPP-PVdC copolymer	3.5	6
HDPE-HDPE + UVab-EVA	3.0	1500
HDPE-HDPE + TiO_2-EVA	3.0	1500
HDPE + TiO_2-HDPE + Br[c]-HDPE	3.0	1500
OPP-LDPE-Foil-LDPE-HDPE-EVA	0	0

Source: Kubiak, C.L. et al., *J. Food Prot.*, 45, 801, 1982.

[a] Measured at 37.8°C and 90% relative humidity.

[b] Measured at 22.8°C and 0% relative humidity.

[c] Brown-pigmented light barrier.

Walnut kernels retained acceptable quality for about 2 months in LDPE pouches under air, 4–5 months in PET-LDPE laminate under N_2 and at least 12 months in SiO_x-coated PET-LDPE pouches under N_2 at 20°C, with samples stored in the dark retaining slightly higher quality than those exposed to light (Mexis et al., 2009). The effect of parameters investigated followed the sequence: temperature > package O_2 barrier > lighting conditions.

The effects of storage temperature, packaging material OTR and variety on the oxidative stability of vacuum-packaged walnut kernels were studied over a 12 months storage period by Bakkalbaşı et al. (2012). The effect of storage temperature on lipid oxidation was greater than the effect of packaging material OTR. It was concluded that for vacuum-packed walnut kernels in PA-LDPE pouches (OTR 63 mL m^{-2} day^{-1} at 23°C), storage at 20°C protected against oxidation for 12 months.

Mexis et al. (2011) found that acceptable conditions for packaging and storage of nonirradiated and irradiated raw almonds for 12 months at 20°C with N_2 MA were with an O_2 absorber, irrespective of lighting conditions (dark and 825 lx), packaging material O_2 barrier (OTRs of 0.3 and 22 mL m^{-2} day^{-1}) and irradiation dose, although lower doses (1.0 kGy) gave better sensory results than higher doses (3.0 kGy).

An economical method for packaging peanuts and pecans for long term storage utilizes the CO_2 adsorption properties of these commodities and involves placing them in plastic pouches impervious to air and CO_2, flushing with CO_2 and then heat sealing the pouches. CO_2 is adsorbed into the pores of the commodities resulting in the formation of a vacuum inside the pouches. Both shelled, raw peanuts and shelled, roasted and blanched peanuts are protected from any significant deterioration of flavor and other quality factors for up to 12 months.

The formation of a collapsed, tight package a few weeks after vacuum-packaging of cereals, grains and nuts due to the adsorption of CO_2 is well documented. If these products are packaged in CO_2 in a plastic bag of low gas permeability and the bag is sealed, the package volume gradually decreases as CO_2 gas is absorbed and finally a skintight package is obtained.

20.6.2 Extruded and Puffed Snacks

20.6.2.1 Manufacture

Extrusion has provided a means of manufacturing new and novel products and has revolutionized many conventional snack manufacturing processes. The most popular and successful extruders used in the production of snack foods have been single-screw extruders, although twin-screw extruders are also used. The extruder must exercise a number of functions in a short time under controlled, continuous or steady-state operating conditions. These functions may include heating, cooling, conveying, feeding, compressing, reacting, mixing, melting, cooking, texturing and shaping (Huber, 2001).

The majority of extruded snacks on the market fall into the category of expanded snacks. They are usually light with a low bulk density and are seasoned with an array of flavors, oils and salt. A typical manufacturing process would consist of blending of the ingredients with water prior to being fed into the extruder. As the mix passes through the extruder, it is compressed, with the work performed on the mix during extrusion being transformed into heat. The combination of pressure and heat causes the mix to become very viscous, and as it passes through the extruder heads, the superheated moisture instantaneously vaporizes, resulting in puffing of the product.

The moisture content of the extruded product is normally between 8%–10% on a wet basis and it must be reduced to 1%–2% to give the desired product crispness. Additional drying at temperatures up to 150°C for 4–6 min is used. Sometimes, the product is subsequently fried in oil to remove moisture and develop a desirable flavor. The product is then cooled and any fines removed prior to coating with flavors. This is achieved by first spraying the product with vegetable oil and then dusting with a variety of dry flavors and/or seasonings. Alternatively, the oils, flavors and seasonings may be mixed together and applied to the extruded product as it is tumbled in a flavor-application reel.

Puffed snack foods such as popcorn were originally made by placing grains of corn onto very hot plates. This caused the moisture in the grains to suddenly expand into steam, thus causing the grain to be puffed and simultaneously cooked. This method was refined by heating the grain in a quick-release but hermetically sealed cylinder where the sudden release of pressure caused the grain to puff or expand. A similar principle is used in extrusion. The efficiency of the process has been improved so that many cereals can now be puffed up to four to eight times their original size; these expanded original-texture grains are used in many snack products.

20.6.2.2 Indices of Failure

The major index of failure for extruded and puffed snacks is loss of crispness. The critical a_w for puffed corn curl has been reported as 0.36 which corresponds to a moisture content of 4.2 g H_2O per 100 g solids (Katz and Labuza, 1981). The initial a_w of this product was 0.082 with a corresponding moisture content of 1.83 g H_2O per 100 g solids. For popcorn, initial and critical a_ws were 0.062 and 0.49, with corresponding moisture contents of 1.70 and 6.1 g H_2O per 100 g solids. The sensory crispness intensity of popcorn as a function of a_w, with the critical a_w of 0.49 marked as a_c, is shown in Figure 20.5.

The critical a_w for extruded rice snacks has been reported to be 0.43, which corresponds to 6.5% moisture content (Chauhan and Bains, 1990). A report on the effects of a_w on the textural characteristics of puffed rice cakes indicated that rice cake lost its crispness and became tough as the a_w increased above 0.44, a critical point with respect to texture (Hsieh et al., 1990). Rice cakes with a_w between 0.23 and 0.44 were crisp and low in hardness. Data such as this is essential before selection of a suitable packaging material can be made.

The development of stale and/or oxidized and rancid flavors and odors can also be a problem limiting the shelf life of certain extruded and puffed snacks.

20.6.2.3 Packaging

Many extruded and puffed snack foods are packaged in an identical material to that discussed earlier for fried snack foods. However, because the major index of failure is loss of crispness, a package that provides a good barrier to water vapor is the primary requirement. Some extruded and puffed

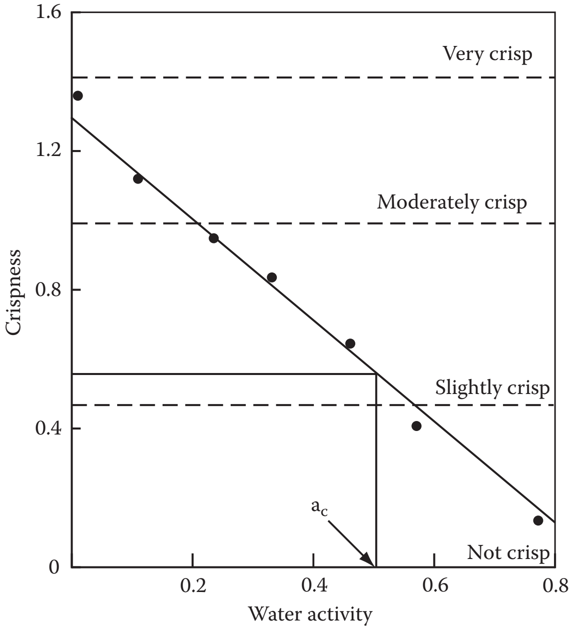

FIGURE 20.5 Sensory crispness intensity of popcorn as a function of water activity; the critical a_w of 0.49 is shown as a_c. (From Katz, E.E. and Labuza T.P., *J. Food Sci.*, 46, 403, 1981.)

snacks are comparatively less sensitive to O_2 than fried snack foods and the O_2 barrier requirements of the packages are consequently less stringent.

20.6.3 FRUIT-BASED SNACKS

A large variety of dried fruits, usually with added nuts and honey, sugar or syrup, are used in the manufacture of this type of snack food. Their composition is infinitely variable, leading to the development of bars with a wide variety of flavors and textures. Generally, these products are in the intermediate moisture category and have a_ws in the range of 0.20–0.40. This is because of their relatively high sugar content (25%–30%) mainly in the form of glucose, sucrose and fructose from several ingredients such as corn syrup, glucose syrup, sweetened condensed (evaporated) skim milk, raw cane sugar and invert sugar syrup.

Also in this category are snacks based largely on flaked cereals such as oat flakes or wheatflakes or puffed cereals such as rice, to which dried fruits, nuts and carob chips are also added to produce variations in flavor and texture. Again, many of these snacks have a chewy texture and an a_w which places them in the intermediate moisture category. The fat content of these chewy bars can be as high as 24%.

Packaging materials for these fruit-based snacks must provide a barrier to water vapor ingress to avoid the development of stickiness as a result of moisture uptake by the sugar in the product. In very dry atmospheres, moisture loss could be a problem. Before the packaging requirements can be specified with any degree of precision, the MSI for this type of product would be required.

20.7 CONFECTIONERY

20.7.1 SUGAR CONFECTIONERY (CANDY)

20.7.1.1 Manufacture

The words “candy” and “confectionery” are often used interchangeably to mean a sweet sugar- or chocolate-based snack or dessert food. Strictly defined, the word *candy* refers to products containing sugar as the dominant component and does not include chocolate products. *Confection* is a more general term referring to any sweet product manufactured from sugar and other ingredients. Products falling within the latter definition will be discussed in this section.

Confectionery has four major basic ingredients: sucrose, glucose, fructose and water. These can be combined with flavorings and colorings to make confections such as fondants and boiled sweets. When milk solids, fat, proteins and modified starches are added as well, products such as jellies, pastilles, toffees and caramels can be produced. The primary difference between the various confectionery products is in the amounts and types of sugars and in the amount of water. In one group (which includes the hard candies and soft, chewy products), uncrystallized sugars are present in a very viscous solution, which is handled like a solid at room temperature. In the other group (which includes fondant crèmes and other crystallized or grained products), sucrose is present in crystalline form, usually as microscopic crystals dispersed in syrup.

Sugars impart the texture necessary to distinguish one confection from another and to provide a unique experience to the consumer. Whether found as crystal, glass or fluid solution, the key to making high quality candy is understanding and controlling the transitions of sugar (Hartel et al., 2011). During processing, sugars in confectionery formulations typically go through one or more phase transitions, depending on the nature of the product. Changes in phase behavior may also occur during storage, usually with a negative effect on shelf life. The physical state of the sweetener can have a critical influence on the attributes of the confection; that is, crystals affect both appearance and textural properties.

Hard candies (also known as *boiled sweets*) are made almost entirely of sugar, typically combinations of sucrose, glucose and fructose. The mixture of sugars is heated under vacuum to reduce the moisture content to about 1%, after which flavors, colors and acid (normally citric) are mixed in, and the plastic mass formed into the desired shape. After cooling to set, the sweets are packaged as rapidly as possible, preferably while still warm.

Toffees and caramels are made by boiling sucrose, glucose syrup, condensed milk, vegetable fats and salt. Other ingredients may include cream, butter and various flavorings, although the inherent flavor is due to the Maillard nonenzymic browning reaction between reducing sugars and milk proteins (Jackson, 1995). After cooling to about 45°C–50°C, the toffee is cut and packaged. Because caramel is a dispersion of fat globules in a high solids, highly supersaturated, viscous sugar matrix that cannot crystallize, all the component sucrose molecules, rather than just those in the syrup phase, influence the a_w.

Confections such as fondant and fudge are composed of sucrose in the form of crystals suspended in a saturated sugar solution. A typical composition of base fondant is about 75% sucrose, 15% glucose and 10% water. The mixture is boiled at 120°C and cooled rapidly to about 50°C when it is subjected to violent agitation to cause rapid nucleation and crystallization. Fudge is basically a toffee or caramel with a high sugar content, which has been deliberately crystallized during processing. Typically, caramel is cooked to about 120°C, cooled to about 50°C and then fondant added to initiate crystallization; it is then cooled to allow crystallization to occur (Edwards, 2000).

The solid crystals in fondant and fudge have no effect on a_w, and the phases are stable provided that the system is protected from atmospheric moisture by suitable packaging materials. The a_w of the syrup phase is related to both its composition and to any water loss or gain that may have occurred; a_ws of 0.78 and 0.65 having been quoted for fondant and fudge, respectively (Nelson, 1995).

20.7.1.2 Indices of Failure

An important difference in the indices of failure between the various candies is that crystallized products tend to dry out under normal storage conditions, while uncrystallized products tend to pick up moisture from the atmosphere. The a_ws of various types of sugar confectionery is presented in Table 20.5. Although not the only mode of failure, moisture migration is arguably the major determinant of the end of acceptable shelf life for many confections (Ergun et al., 2010). Thus, shelf life testing in confections often evaluates changes in physicochemical properties related to moisture changes.

TABLE 20.5
Water Activities of Various Kinds of Confectionery

Type of Product	Average a_w	Usual Limits
Boiled sweets	0.28	<0.30
Toffee	0.47	<0.48
Caramels	0.50	0.45–0.55
Nougat	0.55	0.50–0.60
Gums and pastilles	0.60	0.51–0.64
Liquorice	0.64	0.53–0.66
Fruit jellies	0.65	0.60–0.70
Fudge	0.65	0.60–0.70
Turkish delight	0.66	0.60–0.70
Marshmallow	0.72	0.63–0.73
Fondant	0.78	0.75–0.84

Source: Adapted from Nelson, C., Wrapping, packaging and shelf life evaluation, in: *Sugar Confectionary Manufacture*, 2nd edn., Jackson, E.B. (Ed.), Blackie Academic & Professional, London, U.K., pp. 353–367, 1995.

One of the major defects in hard candy confections is *graining*, or sugar recrystallization. Hard candies are a metastable sugar glass and graining during storage can occur for two reasons. First, if crystals are already present within the glassy matrix (formed during manufacturing), they will start to grow if the temperature increases above T_g. This form of graining is called internal graining. Second, a hard candy can begin to grain when sufficient moisture is adsorbed by the surface to increase molecular mobility to the point where nucleation can occur. As moisture penetrates into the candy, a syrup layer forms at the surface with a reduced T_g due to the higher water content. This form of graining is called external graining. Continued graining occurs as the layer slowly proceeds into the center of the confection. In both internal and external graining, flavor molecules more readily diffuse out of the candy causing a decrease in flavor. Also, the rearrangement of color molecules causes a change in appearance and texture of the candy as graining proceeds (Hartel et al., 2011). If the candies are not individually wrapped, they may stick together as a result of external graining.

Fondants generally have an a_w that is higher than the humidity of the surrounding atmosphere and thus they tend to dry out. This results in increased crystallization. One significant change arising from the loss of moisture is a decrease in volume. If the fondant is coated with chocolate, then this volume decrease causes either collapse of the coating or an air space inside the coating. Both consequences are undesirable, and although a collapsed coating is more apparent, an air space can permit condensation of moisture which leads to a localized area of high a_w where microbial growth could occur.

Two types of flavor changes can occur in confectionery: loss of desired flavor components and development of off-flavors. Packaging has an important role to play in preventing loss of desirable flavors from the product and providing a barrier to the entry of O_2 which can oxidize flavors.

Many confections, notably the hard candies, are brightly colored and therefore color stability is important. The main cause of color fading during storage is bleaching by light. Use of a package which is a complete barrier to light is generally undesirable because the attractiveness of brightly colored confectionery is an important selling point. The use of synthetic, light-stable colors in hard candies is widespread.

20.7.1.3 Packaging

The type of packaging required to protect the confection from moisture uptake will depend on the a_w of the confection and the RH of the ambient atmosphere. The packaging type will also depend on whether or not the confection deteriorates by gain or loss of moisture under these conditions.

It has been customary to wrap boiled sweets, toffees and caramels individually, partly as a hygienic measure, partly to protect them from atmospheric moisture, partly to prevent them from sticking together and partly to avoid the intermingling of the flavors of assortments. Since the wrapping machines operate at very high speeds, the mechanical and electrostatic properties also govern to a high degree the choice of packaging materials to be used (Hooper, 1999). Both ends of the wrapper sleeve are twisted to effect a closure.

Fibrous materials are generally unsuitable since they promote adhesion of the wrapper to the sweet. Materials such as waxed paper, waxed glassine and waterproof, plasticized RCF have been used successfully for many years but the use of cast PP (which holds the twist better than RCF) is now widespread. Although these materials offer some barrier to water vapor, they provide little protection in this situation because the overlap is not sealed. Thus, an outer package that provides a barrier to moisture is required, and this is usually a heat sealed bag made from coated RCF or a polyolefin, although metal containers, glass jars and foil or metallized laminates are also used. In some situations, cartons made from paperboard are used. The board may be coated with LDPE, or the carton may have a plain or waxed glassine liner or one made from thin gauge HDPE.

20.7.2 CHOCOLATE

20.7.2.1 Manufacture

Chocolate is a suspension of finely ground, roasted cocoa beans or cocoa mass and sugar particles in cocoa butter (the lipid fraction of the cocoa mass). Milk chocolate is similar but with the addition of whole milk powder. Cocoa beans are roasted to develop flavor and then ground to liberate some fat. Other ingredients are mixed in and the particles further reduced in size to a maximum of about 30 μm. The final stage is *conching*—agitation under heat (75°C–80°C for plain and 50°C–60°C for milk chocolate) to remove water and unwanted volatile substances, improve flavor and texture and reduce viscosity. During this process, an enormous increase in surface area of the solid particles occurs, and the resulting chocolate mass becomes quite dry. The sugar particles are not easily wetted by the cocoa butter and, although small, are compacted into aggregates (Beckett, 2009).

Although cocoa butter can crystallize in a number of polymorphic forms, only one such form (β or form V) is stable. Chocolate is tempered by heating to 50°C to remove all crystal nuclei and then cooled gradually to about 27°C where crystallization commences. The temperature is then raised to 32°C when only a finely dispersed seed crystal of form V remains. The chocolate is then cooled at a controlled rate when stable crystals form and the surface of the chocolate takes on a good gloss (Bralsford and Le Fort, 1990).

20.7.2.2 Indices of Failure

The amount of liquid fat present in chocolate is significant, not only in determining the sensory (particularly textural) quality, but also in influencing the shelf life of chocolate products (Subramaniam, 2011). The melting characteristic of cocoa butter between 30°C and 35°C is responsible for the fast meltdown of chocolate in the mouth. The solid fat content of cocoa butter decreases from 76% at 25°C to 1% at 35°C and zero at 40°C, making chocolate very sensitive to temperature. If melting and subsequent solidification occur, then the surface texture becomes rough. If the temperature oscillates just below the melting point, then fat will move from the body of the chocolate to the surface, giving rise to a defect known as *fat bloom*: the shiny surface turns dull and, later on, a grayish-white layer starts to develop (Nöbel et al., 2009). Bloom can also arise as a result of using fats in chocolate that are incompatible with cocoa butter and from insufficient tempering during chocolate processing. Storing chocolate below 18°C will prevent bloom from occurring. Generally, there is little that can be done by packaging to prevent such defects occurring.

Sugar bloom is another defect that affects the appearance of chocolate. Although on cursory examination it appears similar to fat bloom, sugar bloom consists of a layer of sugar crystals on the surface. It is caused by exposing the surface of chocolate to air of high humidity and/or by the use of refined sugar having a high moisture content.

Oxidative and lipolytic rancidity are flavor defects, the former coming from oxidation of unsaturated fats and the latter from enzymic hydrolysis of short- and medium-chain triglycerides. Cocoa butter contains tocopherols (liposoluble vitamin E compounds), which act as antioxidants and therefore confer a natural protection against oxidation during storage.

Being high in fat, chocolate is very likely to absorb any foreign odors from the surrounding atmosphere unless adequately protected by suitable packaging materials.

Chocolate is sold in many forms where the product often contains not only chocolate but also other ingredients such as fruits, nuts and caramel which influence the likelihood of different storage defects occurring.

20.7.2.3 Packaging

Suitable packaging for chocolate must provide a good barrier to light, O_2, water vapor and foreign odors (Mohas, 2010). The most common material used to package blocks of chocolate used to be unsealed aluminum foil of 0.009 mm thickness. At this thickness it exhibits “dead wrap” characteristics (i.e., it takes on the shape of the product around which it is placed). No sealing was possible but folding and overlapping of the foil provided adequate protection when covered with a thin, printed paperboard sleeve. In warmer climates, a layer of waxed tissue paper was placed inside the foil to prevent fat staining of the outer package; it was also claimed to offer protection against odor penetration (Minifie, 1999).

It is now more common to package chocolate blocks in a laminate consisting of aluminum foil and LDPE, making it possible to heat seal the package. Such a package is a better water vapor and odor barrier than the foil and the foil-paper packages. Such packages sometimes contain a layer of paper, either between the foil and the LDPE or on the outside of the foil when the latter is laminated directly to the LDPE. In some packages, the foil is replaced by PVdC copolymer, the latter being applied as a thin coating on the LDPE.

Traditionally, almonds and peanuts have been used in confectionery products such as chocolate in the United States, while hazelnuts are more common in Europe. Recently, Mexis et al. (2010) showed that dark chocolate with hazelnuts packaged with an O_2 absorber in a barrier packaging material maintained its aroma, taste and nutritional quality substantially longer than other packaging methods. Chocolate was packaged in either PET-LDPE or SiO_x-coated PET-LDPE under vacuum or N_2 or with an O_2 absorber, and stored in the dark at 20°C for 12 months. “Commercial” control samples for comparison purposes consisted of chocolate packaged in aluminum foil in air while “model” control samples used for sensory evaluation consisted of chocolate packaged in glass jars and stored at −18°C. The chocolate with hazelnuts retained acceptable quality for ~8 months in commercial packages. For samples packaged in PET-LDPE, irrespective of the storage atmosphere, the shelf life was 8–9 months, and for samples packaged in SiO_x-coated PET-LDPE, the shelf life was 11 months, irrespective of storage atmosphere. Finally, for samples packaged with an O_2 absorber, the shelf life was at least 12 months irrespective of packaging material.

Chocolate-coated confectionery such as coated caramel bars are typically packaged in pearlized OPP which is cold sealed longitudinally and at each end; cold sealants avoid the risk of melting the chocolate during the sealing operation.

Packages of individual chocolates are frequently purchased for gifts and special occasions, and this is reflected in the sometimes very elaborate packaging which is used. Thermoformed PVC, HIPS or PET trays with individual cavities for each piece are common, with many of the individual chocolates being wrapped in colored, thin gauge, aluminum foil. Recently, trays made from thermoplastic starch have been used. The trays are placed inside paperboard boxes and overwrapped with RCF or polyolefin film. Sometimes, metal or glass containers are used, which provide an excellent barrier to moisture (Jones, 2009).

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21 Packaging of Beverages

21.1 INTRODUCTION

Beverages are an important part of the diet of all humans and have been since the earliest times. Although the origins of many beverages are unknown, there is no doubt that the range and sophistication of beverages have increased dramatically over recent decades. Much of this growth can be attributed to developments in packaging, which have made it possible for a large national and international trade in beverages to flourish. Today, a wide variety of quite different beverages are consumed in the home, at work and at a myriad of sporting, leisure and entertainment activities, and the full range of packaging media is used (either alone or in varying combinations) to bring these beverages to consumers. This chapter discusses the major categories of beverages, including their manufacture, indices of failure and packaging.

21.2 WATER

21.2.1 INTRODUCTION

In Europe and China, spring and mineral waters have been consumed for centuries by local inhabitants, immigrants and invaders. For example, Evian natural mineral water began its present-day history in 1789 when a French marquis began bottling the "miraculous" waters on his estate bordering Lake Geneva (Lac Léman). Similarly, Perrier water was first bottled as Perrier sparkling mineral water in 1863 (Warburton and Austin, 2000). The very concept of "mineral water" was first defined in Germany in 1911 as water containing at least 1000 mg L^{-1} of dissolved mineral constituents. Over the next 80 years or so, this definition was changed many times, resulting in waters with a lower mineral content also being labeled "mineral." By 1990, the acceptable level had fallen to 200 mg L^{-1} and the market became flooded with pseudo-mineral waters (Diduch et al., 2011). In the United States, if the total dissolved solids content of mineral water is less than 500 ppm or greater than 1500 ppm, the information "low mineral content" or "high mineral content," respectively, must appear on the label (21 *CFR* § 165.110 (a)(3)).

Bottled water is now widely available for sale, and its consumption has risen dramatically over the past 20 years, particularly in countries where clean, potable tap water is available at very low or no cost. The growth in bottled water is influenced by three public concerns or fears: a declining quality from often overworked municipal water supplies, possible toxic contamination of groundwater sources and a general increased interest in personal health. It has also become a "must have" fashion accessory for many consumers. There is a public perception that bottled water is safe, natural and free from additives such as fluoride and chlorine. According to Wilk (2006), the contrast between tap water and bottled water can be seen as a reflection of a contest for authority and public trust between governments and corporations, in a context of heightened anxieties about risk and health. In his view, bottled water is a case where sound cultural logic leads to environmentally destructive behavior. In fact, the U.S. Federal Food, Drug and Cosmetic Act (FDCA) provides that FDA's standards for bottled water must be at least as stringent and qualitative as EPA's standards for public water systems; thus, the maximum contaminant levels for bottled water are very similar to those for tap water (Tarver, 2008).

Bottled water can be divided into nonsparkling or still, and sparkling. It can also be divided into either natural or processed categories, where natural water is bottled directly from underground sources while processed water is tap or well water that is highly filtered or distilled.

Natural bottled waters are sold with the understanding (and in Europe, the legal requirement) that they have not been subjected to any treatment that would remove natural indigenous bacteria, which are believed to have medicinal and therapeutic qualities. It has never been proven that the ingested levels of indigenous microorganisms in bottled water have an adverse effect on health. Despite this, much controversy surrounds the question of the potential pathogenicity of indigenous microorganisms in mineral waters (Warburton, 2002).

Bottled water is defined by the U.S. FDA as water that is intended for human consumption and that is sealed in bottles or other containers with no added ingredients, except that it may optionally contain safe and suitable antimicrobial agents; fluoride may optionally be added within FDA-specified limits (21 *CFR* § 165.110). However, antimicrobial agents are not permitted in many other countries, and in those countries, particularly within the EU, the term “natural mineral water” carries a requirement that the water source must meet certain stringent criteria (see Council Directive 80/777/EC). In particular, it must be free from pathogenic organisms such as fecal coliforms, fecal streptococci and staphylococcal organisms as well as parasites such as *Giardia* and *Cryptosporidium*.

The water may be subjected to a number of treatments including distillation, carbonation, ozonation, chlorination, filtration and so on, depending on the quality of the source water, the type of bottled water being manufactured, where it is being manufactured and local legislation (Senior and Dege, 2011).

21.2.2 INDICES OF FAILURE

The major index of failure in bottled water is microbial growth. The source of water is never sterile and contains sufficient trace nutrients for microbial growth. Various saprophytic bacteria, yeasts and molds are commonly found in water, which may also be contaminated with pathogenic bacteria and parasites (Hocking and Jensen, 2001). In addition, water may become contaminated during transport and processing, with bottles and closures also being possible sources of contamination.

Where legislation permits, water may be treated prior to bottling with chlorine or ozone, the latter being preferred since it is much faster acting than the former. In the EU, assuming that natural mineral water is free from pathogens, the presence of other microorganisms that arise from the environment from which the water is taken is accepted as a normal part of its composition (Ashurst, 2010). These environmental organisms are those characterized by growth in media at 20°C –22°C, although many bacterial species occurring naturally in groundwater will grow over a much wider temperature range. The presence of such flora has given rise to a wide range of questions and debates about effects on health, primarily because the flora is not particularly well characterized. However, since no disinfection that modifies or eliminates the biological constituents of water is permitted, the bacteria must be regarded as natural components in exactly the same way as their chemical counterparts.

The most obvious manifestation of spoilage in bottled water is the appearance of floating pieces of mold mycelium, with *Penicillium* species, together with *Cladosporium* and *Phaeoramularia,* being the most commonly isolated fungi (Hocking and Jensen, 2001). *Pseudomonas aeruginosa*, an organism associated with soil contaminated with human and animal feces, is not generally associated with spoilage of bottled water, but its presence can affect water color, clarity and taste. It is capable of growth to high numbers in minimal nutrient environments such as deionized and demineralized water and has been implicated in food- and waterborne diseases. Most *P. aeruginosa* strains are resistant to commonly used antibiotics and sanitizers/disinfectants but should be inactivated by pasteurization. It has been isolated from bottled waters from Brazil, Canada, France, Germany, Indonesia, Spain and the United States (Hocking and Jensen, 2001).

In non-carbonated water, the numbers of bacteria are known to increase rapidly after bottling. An example given by Ashurst (2010) for natural mineral water showed a level of colony counts of water emerging from the spring as about 1–4 cfu mL^{-1}, and immediately after bottling, the numbers were only slightly higher. During storage at 20°C, bacterial populations increased to reach a peak of more than 10^5 cfu mL^{-1} by the end of 1 week. During the next 4 weeks, bacterial populations then slowly declined or remained fairly constant. At the end of a 2-year storage period, colony counts were still likely to be of the order of 10^3 cfu mL^{-1}.

Solar water disinfection (SODIS) is an effective, simple, household level, point-of-use technology suitable for application in developing countries (Muriner and Kraemer, 2008). Contaminated water is placed in a PET bottle, capped and then exposed to sunlight for at least 6 h. Laboratory and field trials have demonstrated SODIS to be effective against a wide range of waterborne pathogens, with health impact assessments demonstrating significant benefits from consumption of SODIS-treated water. The unavailability of PET bottles has been identified as a potential hindrance to the successful implementation of SODIS.

Biofilm proliferation has been reported on the walls of PVC containers and may be partly responsible for the long-term survival of bacteria in bottled water; several authors have found higher counts and faster growth in bottled water stored in plastic bottles than in glass bottles (Warburton, 2002).

The use of returnable containers for bottled water is common in many countries. Only a limited number of studies have been performed on the contamination risk by microorganisms when classical caustic cleaning is applied to rinse returnable containers. It has been found that under optimal conditions, the following classification could be made in decreasing order of microbial rinsability: glass > PET > PC > PP = PVC > HDPE. Even at optimal rinsing conditions, it was not possible to totally remove all bacteria from the sides of the containers, leading to the recommendation that bottled water should be disinfected by ozonation (Warburton and Austin, 2000).

The presence of dissolved O_2 in many non-carbonated waters is a major contributor to the desirable taste and mouth feel of the water. Loss of much of this dissolved O_2 leads to the water being judged unacceptable by consumers. A further deterioration in bottled water has been the development of a "plastic" taste, which is sometimes found in water which has been packaged in unsuitable plastic containers (Senior and Dege, 2011).

21.2.3 PACKAGING

Glass bottles were long considered the container of choice for sparkling waters and carbonated soft drinks (see Section 21.3.3.1), but, in recent years, PET bottles have gained an increasing share of this sector. The majority of still waters and many sparkling waters are now packaged in plastic containers, and PET is the principal resin with PC being used for large, refillable containers, typically of 11, 19 and 22 L capacity.

Recently, a model of the shelf life of sparkling water packed in PET bottles was proposed using computational fluid dynamics (CFD) and validated by Carrieri et al. (2012). The model considered the bottle weight and storage temperature as variables. The decrease in carbonation (initial values of 4.8–5.4 g L^{-1}) did not appear to depend on bottle weight, although diffusive non-uniformity was observed depending on PET bottle wall thickness variation. The importance of storage at low temperature was confirmed, as the diffusion of gas through PET is accelerated by temperature: the loss at 40°C was 83% higher than at 10°C. This model could be used as a design and verification tool for predicting shelf life in any carbonated beverage, and the results employed to rapidly establish the "best used by" date.

Water packed in PET is normally regarded as being free from taints. The major significant volatile compound in PET is acetaldehyde (AA) which is present as a thermal degradation product formed during the melt condensation reaction and melt processing of PET. AA possesses a distinct odor and taste, generally described as sweet, plastic-like and fruity, and has a low sensory detection threshold that ranges from 20 to 40 ppt. Present manufacturing techniques have dramatically reduced residual AA levels in PET packaging to <1 ppm. AA scavengers are available to reduce AA formation in PET packaging by up to 80%; anthranilamide is particularly preferred because of its low cost, efficiency and ease of incorporation into PET (Bach et al., 2012).

Matsuga et al. (2006) analyzed commercial samples of water bottled in PET from Japan, Europe and North America and showed that AA and formaldehyde (FA) migrated into water from PET bottles. Concentrations of AA ranged from 5.0 to 25.7 ppb and for FA from <0.5 to 3.0 ppb. In commercial water without bacteria, the levels of FA and AA remained unchanged, whereas in natural mineral water containing heterotrophic bacteria, the FA and AA were decomposed. Of the carbonated water samples, one contained bacteria and showed a reduction in FA and AA, while the others had no bacteria and showed no decomposition activity. It was speculated that the existence of bacteria influenced the concentration of carbonate gas.

Antimony trioxide (Sb_2O_3) is used as an additive and initiator in the manufacture of 90% of the PET manufactured worldwide, at a maximum level of 0.035% as Sb. Welle and Franz (2011) reported a mean value of 224 ± 32 ppm Sb in 67 PET bottles from the European market. Although Sb is a potentially toxic trace element with no known physiological function, only a small fraction of the Sb contained in PET bottles migrates into water. Shotyk et al. (2006) reported that 12 brands of bottled natural waters from Canada contained 156 ± 86 ppt Sb, and 3 brands of deionized water contained 162 ± 30 ppt Sb. Comparison of three German brands of water available in both glass bottles and PET containers showed that waters bottled in PET contained up to 30 times more Sb, with a range of 253–546 ppt Sb. One German brand of water in PET bottles had 626 ± 15 ppt Sb 6 months after bottling. The median concentration of Sb in 35 brands of water bottled in PET from 11 other European countries was 343 ppt. All of the waters found to contain Sb were at concentrations well below the guidelines commonly recommended for drinking water, which are as follows: World Health Organization 20 ppb, U.S. EPA and Health Canada 6 ppb, German Federal Ministry of Environment 5 ppb and Japan 2 ppb. The EU SML for Sb is 40 ppb. Cheng et al. (2010) reported Sb leaching into water packed in PET bottles after various treatments that included cooling with frozen water, heating with boiling water, microwaving, incubating with low pH water, outdoor sunlight irradiation and in-car storage. Concentrations after heating and microwaving exceeded 6 ppb.

Genotoxic and estrogenic activities in water bottled in PET have been reported, and these are discussed in Section 22.3.4.1.

21.3 CARBONATED SOFT DRINKS

21.3.1 Manufacture

Traditionally, soft drinks were prepared by dissolving granulated sugar in specially treated water or, alternatively, by diluting liquid sugar with this water. A variety of ingredients including flavoring and coloring agents, acidulants (invariably either citric or phosphoric acid) and preservatives were then added. Other constituents such as fruit juice or comminuted fruit, bodying agents, artificial sweeteners, clouding agents, antioxidants and foaming agents were added, depending on the particular product being made. Recently, "diet" soft drinks in which the sugar has been replaced with an artificial sweetener (typically aspartame) have become very popular.

Soft drinks are now prepared almost exclusively using the premix system whereby the blended syrup, after flash pasteurization if necessary, is mixed with carbonated, treated water prior to delivery to the filler. Although traditionally the product has been cooled to 1°C–3°C before arrival at the filler in order to minimize loss of carbonation and facilitate filling, fillers and ancillary equipment capable of handling the product at ambient temperatures have been introduced.

The degree of carbonation of soft drinks is typically expressed in volumes or g L^{-1} of CO_2. One volume equals approximately 2 g L^{-1}, and at room temperature, each volume produces about 1 atm (101 kPa) of internal pressure. Temperature has a significant effect on internal pressure, with a 4 volume beverage such as a cola rising to 7 atm at 38°C and to 10 atm at maximum storage/pasteurization temperatures (Griff, 2009). The carbonation level of beverages ranges from 1.5 volumes for citrus and other fruit-based soft drinks to 4 volumes for common cola drinks and 5 volumes for club soda and ginger ale.

21.3.2 INDICES OF FAILURE

The three major indices of failure in carbonated beverages are loss of carbonation, oxidation and/or acid hydrolysis of the essential flavor oils and colorings and loss of color and undesirable changes in flavor caused by light. Loss of carbonation is largely a function of the effectiveness of the package in providing a barrier to gas permeation, while oxidation can be largely prevented by the use of high-quality flavorings and antioxidants, deaerating the mix prior to carbonation and minimizing exposure of the product to light. Colorings of both natural and artificial origin may be affected by O_2, and the usual result is a bleaching effect. Many manufacturers add ascorbic acid to act as an O_2 scavenger (Ashurst, 2010).

21.3.3 PACKAGING

21.3.3.1 Glass

From the beginning of the twentieth century, virtually all carbonated soft drinks were packaged in refillable glass bottles, which were sealed with crown cork closures (see Section 10.1.3.1.1). In recent years, nonreturnable glass bottles have replaced refillable glass bottles in many markets. These sometimes have a foam plastic protective label or a paper-polyolefin or all-plastic shrink sleeve, in part as a safety measure to prevent flying glass fragments should the bottle break (see Section 9 5.4 for more details). The crown cork closure has been largely replaced with a roll-on aluminum screw cap on threaded necks with a tamper-evident ring, or a plastic closure (typically PP with or without a liner), which fits and unscrews over the same threads as the roll-on and provides some visible indication of tampering.

21.3.3.2 Metal

Three-piece tinplate containers were used for many years for the packaging of carbonated beverages. The highly corrosive nature of carbonated soft drinks demanded complete protection of the metal container from the product by the use of one or more coatings of an impermeable enamel system. For three-piece cans, this involved spraying an additional coating of enamel (a process known as *sidestriping*) over the inside of the container down the sideseam area after welding. Control of iron migration is critical, because extremely small levels of iron (0.5 ppm) can compromise the flavor of the beverage. One study on the influence of two different compound systems applied during the end seaming operation (can closing) on the iron pickup from tinplate cans after storage with a cola soft drink for 180 days at 37°C found levels between 0.15 and 1.0 ppm depending on the compound/enamel combination (Bernardo et al., 2005).

Today, most carbonated beverages are packaged in two-piece containers usually made from aluminum. The two-piece container has made it much easier to retain the integrity of the enamel layer inside the can and thus minimize corrosion during storage. The cans must be able to withstand continual internal pressure of up to 5 atm.

Metal cans for beverages have an easy-open end consisting of a scored portion in the end panel and a levering tab (formed separately) that is riveted into a bubble-like structure fabricated during pressing. The aluminum alloy used to manufacture easy-open ends for beverage cans is specially developed to give the required mechanical properties but is subject to environmental stress cracking (ESC) corrosion due to reaction with moisture. The score area is particularly susceptible because of the tensile stress to which this part of the end is subjected (Page, 2006).

Container lightweighting and design have been the subject of much development work, and quadruple necking is now standard on many aluminum beverage cans. This has resulted in cost savings in the reduced aluminum required for the end, and smaller overall pack area as well as reduced weight. The introduction of a single-stage process of spin-necking has resulted in a smooth, conical-shaped top section.

21.3.3.3 Plastics

As early as the 1960s, the Coca-Cola™ and Pepsi-Cola™ companies were seriously considering the use of plastic bottles for soft drinks, and they began to develop their ideas with major polymer manufacturers in the United States. It soon became apparent that only the polyester and nitrile families of plastics had the necessary physical and chemical characteristics required. Because the nitrile plastics could be made into bottles using existing blow molding equipment, while PET could not because of its inclination to crystallize and go hazy at higher temperatures, early market development work in the 1970s was carried out with nitrile bottles. Coca-Cola successfully launched a 950 mL nitrile bottle in 1975, but the release in 1977 of toxicological data showing that AN monomer could be carcinogenic at high dosage led to the removal of the nitrile bottle from the market (Turtle, 1984).

Meanwhile, attempts to successfully manufacture PET bottles using a stretch blow molding process were continuing. In the spring of 1977, the plastic PET bottle for soft drinks was launched by Pepsi-Cola, followed later by Coca-Cola and other beverage producers. It has been described as probably the biggest single development in the soft drinks industry since the introduction of the ring-pull can a decade earlier (Turtle, 1984). Today, the greatest volume of soft drinks is packaged in PET bottles which have achieved their market share mainly at the expense of glass, albeit in an enlarged total market. The early designs had a round base which necessitated a flat base cup, usually injection molded from high density polyethylene (HDPE) and fixed to the bottle with hot-melt adhesives. The increase of PET recycling schemes accelerated the introduction of the petalloid base, thus obviating the need for a base cup. Although more material is required for a petalloid base, separation of the base cap is not required prior to recycling of the PET bottle.

Stress cracking of PET bottles filled with carbonated soft drinks is a complex process that is influenced by a large number of variables, including climate, chemistry, polymer quality and bottle engineering design. There is a growing awareness that "alkalinity," including naturally occurring water alkalinity, is connected to stress crack failure of PET bottles (see Section 2.3.6.4.1).

The continuing trend for larger and larger containers of soft drink has helped penetration of the PET bottle. The 1 L glass bottle is considered to be near the limit of size and weight, above which it becomes difficult to handle easily, particularly by children. In contrast, PET bottles up to 5 L in size are now available, resulting in considerable savings in container cost per unit volume. In addition, the larger the bottle, the more CO_2 is retained per unit of time because of a smaller surface area:volume ratio (i.e., a reduced area for permeation).

The factors that influence the taste and odor of carbonated beverages packaged in plastic containers are depicted schematically in Figure 21.1. Most of these factors are applicable to many other foods or beverages packaged in plastic containers. Although O_2 pickup is a very critical item with beer, soft drinks are much less sensitive and a maximum ingress of 20 ppm for citrus-flavored soft drinks and 40 ppm for cola drinks has been suggested, together with a limit for water loss of 1%, the latter based primarily on maintaining labeled contents. The criteria for flavor absorption and permeation losses are necessarily general because of the great variety of flavorants and wide differences in sensory effects.

Compared to glass, there is a loss of CO_2 through the bottle walls which must be allowed for. While increasing the wall thickness will decrease the rate of CO_2 transmission, this will also increase the cost of the bottle, and so a compromise has been sought. In addition, PET (like most thermoplastics) exhibits the phenomenon of creep, and this occurs to the greatest extent in the first few days after the bottles have been filled. In addition, there will be an elastic deformation which,

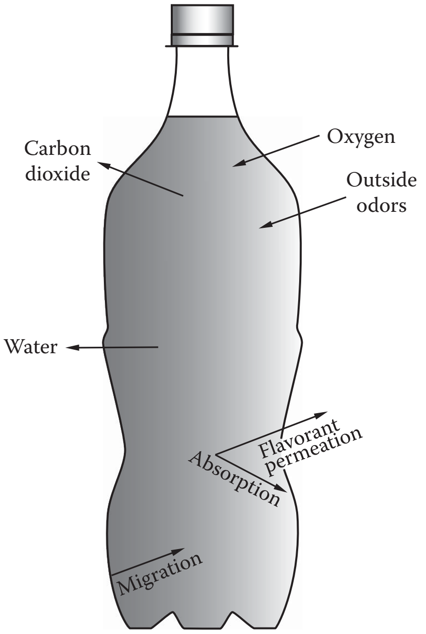

FIGURE 21.1 Factors influencing taste and odor of carbonated beverages packaged in plastic containers.

unlike the creep effect, will not be permanent but will disappear when the bottle is opened and the internal pressure is released. In combination, both these effects will produce an increase of about 2.5% in the volume of the bottle over the first 3–4 days after filling, given normal storage conditions.

A typical carbonation loss for 2L containers shows an initial loss of about 0.3 volumes in 3–4 days from the initial 4 volume figure, owing to the volume increase and absorption of CO_2 by the container wall. Thereafter, the rate of CO_2 loss becomes steady at about 0.04 volumes per week, giving a carbonation value around 3.4 after 12 weeks. The maximum shelf life for a 1.5–2L bottle is around 16–17 weeks by which time the carbonation will have dropped to a still acceptable level of 3.1–3.2 volumes (Turtle, 1984).

The PET bottle is usually fitted with either a standard aluminum roll-on closure or a pre-threaded plastic cap, both either in the standard or pilfer-proof form. The cap is ideal for use with PET bottles because its main sealing surface is on the inside bore of the neck finish, and this is very precisely controlled with regard to diameter and smooth surface finish during injection molding and has almost nil ovality (Turtle, 1984).

21.4 COFFEE

21.4.1 MANUFACTURE

The fruit (called a *cherry*) from trees of the genus *Coffea* (the two most important species are *C. arabica* and *C. robusta*) is a small pod that contains two coffee beans. The outer skin and pulp layers are removed using one of two processes: a "dry" method where the cherries are dried and then passed through a hulling machine, which removes the outer skin, dry fruit and parchment; and a "wet" method in which the beans are softened in water, depulped mechanically, fermented in large tanks to remove a mucilaginous parchment layer which encases the beans and then dried. Milling removes the parchment shell, leaving a gray-green colored bean.

Three operations are needed to convert green coffee beans into a consumable beverage—roasting, grinding and brewing. Roasting develops the characteristic flavor and headspace aroma of coffee, while grinding is necessary so that both the soluble solids and volatile flavor substances can be sufficiently extracted by infusion or brewing with hot water to provide a beverage of required strength, either for immediate consumption or an extract for subsequent drying to make instant coffee.

Roasting of coffee beans involves rapid heating to raise the bean temperature to about 180°C. Roasting is normally carried out under atmospheric conditions with hot combustion gases and excess air and results in both chemical and physical changes in the green beans (Eggers and Pietsch, 2001). The chemical changes give rise to the characteristic flavor and aroma of roasted coffee, and, in addition, CO_2 is formed from decomposition of carbohydrates and other chemical reactions including the Maillard nonenzymic browning reaction. These latter processes have important implications for the packaging stage. The roasted whole beans may be packaged directly or else ground first prior to packaging. To maximize the retention of flavor volatiles within the roasted and ground coffee, cryogenic grinding (i.e., at sub-zero temperatures with the use of CO_2 or liquid N_2) is recommended.

The bulk density of ground coffee is assessed in two ways—free fall or packed measurement. Values will differ according to the blend, degree of roasting (decreasing with increasing severity), degree of grinding (increasing with increasing fineness) and moisture content. A fine grind coffee may have a bulk density of 0.39–0.47 g mL^{-1} in free fall (Clarke, 1987). Bulk density is clearly of importance from a packaging point of view, because coffee is sold by weight, and if the bulk density varies, the headspace in the package will also vary.

Instant coffee is produced by extracting both soluble solids and volatile aroma/flavor compounds from roasted and ground coffee beans with water. Extracts of around 25% w/w soluble solids concentration are obtained, and these extracts are further concentrated using evaporation or freeze concentration and then dried using either spray drying or freeze drying. The latter is more common and is typically followed by agglomeration to produce granules of around 1400 µm on average. The agglomerates are then dried in a fluidized bed to the desired final moisture content. Freeze-dried coffee has a longer shelf life than spray-dried coffee, although the reason for this difference is not clear.

21.4.2 INDICES OF FAILURE

The major index of failure for coffee is staling, defined as “a sweet but unpleasant flavor and aroma of roasted coffee which reflects the oxidation of many of the pleasant volatiles and the loss of others” (Buffo et al., 2004). The aroma degeneration during staling has been described as changing from flat to old to sharply rancid, with a cocoa odor appearing in the advanced stage. Concurrently, the taste of the coffee changes from flat to bitter, old and rancid, at which stage it should no longer be sold. The extent of staling is increased by increased moisture content and storing at higher temperatures.

O_2 is believed to be absorbed by roast and ground coffee which provides a reservoir for O_2 to cause subsequent deterioration. It has been observed that in the vacuum packing of roasted coffee, the in-package O_2 value may in fact rise after several days as a result of desorption into the vacuum space, followed by its fall again during storage. There is little information on the precise relationship between the in-package percentage O_2 content and stability for roast whole beans (RWB) (Clarke, 1987). However, for roast and ground (R&G) coffee, there is some evidence of a linear correlation between the logarithm of the O_2 content and the time to end of shelf life for a constant quality level. For example, for a closed package at 0.5% initial O_2 content by volume, stored at 21°C, the corresponding shelf lives were 6, 12–17 and 20–25 months for high, medium and low flavor quality criteria, respectively; at 1% initial O_2 content, the shelf lives were 4, 9–17 and 14–20 months, respectively (Ratke-Granzer and Piringer, 1981). Extrapolation to 21% O_2 gave a shelf life of 10–15 days for medium flavor quality. Differences would be expected for coffees of different grind and roast degree and blend. Storage temperature would also have an important effect on shelf life.

Another study seeking to determine the shelf life of R&G coffee found that shelf life decreased with an increase in O_2 partial pressure, a_w and temperature (Cardelli and Labuza, 2001).

Oxygen had the greatest effect with an approximately 20-fold reduction in shelf life when the partial pressure was increased from 0.5 to 21.3 kPa (air). Increasing a_w by 0.1 led to a 60% decrease in shelf life, while a temperature increase of 10°C decreased shelf life by 15%–23%. Storing the coffee in air at 4°C gave a 44% increase in shelf life compared with that at 22°C.

Roast coffee will also gradually release its volatiles into the vapor phase, and once a certain proportion of the volatiles has been released, the coffee will be regarded as unacceptable. The physical and chemical changes occurring in roasted coffee during storage have been reviewed by Nicoli and Savonitto (2005).

Another reaction that is not strictly deterioration is the evolution of CO_2. During the roasting process, a large quantity of CO_2 is emitted both from the pyrolysis of the beans as well as the heating gases. The beans absorb a large amount of the CO_2 and part of this CO_2 is freed when the cells are crushed by grinding. During the first 24 h after grinding, CO_2 is given off quite rapidly. Fine grind coffee (500–600 μm) degasses more rapidly than coarse grind (800–1000 μm) coffee, and thus the latter presents more of a problem when vacuum packed.

The major index of failure in instant coffee is caking as a result of water vapor ingress; this occurs when the moisture content reaches 7%–8% or around 0.4 a_w (Figure 21.2). Instant coffee typically has a moisture content of 2%–4% at the time of packing, which corresponds to a very low a_w of <0.1, and therefore a package with a very low water vapor transmission rate (WVTR) is necessary. Some instant coffees have a surface application of coffee oils carrying aromatics which enhance the headspace aroma, and these are susceptible to flavor deterioration from O_2 and moisture pickup.

21.4.3 PACKAGING

21.4.3.1 Roasted Whole Beans

Depending on the shelf life required, the choice of packaging material has to be considered in regard to water vapor ingress, O_2 permeability, CO_2 and volatile component egress and grease resistance if oily, dark-roasted beans are being packaged. The major problem with the packaging of RWB is the evolution of CO_2.

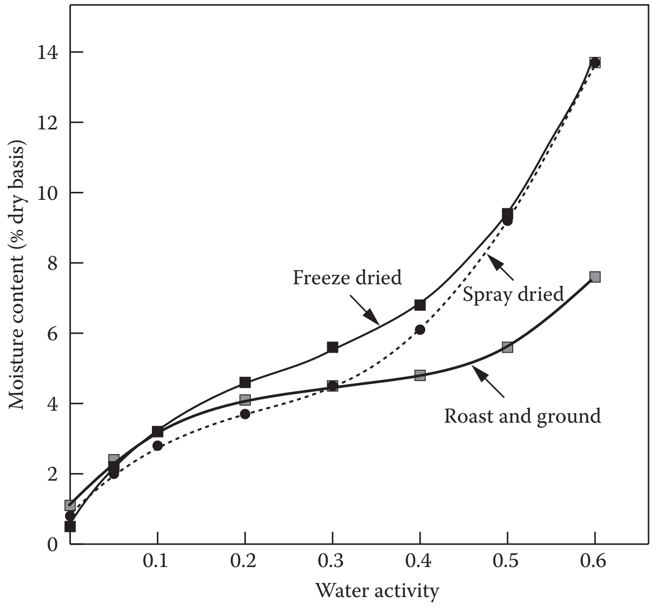

FIGURE 21.2 Moisture sorption isotherms for spray-dried and freeze-dried instant coffee and roast and ground coffee at 20°C. (Drawn from data presented in Hayakawa, K.-I., Matas, J., and Hwang, M.P., *J. Food Sci.*, 43, 1026, 1978.)

The quantity of CO_2 entrapped in RWB is of the order of 2–5 mL g^{-1} (measured at standard temperature and pressure) and probably higher, depending on the method of measurement (Clarke, 1987). Thus, when RWB are placed within a closed package, the CO_2 released will have to be contained within the available headspace inside the package or, depending on the nature of the packaging material, permeate through the package.

Some useful calculations have been presented to illustrate the magnitude of the packaging problem and assist in evaluating alternative packages (Clarke, 1987). Assuming that 100 g of RWB are placed in a package, they will occupy about 330 mL, where about 150 mL is occupied by the beans themselves but only 75 mL by the solid material of the beans because their internal porosity is 50%. If it is further assumed that the internal volume of the package is 10% greater than that occupied by the beans, then the total package volume will be 366 mL, of which $366 - 150 = 216$ mL will be available for take-up of released CO_2. Every 100 mL of CO_2 introduced inside the package will increase the total internal pressure by $100/216 = 0.46$ atm. From 100 g of RWB, up to 500 mL of CO_2 could be released, generating a total internal pressure of 2.3 atm.

Five possible solutions to the problem created by CO_2 release from RWB have been suggested (Clarke, 1987):

1. Use a sufficiently rigid container to withstand the increase in internal pressure—this was considered to be impractical.
2. Use a packaging material either sufficiently permeable to CO_2 or fitted with a one-way valve.
3. Use a package under vacuum—this would not solve the problem since even if a full vacuum were obtained in the package, it might well be inadequate to cope with the quantity of CO_2 released.
4. Use a package with a very large headspace—this was judged to be commercially unacceptable.
5. Allow a substantial release of CO_2 by holding the beans before packing.

21.4.3.2 Roasted and Ground Coffee

Substantial quantities of CO_2 are released on grinding, especially with the finer grinds. For example, estimates have been given that 45% is released within 5 min of grinding for a fine ground coffee, while others have determined that 30% is lost within 5 min of grinding to an average particle size of 1000 µm, and 70% at 500 µm.

O_2 is a prime determinant of shelf life, and there are three main ways of lowering its concentration inside a package. The first method is to apply a high vacuum immediately after filling into the package and then sealing. The second is to flush the R&G coffee and package with an inert gas immediately prior to sealing. The third is to place an O_2-absorbing sachet inside the package.

When used by consumers, packages of R&G coffee will be opened and closed frequently. In such situations, the rate of coffee degradation increases rapidly owing to modification of the conditions inside the package as a result of interaction with air and moisture. In such situations, the shelf life becomes essentially that of an air pack. This is referred to as *secondary shelf life* and represents the length of time after opening of the package during which coffee maintains acceptable quality (Nicoli et al., 2010). The end of the secondary shelf life of R&G coffee at 30°C as a function of a_w was determined by Anese et al. (2006) based on consumer rejection methodology, choosing as the acceptability limit rejection by 50% of consumers. The end of secondary shelf life was almost constant, at around 20 days, at a_w values below 0.36. At higher a_w values, the secondary shelf life greatly decreased to about 13 days at an a_w of 0.44.

21.4.3.2.1 Metal Cans

The oldest type of commercial package for R&G coffee is the vacuum-packed tinplate can. It provides impermeability to water vapor, gases and volatiles and can be made with a scored, removal aluminum end over which a threaded screw cap is placed. After filling, a high vacuum is pulled on the can; this should be at least −95 kPa (71 cm Hg) to give an O_2 content of less than 1%. After sealing, evolution of CO_2 gas will reduce the vacuum until atmospheric pressure is restored. It is important that pressure does not build up inside the container during storage; to prevent this from occurring, the R&G coffee must be degassed in bulk to reduce its CO_2 content to an acceptable level. The type of calculation required to ensure that pressure will not develop during storage of the packaged coffee has been presented elsewhere (Clarke, 1987).

Inert gas packing of R&G coffee in metal containers is also practiced. The usual procedure is to first apply a vacuum and then release it with an inert gas, typically N_2. In order to prevent excessive pressures developing in the can, it is necessary to degas the coffee to a much lower level than for high vacuum packing. Alternatively, a relatively low vacuum can be applied to the gas-purged can before finally sealing (Clarke, 1987).

21.4.3.2.2 Hard Packs

As an alternative to the metal can, so-called hard or shape-retentive packages of flexible laminated materials shaped into bags have been developed and widely used. These packs are called "hard" because on application of a high vacuum after filling and sealing, the material collapses onto the coffee to form a "brick," which is hard to the touch. However, if significant quantities of CO_2 are evolved and/or air enters from the atmosphere, the bag will become "soft." This is an undesirable condition since consumers may erroneously perceive that the coffee has deteriorated, although this is not necessarily the case.

Many flexible laminates used for this type of package used to contain a central layer of aluminum foil, but this has been replaced in many situations by a metallized layer. A typical early construction was PET-alufoil-LDPE 12-12-70 μm, while contemporary structures are mPET laminated to low density polyethylene (LDPE). Most U.S. coffee roasters employ a more durable four-ply structure, which utilizes BOPP or OPA in addition to OPET, alufoil and LDPE.

The internal pressure at which the packs will become noticeably soft is of the order of 0.5–0.75 atm (50–76 kPa) (Clarke, 1987). This means that coffee that has been satisfactorily packaged in metal containers will need to be degassed to a greater extent before packing in laminate packs if a similar shelf life is desired. Degassing times range from 1 to 30 h depending on the degree of roasting and the fineness of the grinding.

Another approach to avoid the problem of softening of the package and/or permit the packaging of freshly ground coffee is to include inside the package a sachet containing an absorber for CO_2. The use of such sachets is now quite widespread.

21.4.3.2.3 Soft Packs

These packs or pouches (sometimes referred to as *pillow packs*) are similar to those which were described earlier for the packaging of RWB, and similar considerations apply. No vacuum is used and the O_2 content is reduced by flushing with an inert gas immediately prior to sealing. To provide an adequate shelf life, the packaging material must provide a good barrier to gases and water vapor. Again, adequate degassing of the ground coffee must be carried out prior to packing to avoid pressure building up inside the package.

The use of sachets containing an absorber for CO_2, as described earlier for hard packs, is also possible for soft packs. However, it has become more common to incorporate a one-way valve into the side of the package which opens and releases CO_2 when a certain internal pressure is exceeded. The increase in internal pressure caused by CO_2 initiates opening at a pressure of 0.00345 atm (350 Pa), allowing the CO_2 to escape. When the overpressure declines to about 0.0005 atm, the valve closes again. It should be noted that volatiles also escape through the valve, leading to beverages with diminished sensory quality.

A recent innovation in the R&G coffee sector is the coffee pod, which contains the optimal quantity of coffee for a single-cup preparation. The Easy Serving Espresso pod, or ESE pod, is one example. It looks like a small disk and contains 7 g of coffee prepacked in its own paper filter. Coffee pods are generally individually sealed in a high barrier metallized secondary package flushed with an inert gas (typically N_2) prior to sealing. More recently, coffee capsules have been introduced into the market. Designed for specific espresso machines, capsules have different shapes and may contain varying amounts of coffee, ranging from 5.0 to 7.5 g. The capsules are generally made of aluminum foil coated on the inside with a protective film. Before sealing, they are saturated with N_2 to improve shelf life (Nicoli et al., 2010).

21.4.3.3 Instant Coffee

In a review of the limited shelf life data and accompanying information on instant coffee, it was concluded (Clarke, 1993) that provided the moisture content was maintained at less than 4%–5% w/w, coffee will retain its original quality for at least 2 years at ambient (temperate) conditions. With more sophisticated products (i.e., with higher retained levels of volatiles), a shelf life of at least 18 months is possible, provided that the initial O_2 in the headspace is less than 4.0%.

Alves and Bordin (1998) investigated the shelf life of portion packs (25 and 50 g) of instant coffee at 30°C and 80% RH in three different plastic structures. The surface areas of the packs were 8 × 11 cm for 25 g and 10 × 16 cm for 50 g. The structure of the packages, their WVTR and the shelf life of the coffee at 30°C and 80% RH are shown in Table 21.1. The end of shelf life was when the moisture content had reached 7.8%, at which time powder agglomeration or caking occurred. Data on the shelf life of agglomerated and powdered instant coffee packed in PP and PET pots were presented in a later paper (Alves et al., 2000), the shelf life in the former being up to 2.5 years, compared to 4 months in the latter.

Ocampo and Giraldo (2006) reported that instant coffee packed in glass was rejected by 50% of consumers after approximately 2 years of storage at 18°C. Flexible materials containing aluminum foil (i.e., PET-alufoil-LDPE) as an O_2 and moisture barrier may also be very effective, giving shelf lives of around 1 year. However, a much lower shelf life is obtained when instant coffee is stored in other plastic materials.

For many years, instant coffee for the retail market was packaged in either tinplate cans or glass jars of various shapes. A laminated paper or metal foil diaphragm sealed to the rim of the container provided an effective barrier to water vapor and O_2, over which was placed a tight-fitting metal lid in the case of tinplate containers, and a screw cap of plastic or metal in the case of glass jars. More recently, "refill" packs of instant coffee packaged in flexible laminates of PET-alufoil-LDPE or metallized PET-LDPE have reduced the quantity of coffee packaged in metal containers and glass jars. The contents of such packs after opening in the home are refilled into glass or metal containers, and adequate shelf lives are generally obtained.

TABLE 21.1
Shelf Life of Instant Coffee in Plastic Packages

Package Structure	WVTR (g m^{-2} day^{-2})	Shelf Life (Days)	
		25 g	50 g
LDPE (30 µm)	6.1	15	16
BOPP-BOPPP[a] (20 µm-40 µm)	1.2	84	94
MetPET-LDPE (12 µm-70 µm)	0.9	108	112

Source: Alves, R.M.V. and Bordin, M.R., *Cienc. Tecnol. Aliment.*, 18, 19, 1998.

[a] Biaxially oriented pearlized polypropylene.

21.5 TEA

Tea is the most widely consumed drink in the world after water. The appealing characteristics of tea as a beverage are its taste, aroma and color. Polyphenols (such as catechins) and amino acids (such as theanine) are the main contributors to the unique taste and color of tea. The components of essential oil in fresh tea leaves and volatile compounds developed during the manufacturing process form the characteristic tea flavor.

Although many types of tea are available around the world, teas may be classified into three general categories according to the manufacturing process used: fermented (black tea), semifermented (oolong and pouchong) and nonfermented (green tea). The different manufacturing conditions result in differences in taste, aroma and color as well as in storage stability and shelf life.

21.5.1 MANUFACTURE

21.5.1.1 Black Tea

Black tea goes through four processes: withering, rolling, fermentation and firing. After picking, the leaves are placed on trays to wither or dry for about 18 h. Heat may be applied to reduce the time to 6–8 h. The leaves are then rolled, which distorts the shape and crushes the cell walls, releasing oxidizing enzymes. The leaves are then spread out and held at ambient temperature and saturated humidity for about 13 h. This is the fermentation stage and results in the leaves changing from green to copper-red, as well as developments in the flavor. The final stage is heating to 82°C–93°C to denature the enzymes and stop fermentation. The moisture content is reduced to about 3%.

Oolong and pouchong teas are semifermented teas, with the fermentation process typically lasting 5–6 h, after which the leaves are heated with agitation in a pan at 200°C until the desired final moisture content is reached.

21.5.1.2 Green Tea

After picking, the leaves are steamed (Japanese type) or panned (Chinese type) to inactivate polyphenoloxidase and other enzymes responsible for fermentation. The leaves are then rolled and dried by a process similar to that used for black tea.

21.5.2 INDICES OF FAILURE

21.5.2.1 Black Tea

During storage, black tea consumes O_2 and evolves CO_2. The major indices of failure for black tea are (1) loss of volatile components; (2) changes in catechins, amino acids, theaflavins and other pigments; and (3) increases in undesirable taints arising from oxidative reaction products from fatty acids, and oxidation and condensation products from soluble polyphenols such as catechins and theaflavins. All these reactions are accelerated by increases in tea moisture content, elevated temperature and exposure to light. Although lipid oxidation is insignificant except under hot, dry conditions, oxidation of free fatty acids released during storage occurs during brewing and has a profound influence on the quality of the liquor. Exclusion of light is clearly important because photooxidation of lipids and nonenzymic browning reactions, both of which contribute to quality loss in black tea, are accelerated by light.

21.5.2.2 Green Tea

The major indices of failure for green tea are (1) change in color from bright green to olive green and then brownish green, (2) change in characteristic leafy and refreshing odor to dull and heavy odor and (3) changes from a well-balanced, complex taste to a flat taste lacking in characteristic briskness. All these reactions are accelerated by moisture, O_2, elevated temperatures and exposure to light, much as in the case of black tea.

21.5.3 PACKAGING

A moisture sorption isotherm for oolong tea is depicted in Figure 21.3. Despite a number of MSIs for tea published over the past 40 years, there are no published data on the critical moisture contents and a_ws, making it difficult to specify the required barrier properties of a suitable package. Given that the initial moisture content of tea is 3%–4%, a good water vapor barrier is required to prevent a relatively rapid increase in moisture content. However, a reduction in the levels of various chemical constituents is more likely to contribute to the end of shelf life of tea than an increase in moisture content. The volatile fraction of black tea shows an overall decline during storage that is accelerated by moisture uptake and, to some extent, storage at elevated temperatures.

Loose tea is packaged in a multitude of different shapes, sizes and types of materials, the most common being a paperboard carton with either an aluminum foil liner or an overwrap of PP or RCF. Metal containers with snap-on lids are also used for some premium products. Tea bags have now become the most popular form of retail packaging, and considerable development has gone into improving the tissue paper used for this type of package, with porous wet-strength paper being required. Once filled, the tea bags must be placed inside a package that provides an adequate barrier to water vapor. Paperboard cartons overwrapped with PP or RCF are the most common.

The storage stability of green tea is the lowest among the various teas including black tea, oolong tea and pouchong tea. To most effectively protect the quality of green tea during storage, N_2 flushing or vacuum packaging is recommended.

Changes in biologically active green tea catechins during long-term storage of commercial tea leaves in the dry state were evaluated by Friedman et al. (2009). Samples of eight commercial green tea leaves of unknown history sold as tea bags in the United States, Korea and Japan were stored at 20°C for up to 6 months. The results suggested that the consumer needs to be aware about possible adverse consequences of long-term storage of commercial tea brands because even in the absence of moisture, the quality of teas may degrade with time.

Lee and Chambers (2010) studied how flavor changes in green teas that are stored over a period of 2 years (a typical shelf life for green tea products in loose leaf form). Two Korean green teas were packaged in metallized multilayer plastic films and stored at an ambient temperature of ~20°C. Samples were evaluated by highly trained panelists at 3, 6, 12, 18 and 24 months. Green tea changed minimally during the first year of storage and changed slightly more during the second year. However, these changes appeared to be minimal when the samples were packaged in metallized multilayer plastic films. Unfortunately, specific details about the barrier properties and composition of the packaging material and changes in the moisture content over time were not given.

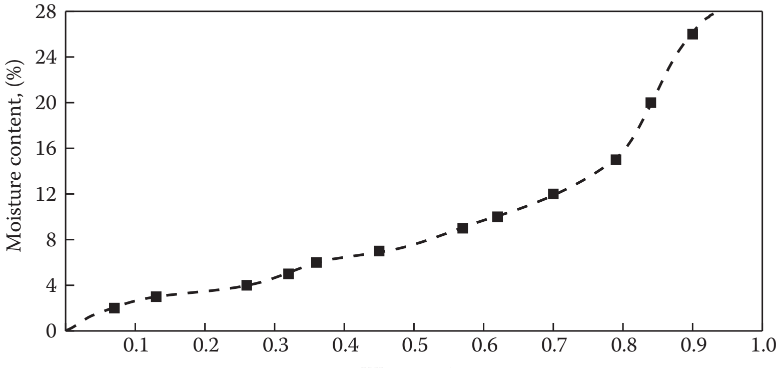

FIGURE 21.3 Moisture sorption isotherm for oolong tea at 25°C. (From Chen, C. and Weng, Y.-K., *Food Bioprocess Technol.*, 3, 226, 2010.)

Ready-to-drink (RTD) teas are a growing segment in the beverage category, brought about by improvements in the flavor of these products, their perceived health benefits and convenience. Kim et al. (2011) evaluated the impact of packaging materials on green tea polyphenolics and antioxidant capacity. RTD infusions were packed in glass, PET and a PET-PP retortable pouch (RP) and stored in the dark at 3°C for 12 weeks. Concentrations of the three major polyphenolics were better retained in glass bottles as compared to other packages over 12 weeks, while the antioxidant capacity was better retained in glass and PET versus RP. Because commercial RTD teas generally have a relatively long retail shelf life, significant losses in polyphenolic compounds or antioxidant capacity are to be expected, even under refrigerated conditions. Packaging materials with different OTRs are likely to be a significant shelf life predictor due to the relationship between O_2 permeability and antioxidant polyphenolic degradation observed in these trials.

21.6 JUICES

21.6.1 MANUFACTURE

Although fruit juices were originally developed to use up surplus fresh fruit production, fruit (in particular citrus and apple) is now specially grown for juicing. A variety of different types of juice is available. These include clear clarified juices such as grape, apple and blackcurrant; light cloud juices like pineapple; heavy cloud juices containing cellular material in suspension such as orange and grapefruit juices; pulpy juices such as tomato-based products; and nectars made by pulping whole fruits like peaches, apricots and comminuted citrus products.

The quality of a juice depends essentially on the species and maturity of the fresh fruit. The main factors that influence the quality are the sugar:acid ratio, the aroma volatiles, the phenolic components and the ascorbic acid content. Satisfactory fruit juice production depends on sound judgment of the raw materials and the blending procedures adopted. Details of the juice extraction and subsequent processing operations used are outside the scope of this book since they tend to be specific for the different types of juices; the reader is referred to standard texts on the subject for more specific information (Ashurst, 2005; Barrett et al., 2005).

A key step in the processing of fruit juices from the packaging point of view is the *deaeration* step. This is important both to minimize oxidative reactions in the juice and reduce corrosion if the juice is subsequently packaged in a metal container. O_2 in air, present in the spaces between the juice vesicles and from the surroundings, saturates the juice during extraction, producing oxidation reactions that often result in browning, changes in aroma and loss of nutritional value. These reactions are exacerbated by the increase in temperature during pasteurization and reduce the overall quality of the juice during storage (Garcia-Torres et al., 2009).

Pasteurization involves heating the juice in tubular or plate heat exchangers to temperatures in the region of 85°C–100°C for 2–45 s. Pasteurization was originally used as a means of controlling microflora, but it is also important for stabilizing the cloud of orange juices, as consumers regard orange juices without a stable cloud as inferior and unacceptable. Although pasteurization ensures the safety and extends the shelf life of orange juice, it often leads to detrimental changes in the sensory qualities of the product.

21.6.2 INDICES OF FAILURE

The five key indices of failure in juices are microbiological spoilage, nonenzymic browning, oxidation resulting in loss or degradation of flavor components and nutrients (essentially ascorbic acid), absorption of flavor compounds by the package (scalping) and, in some cases, cloud loss. Although preservatives were commonly added to fruit juices to overcome microbiological problems, the recent consumer preference for preservative-free foods has seen their use diminish. Instead, attention to good manufacturing practice in the plant, coupled in many cases with aseptic processing and packaging, has obviated the need for them.

The rate of browning and nutrient degradation in fruit juices is largely a function of storage temperature, although the rate is partly dependent on the packaging material. For example, Mannheim et al. (1988) compared the quality of citrus juices aseptically packaged in plastic-alufoil-paperboard laminated cartons and glass containers and found that the extent of browning and loss of ascorbic acid was greater in cartons than in glass, presumably because of O_2 permeation into the carton. Ahrné et al. (1997) reported OTRs for a 1 L laminated carton (surface area not given) of 0.009 mL pack^{-1} day^{-1} at 10°C, 0.014 at 20°C, 0.023 at 30°C and 0.038 at 40°C and noted that O_2 permeation occurred mainly through the seals. Assuming an inner surface area of 495 cm^2 (0.0495 m^2) for the cartons analyzed by Ahrné et al. (1997), 0.009 mL pack^{-1} day^{-1} corresponds to an OTR of <0.18 mL m^{-2} day^{-1} at 10°C, 0.28 at 20°C, 0.47 at 30°C and 0.77 at 40°C (Lopez-Gomez et al., 2010).

Pasteurization was originally used as a means of controlling microflora. The acid conditions that prevail in most fruit juices will not support pathogens and tend to inhibit organisms in general, although acid-tolerant types may germinate and cause spoilage. The low pH conditions assist pasteurization so that 80°C for 30 s is adequate for virtually all juices except for the less-acid fruits such as apricot and tomato.

The sorption of key aroma and flavor compounds by plastic packaging in contact with juice is referred to as “scalping” (Sajilata et al., 2007). Because of its lipophilic nature, the oil fraction of orange juices will be absorbed by many nonpolar packaging polymers. Factors that affect absorption include molecular size of the aroma compounds and polarity and solubility properties of both the polymer and the aroma compounds.

Pasteurization is also important for stabilizing the cloud of certain juices (typically orange, grapefruit and tomato) because cloud particles impart characteristic flavor, color and mouthfeel, and consumers regard clarified versions of these juices as inferior and unacceptable. Such a reaction is based largely on tradition because lemon, lime and apple juices are invariably preferred in the clarified state but can be (and sometimes are) made to have a stable cloud. The major enzyme responsible for destabilizing the cloud is pectinmethylesterase, and it must be inactivated as soon as possible after extraction of the juice. This is generally done by pasteurizing the juice at 90°C–95°C for 15–30 s, the precise time depending on the pulp content. Recently, nonthermal methods such as high pressure processing have been commercialized for inactivating microorganisms and enzymes in fruit juices.

The oil fraction of citrus juices contains many volatiles which have a major impact on citrus aroma and flavor. These oil-based flavor compounds are relatively easily oxidized, resulting in the development of undesirable, terpene-like off-flavors. This form of flavor deterioration can be minimized by removing O_2 from the juice prior to packaging, avoiding high pressures during juice extraction so as to limit oil transfer to the juice and using a package that is a good barrier to O_2.

21.6.3 PACKAGING

From a packaging point of view, there are three categories of juices: single strength (10°–13° Brix), concentrated juices (42° or 65° Brix) and nectars (20°–35° Brix).

The traditional packaging procedure for single strength juices involved heating the deaerated juice to around 90°C–95°C in a tubular or plate heat exchanger, filling the hot juice directly into metal cans, sealing and inverting the cans, holding them for 10–20 min and then cooling. This hot-fill/hold/cool process ensured that the juice was commercially sterile and provided that the seams were of good quality, the cans had an acid-resistant enamel coating and the juice had been properly deaerated, a shelf life of at least 1–2 years was attainable. However, because of the acidic nature of fruit juices, any imperfections or scratches in the enamel coating or tin layer resulted in rapid corrosion, dissolution of metal into the juice, production of H_2 and container failure due to swelling. The use of glass containers obviated these problems provided that the container closure (typically metal) was resistant to attack by the juice.

The use of glass bottles for the packaging of fruit juices was widespread and is still used for high quality, single serve juices. The hot-fill/hold/cool process has to be applied with care to avoid breakage of the glass containers. Gable top cartons consist of paperboard coated on both sides with polyolefins; aluminum foil or EVOH may be incorporated into the structure to improve its O_2 barrier and extend the shelf life to 4–6 weeks. Although the cartons are handled under nonsterile conditions, steps are taken to avoid recontamination. The filling temperature of the juice is typically 4–5°C to minimize microbial growth, although foaming can be a problem at this low temperature. The cartons are filled to leave a positively controlled headspace, and an inert gas such as N_2 can be injected immediately prior to sealing to remove O_2 from the headspace.

Fruit juices and concentrates can be packaged aseptically into plastic-alufoil-paperboard-laminated cartons. These products are then held at room temperature and the shelf life and nutrient composition are greatly influenced by the barrier properties of the carton, the interactions of the juice with the carton and the storage environment. The end of shelf life is typically 6–8 months and is related to the extent of nonenzymic browning and the sorption of key aroma and flavor compounds by the plastic in contact with the juice.

The stability of aseptically packaged fruit juices in cartons and LLDPE pouches with either EVOH or PVdC copolymer barrier layers was investigated by Alves et al. (2001). The OTRs in mL m^{-2} day^{-1} were <0.1 for the cartons, 0.3 and 0.6 for the pouches containing EVOH at two thicknesses and 2.9 for those with PVdC. The performance of the packages with EVOH was virtually equivalent to that of the cartons throughout the storage period studied (90 days at 25°C).

Two flexible packaging formats are used for juices and especially for sports drinks. One consists of a stand-up pouch (SUP) constructed (from inside to out) of LDPE-alufoil-PET with a drinking straw attached to the side of the pouch; the sharpened end of the straw is used to pierce a specially prepared area on the pouch. Another is made up of four panels or sections combined to form a SUP with two side gussets, and a variety of laminate constructions are available. For beverages, the most common structure (from inside to out) is LDPE-PET-alufoil-PET. For specific applications, EVOH, OPA or PP can be included in the structure. A HDPE neck and straw is sealed into the top portion of the pack, which is filled through the neck and then sealed by a tamper evident closure. The packs can be cold or hot filled (up to 95°C) and pasteurized after filling if required.

Extrusion blow molded HDPE bottles have been used for many years to package fruit juices and drinks. As HDPE is a poor barrier to O_2, such bottles can be used only for chilled juices with a shelf life of up to 3 weeks. The barrier properties can be improved by incorporating a layer of EVOH copolymer or PA, permitting shelf lives of up to 6 months, depending on the choice and thickness of the barrier layer.

Developments in barrier coatings for PET have led to increasing use of PET bottles for fruit juices and drinks. Berlinet et al. (2006) evaluated three different commercial 330 mL PET bottles: standard monolayer PET (PET1), multilayer PET containing an O_2 scavenger and complexed with nylon-MXD6 (PET2) and plasma-treated (internal amorphous carbon coating) PET (PET3). The O_2 permeabilities of the PET bottles were 0.0632, 0.0058 and 0.0056 *barrer* for PET1, PET2 and PET3, respectively. Glass bottles (500 mL) were used as the reference packaging. The bottles were stored at 20°C under artificial light (750 lx), and after 9 months, ascorbic acid had decreased from 383 to 310 mg L^{-1} in glass, 132 mg L^{-1} in PET1, 255 mg L^{-1} in PET2 and 230 mg L^{-1} in PET3, as shown in Figure 21.4. In the EU, orange juice must have ≥200 mg L^{-1} ascorbic acid at the end of shelf life. Thus, juice in PET1 would be unacceptable after 9 months, a result confirmed by Ros-Chumillas et al. (2007). In a later study, Berlinet et al. (2008) investigated the loss of aroma compounds from orange juice by permeation through the bottle (PET1 and PET2) and the cap. The results showed that permeation took place mainly through the cap. The use of an HDPE multilayer cap with an internal barrier layer of LDPE-EVOH-LDPE considerably limited the permeation of the aroma compounds, regardless of which PET bottle was used.

In the United States, the production of frozen concentrated orange juice has become a huge industry. The 42° Brix juice is usually held at −12°C at which temperature it is still liquid. Typical packaging materials for this product consist of spiral wound paperboard tubes with aluminum ends or aluminum cans.

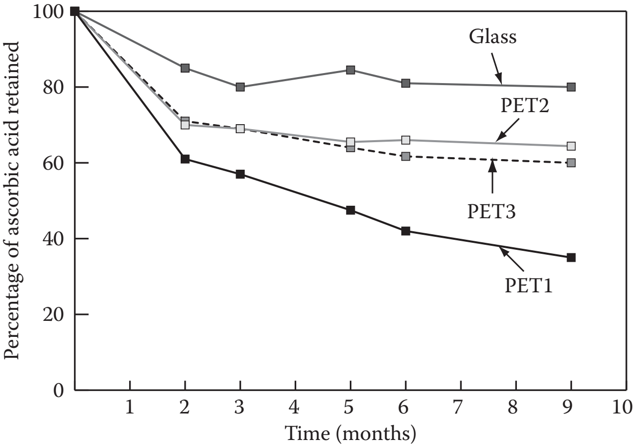

FIGURE 21.4 Percentage of ascorbic acid retained in orange juice stored for 9 months at 20°C under artificial light in glass and three types of PET (see text for details). Initial concentration was 383 mg 100 L^{-1}. (From Berlinet, C., Brat, P., Brillouet, J.-M., and Ducruet, V., *J. Sci. Food Agric.*, 86, 2206, 2006.)

21.7 BEER

21.7.1 Manufacture

Beer is an alcoholic beverage made by brewing and fermentation from cereals (usually malted barley) with added hops to give a bitter flavor. Two major technological steps are required to complete the transformation of the raw material into the finished product: controlled germination (i.e., malting) which allows the ultimate production of a fermentable extract through the activities of enzymes formed during seedling growth and fermentation.

Malted barley is crushed and "mashed" by mixing with water at temperatures of up to 67°C, resulting in rapid degradation of solubilized starch and less extensive hydrolysis of other high MW substances. This is followed by a leaching process, which completes the separation of the solutes from the spent grains. The resulting "sweet wort" is boiled in a copper or kettle together with hops (*Humulus lupulus* L.), after which the spent hops and precipitated high MW material are removed. The specific gravity of the wort rises as increasing amounts of sugars are extracted. After adjustment to the desired specific gravity, a selected strain of yeast is added. As the yeast grows and ferments the sugars of the wort, alcohol is formed and the specific gravity falls.

At the end of fermentation, the yeast is separated from the immature or "green" beer which is allowed to mature for an appropriate period. Before it is ready for consumption, freshly fermented beer must undergo a number of changes, including the elimination of certain fermentation products, supersaturation with CO_2, separation of yeast cells and removal of some of the polyphenolic and other material that will eventually give rise to turbidity in the beer. After centrifugation and filtration to remove residual yeast and assorted detritus from conditioned beer, followed by pasteurization and possibly other treatments, the beer is ready for packaging (Briggs et al., 2004).

The most common procedure for bulk beer is flash pasteurization where the beer is held at 70°C for ~20 s before cooling and packaging. Tunnel pasteurizers are used with bottled and canned beer where the containers travel through an enclosed area in which they are sprayed with hot water, left for an appropriate time and then treated with a cold water spray.

21.7.2 Indices of Failure

The vast majority of beers are never better than when they are first filled into their containers (Bamforth and Krochta, 2010). The major indices of failure involve the production of off-flavors and off-colors due to oxidation, which is accelerated by light, transition metal ions (e.g., iron, copper and aluminum) and heat. Oxidation of alcohols, iso-α-acids and fatty acids in beer produces carbonyl compounds that are detectable in sensory tests at low levels (Kuchel et al., 2006). In addition to residual O_2 from the brewing process, O_2 can find its way into packaged beer from three sources: (1) O_2 in the package headspace that is not removed during the filling operation, (2) penetration of O_2 through the package closure and (3) permeation of O_2 through the packaging material (Bamforth and Krochta, 2010). Even very low levels of O_2 (≤1 ppm) can lead to detectable flavor and color problems in beer. Typically, commercial brewers use a measurement of total package oxygen (TPO) which includes both the dissolved O_2 in the liquid and the amount of O_2 in the headspace of the package, typically a bottle or can. Continual improvements in packaging capabilities have brought the TPO down to <50 ppb (Kuchel et al., 2006).

Beer is sensitive to light, especially in the 350–500 nm range, and clear and green glass bottles allow penetration of light at these wavelengths, resulting in nauseous off-flavors. Such beer is said to be "sunstruck" and the taste and aroma are referred to as "skunky." The compound responsible is 3-methyl-2-butene-1-thiol, which has a flavor threshold of 4–35 ppt. One strategy to overcome this problem is to use specialized reduced hop extracts that do not yield this breakdown product (Stewart and Priest, 2011). The more obvious solution in the present context is to avoid packaging beer in clear and green glass bottles if it is likely to be exposed to light.

One of the major oxidative reactions is the oxidation of linoleic acid (introduced into the wort from the malt) to yield the unsaturated aldehyde *trans*-2-nonenal which gives beer a "cardboard-like" flavor; it has a flavor threshold of 0.1 ppb and has been associated with human body odor. Flavor loss is accelerated in the presence of light and certain metal ions. Early on, it was assumed that it was mainly *trans*-2-nonenal that was responsible for sensory changes, but it is now evident that a myriad of flavor compounds is responsible (Vanderhaegen et al., 2006).

Because the fermentation process itself consumes O_2, brewing reduces the level of O_2 in beer down to 40–50 ppb prior to packaging. However, during the filling process, air enters the package and the level of O_2 can reach 250–500 ppb, which corresponds to 0.1–0.2 mL of O_2 per 355 mL bottle or can. This results in a shelf life for the beer of 80–120 days and even then significant flavor deterioration is likely to occur. Brewers would like to be able to reduce the O_2 level in beer to less than 50 ppb immediately after packing and hold it at that level for as long as possible. Use of a double evacuation technique with glass bottles which involves flushing with CO_2 can essentially eliminate any addition of O_2 to beer during the filling operation (Bamforth and Krochta, 2010).

One method by which flavor compounds can be depleted in beer is from sorption by the packaging material. Some of the more nonpolar flavor compounds in beer are more soluble in soft plastics such as the PVC liners in crown corks than in water. The degree of partitioning into such materials is a function of the polarity of the molecule in question, the volume and chemical composition of the plastic or other lining material, the volume and alcohol content of the beer and the temperature. For many bottled beers, loss of hop flavor to the packaging material occurs and may be a major source of hop flavor loss.

Owing to its low pH (<4.4), microbial degradation is not usually a problem with beer, and the use of pasteurization and aseptic cold filtration excludes wild (i.e., noncultured) yeasts that could thrive.

21.7.3 PACKAGING

21.7.3.1 Glass

The traditional packaging media for beer is the glass bottle sealed with a crown cork (see Section 10.1.3.1.1). Pasteurization of the beer in the bottle after sealing is the most common means of securing microbial stability. The aim is to heat the beer to a high enough temperature and hold it there long enough to destroy any beer spoilage organisms. The brewing industry has developed its own standard measure of the effectiveness of the pasteurization process and uses the term *pasteurization units* (PUs) where one PU is equivalent to holding beer at 60°C for 1 min. About 10 PUs is regarded as a suitable heat treatment for most bottled beers produced under good manufacturing practices.

The crown cork closure is made of tinplate or electrolytic chrome-coated steel and contains a compressible lining material, the composition of which has changed over the years from solid cork to composition cork, plastic and aluminum foil in various combinations. Today, the use of cork-based linings is relatively rare, and most crown closures are lined with PVC (often foamed) or sometimes HDPE. Where cork is still used, it is common to laminate it to aluminum foil to improve its barrier properties.

The material properties as well as the shape of the lining have a great effect on the rate of O_2 permeation through crown cork linings. Linings with aluminum foil provide a perfect barrier. Although PVC linings are normally foamed to different degrees, they appear almost solid after closing and permeation rates are almost identical. Ingress of O_2 does not appear to be measurably influenced by the condition of the glass sealing surface or the amount of pressure used in applying the crown to the bottle. The total ingress of O_2 through closure linings ranges from 0.6 to 1.2 μL day^{-1} or 2.0 to 8.4 ppb day^{-1} for a 355 mL bottle. If no O_2 is added to a bottle of beer during filling, the resulting shelf life for the beer would be 4–13 months for a maximum O_2 ingress of 1 ppm.

In an attempt to extend the shelf life of bottled beer, O_2-absorbing materials have been incorporated into the lining material of crown seals to remove O_2 present in the headspace at the time of filling as well as absorbing O_2 permeating into the bottle through the crown closure. The linings containing the O_2 absorber can be used in metal crowns as well as roll-on metal and screw-on plastic caps. They also find limited application in the fruit juice and carbonated beverage industries. It is recognized that pry-off crown closures provide a tighter seal than do twist-off crowns.

21.7.3.2 Metal

The first successful canning of beer occurred in 1933 in Newark, New Jersey, when 2000 cans were produced for a test market. In January 1935, the first beer cans went on sale—Kruegers Finest Beer and Kruegers Cream Ale. By the end of 1935, no less than 36 American breweries were canning beer.

The greatest problem with using cans for beer packaging was preventing the pickup of metal ions from the tinplated steel and lead solder of the early three-piece cans. The metal ions resulted in undesirable metallic flavors and the rapid onset of haze or "metal turbidity" as it was called. Although several reasonably successful enamel coatings were developed and used, it was not until the development of epoxy-phenolic resin linings around 1960 that a truly effective lining capable of eliminating metal pickup over a long term was found. These linings resulted in less than 0.3 ppm iron pickup over a 6 month period.

Until the late 1950s, tinplate was used almost exclusively. However, three-piece aluminum cans were launched in 1958 by Primo of Hawaii and in 1959 by Coors. This was followed in 1963 by some test markets of two-piece D&I aluminum cans. This latter type of can began to be mass produced in 1966.

Aluminum was used for beer can ends by Schlitz in 1960 when it introduced the "soft top" can to facilitate opening with a special tool known as a "church key." A detachable pull-tab aluminum end was developed in 1962 by Ermal Fraze of Dayton, Ohio (see Section 7.7.5.1). It was test marketed and emerged in 1965 as the ring-pull tab. However, because it was detachable, it resulted in litter, and so, in 1975, a patent was granted for a can end with an inseparable tear strip that is the familiar stay-on tab in use today.

Aluminum cans provide a total barrier to light and prevent ingress of O_2 or egress of CO_2. Any oxidation leading to off-flavors, off-colors and haze is due to O_2 remaining in the beer after the brewing process and any O_2 added during the filling operation. Thus, the extension of shelf life of beer in cans appears to be dependent on reducing levels of O_2 exposure from these two sources (Bamforth and Krochta, 2010).

The use of foam-producing widgets, originally developed for stout beer packaged in metal cans, has been described in Section 15.3.5.

21.7.3.3 Plastics

The end of shelf life for beer is when O_2 ingress exceeds 500 ppb and CO_2 egress 10%. The shelf life of beer at 21°C in a standard monolayer PET bottle was shown to be only 3 weeks before ingress of 500 ppb O_2 and 4 weeks before 10% loss of CO_2 (Boutroy et al., 2006). To overcome these problems, a variety of barriers are offered commercially including amorphous carbon on the inside, SiO_x on either the inside or outside and O_2-absorbing compounds as the middle layer in the bottle wall (see Section 5.5.2). The improved barrier to O_2 resulting from an amorphous carbon coating on PET bottles is shown in Figure 21.5. Today, a small but increasing quantity of beer is packaged in PET bottles with a barrier to provide acceptable shelf life, and this market sector is expected to expand rapidly over the next decade, mainly at the expense of glass bottles.

Interior DLC or amorphous carbon coatings were shown by Shirakura et al. (2006) to reduce O_2 and CO_2 transmission rates of PET bottles by 95% and 90%, respectively, with a resulting reduction in stale flavor (Table 21.2). Boutroy et al. (2006) reported that PET bottles with an amorphous carbon coating of 100 nm showed a shelf life at 21°C of 25 weeks based on ingress of 500 ppb O_2 or 38 weeks based on 10% CO_2 loss.

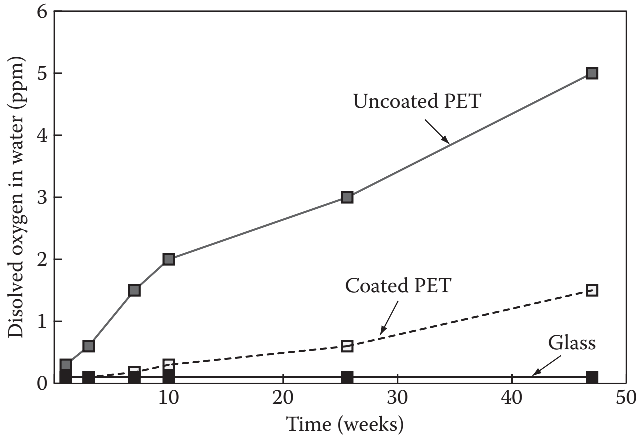

FIGURE 21.5 Dissolved O_2 in water versus time of uncoated and amorphous-carbon-coated PET bottles compared to a glass bottle. (From Boutroy, N. et al., *Diamond Relat. Mater.*, 15, 921, 2006.)

TABLE 21.2
Bottle O_2 Transmission Rate (OTR), CO_2 Transmission Rate (CDTR) and Bottled Beer Sensory Evaluation After Storage for 2 Weeks

	OTR (mL Bottle^{-1} Day^{-1})		CDTR (g Bottle^{-1} Day^{-1} atm^{-1})		Stale Flavor[a]	
	30°C	40°C	30°C	40°C	30°C	40°C
PET bottle	0.1132	0.2167	0.0048	0.0071	6.5	7.1
DLC-coated PET bottle	0.0043	0.0061	0.00044	0.00059	4.7	5.0
Glass bottle	0	0	0	0	3.9	5.7

Source: Adapted from Shirakura, A., Nakaya, M., Koga, Y., Kodama, H., Hasebe, T., and Suzuki, T., *Thin Solid Films*, 494, 84, 2006.

[a] 0, Not perceptible; 9, very strongly perceptible.

21.8 WINE

21.8.1 INTRODUCTION

Unlike most other foods and beverages, consumers generally expect wines to improve with age. However, this change is neither universal nor everlasting and varies from wine to wine, and expectations differ from consumer to consumer. Most wines improve only for a few months to a few years before showing irreversible loss in quality, and the changes are difficult to predict precisely. Thus, the required shelf life can be a few weeks to many years. Wine quality is a mix of extrinsic and intrinsic factors, and with prices ranging from as little as \$2 to more than \$1000 per bottle, it is not surprising that there is a significant variation in consumer quality expectations (Reeves, 2010).

21.8.2 CLASSIFICATION

Wine is a beverage resulting from the fermentation by yeasts of the juice of the grape with appropriate processing and additions. Wines can be assigned to one or the other of two major groups—table wines and fortified or appetizer wines. In the first group, the fermentable sugar has been largely consumed so that further fermentation by yeasts is prevented; spoilage organisms should not develop if the wine is kept anaerobic. Owing to the natural limit of sugar present in wine grapes, the alcohol content of such wines is normally about 12%–14%. The major subclass of these wines is the still wines, which have no evident CO_2. Further subdivision depends on color and residual sugar. It is possible to produce microbiologically stable wines having a moderate or high amount of residual sugar. The other major subclass of table wines is the sparkling wines. These have undergone two complete fermentations, where the CO_2 of the second fermentation is retained. Sometimes, cheap sparkling wines are produced by carbonation of still wines.

The second major group includes the dessert and appetizer wines which contain 15%–21% alcohol. The nature and keeping quality of these wines depend heavily on the addition of spirits (alcohol) distilled from wine, the amount of extra alcohol added being sufficient to prevent spoilage by further growth of yeasts or other microorganisms. There are three major subclasses in this group: sweet wines in which the addition of wine spirits serves to arrest the yeast fermentation with part of the sugar unfermented; sherries, which may be sweet or dry and are characterized by flavors induced by various types and degrees of oxidation; and flavored wines such as vermouths and trade-named proprietary specialty wines.

21.8.3 WINEMAKING

After harvesting at the correct stage of maturity, the grapes are destemmed, crushed and sulfur dioxide added to inhibit the growth of undesirable microorganisms, inhibit browning enzymes and serve as an antioxidant. If white wine is being made, the next step is the separation of the fluid must from the pomace (skins, seeds and part of the pulp). This is usually achieved by holding the crushed grapes in a large tank fitted with a screen through which free-run juice can pass. Juice is removed from the remaining material using a press. If red wine is being made, the separation occurs during fermentation; after the fermented juice has been run off, the remaining material is pressed to increase the yield and concentration of extractives.

Fermentation commonly occurs in large tanks in which the must is inoculated with selected yeasts. After fermentation has been completed, the wine is allowed to settle so that yeast cells and other fine suspended materials (known as *sediment* or *lees*) can collect at the bottom of the container. The relatively clear wine is then racked off its lees and stored in tanks or casks. Several additional rackings, along with finings, filtrations and stabilization treatments, may be required to produce wine that is and will stay clear until consumed. It is usual to age red (and some white) wines in wooden barrels for varying periods of time (up to 2 years in some instances) prior to blending and filling into the final package (Jackson, 2008).

Sparkling wines are made by fermenting for a second time wine that has been stabilized and fined beforehand. Yeast is added, together with fermentable sugar (typically sucrose), a rule of thumb being that 4 g of sugar per liter of wine will produce 1 atm of CO_2 pressure on fermentation; a final pressure of 6 atm is usually desired. For bottle-fermented sparkling wine, the wine is filled into champagne-type bottles, which are sealed with large wired- or clamped-on corks especially made for sparkling wines, or with plastic-lined crown seal caps. The sealed bottles are then stacked horizontally in a cool place to ferment (a process which typically takes several weeks) and then left undisturbed for 1–4 years to allow the wine to age.

The bottles are then placed on racks and a process (known as *riddling*) begins to remove the yeast sediment. By a process of turning and tilting each bottle, the sediment is moved into the mouth of the bottle. Following this, the neck of the bottle is placed in a bath at −15°C, which results in the formation of an ice plug containing the sediment. The bottle is then turned about 45° from the vertical and opened, whereupon the ice plug is pushed out by gas pressure. The *dosage* (syrup to adjust the sweetness of the wine) is then added, the level of wine is replenished if necessary and the bottle recorked with its final natural cork or plastic stopper which is wired into place. Today, automatic equipment is used in many wineries to perform these tasks.

21.8.4 INDICES OF FAILURE

The major index of failure in wines is oxidation resulting in dull, flat, "oxidized" flavors. With their lower levels of phenolics, white wines are more prone to oxidation and exhibit a loss of freshness, fruitiness and the development of browning and undesirable flavors. With red wines, the situation is more complicated, and some red wines are even given small, controlled doses of O_2 during maturation in a process termed *micro-oxygenation* with the objective of improving wine color, aroma and texture (Reeves, 2010). Oxidation in red wines involves condensation polymerization reactions between tannins and anthocyanins, resulting in loss of pigmentation and changes in color.

As discussed in Chapter 10, the style and development of wine is strongly influenced by the choice of closure because of the different O_2 barrier properties of the closures. Experts disagree as to whether some amount of O_2 benefits wine maturation after bottling, and some consider that a certain degree of oxidation is desirable in some wines (e.g., tannic reds, sherries and tawny ports) and undesirable in others (e.g., most whites and rosés). Oxidation reactions are assumed to play a dominant role in wine aging and seem to be related to measured values of O_2 transfer through various types of closures.

21.8.5 PACKAGING

Immediately prior to packaging, a small amount of sulfur dioxide may be added to the wine which is then given a final filtration. The potentially harmful effects of oxidation by air in the headspace of the package and dissolved in the wine are minimized or prevented by various procedures. The wine may be stripped of dissolved O_2 by passing bubbles of N_2 through it, and the package may be purged with N_2 or Ar and filled so as to displace the gas without introducing air. Other antioxidants (such as ascorbic acid) or other microbial inhibitors may be used, and the wine may be pasteurized or filtered through a membrane so as to be effectively sterile as it is packaged.

21.8.5.1 Glass

The most common form of packaging used for wines is the glass bottle sealed with natural cork. Cork is the outer bark of the cork oak tree (*Quercus suber* L.) and is tough, light and elastic. They are typically sterilized by exposure of damp corks in sealed plastic bags to SO_2, which seems to inactivate any microorganisms of concern. However, this treatment has no influence over the development of cork taint.

Copete et al. (2009) reported the incidence of halophenols and haloanisoles in aged Spanish red wines, with the most abundant being 2,3,4,6-tetrachloroanisole (TeCA) and TCA (6.8% and 5.3%, respectively). Of total wines sampled, 16.1% were contaminated with one or more compounds, with the most contaminated wines being those aged for at least 12 months. The cork stopper was not the only source of the tainting compounds; other possible sources were the wooden materials used during winemaking.

A variety of alternatives to the traditional cork closure have been developed, and these were discussed in Section 10.1.3.2. There is no doubt that closures have an important influence on wine quality during aging in bottles, and the increasing diversity of wine closures and their effect on wine development after bottling has been the subject of intense research. A review by Silva et al. (2011) focused on the impact of closures on wine quality during bottle storage and discussed the effectiveness of closures in protecting wine and the impact of closures on wine organoleptic properties. The role of closures in the removal and/or addition of undesirable compounds from/to wine was also discussed.

Variables such as closure type, gas flushing of empty bottles with inert gas, filler style, equipment maintenance, filler speed and preclosure headspace flushing affect the DO level in bottled wine (Reeves, 2010). An empty bottle contains 750 mL of air or over 200 mg O_2, and flushing bottles with 1–2 volumes of inert gas (CO_2, N_2 or Ar) may reduce the potential O_2 contribution from the bottle to 1–3 mg L^{-1}. Once the bottle is closed, it contains O_2 from the original bulk wine, headspace O_2 remaining after any gas flushing or vacuum application at the time of closure application and any O_2 within a cellular structured closure if such was used.

Headspace height depends on the wine filling level (55–63 mm) and on the length of the cork stopper (38, 44, 49 or 53 mm). Generally, a 15 mm headspace is maintained to avoid partial cork ejection in the case of headspace gas compression caused by thermal expansion of the liquid. This corresponds to 1–2 mg of O_2 available for dissolution in wine (or 1.3–2.7 mg L^{-1}) if a vacuum has been drawn in the neck of the bottle (Karbowiak et al., 2010). During the corking operation, the closure compresses the headspace atmosphere and, if no vacuum is drawn, this displacement creates a potential increase of O_2 dissolution into wine that could lead to a fourfold increase of O_2 uptake. Because cork contains between 80% and 85% of air in its cellular structure, a classical closure, with pre-compression dimensions of 44 mm length × 24 mm diameter, already contains about 4.8 mg of O_2 which represents a potential source of O_2 that could slowly diffuse into the headspace, even if the headspace has been sparged with inert gas (Karbowiak et al., 2010). With O_2 playing a pivotal role in the development and longevity of bottled wine, the O_2 level in the newly packaged wine and the quantity that subsequently ingresses are key determinants of shelf life (Reeves, 2010).

Because many types of wine are damaged by sunlight, the bottles are usually of colored glass, commonly dark green or brown. Bottled wine with cork closures is normally stored in the horizontal position so that the corks are kept moist, as it is assumed that this provides a better barrier to the ingress of O_2. However, a recent review (Karbowiak et al., 2010) concluded that there is no consensus on the effect of bottle position on O_2 mass transfer and wine aging over time and cited contradictory research findings to support their conclusion.

In champagne and sparkling wine, the concentration of dissolved CO_2 is an important parameter because it directly affects the sensory properties. Consequently, keeping the dissolved CO_2 molecules as long as possible inside the bottle during aging is an important challenge for champagne and sparkling winemakers. Natural cork stoppers are commonly used for champagne corking, but they are not completely hermetic with regard to gas transfers. Liger-Belair and Villaume (2011) reported losses of dissolved CO_2 close to 30% (11.5–3.5 g L^{-1}) in champagne aged for 75 months at 12°C. Both champagne temperature and bottle volume were found to be key parameters with regard to the kinetics of CO_2 losses through the cork, with smaller bottles showing a greater loss (Figure 21.6).

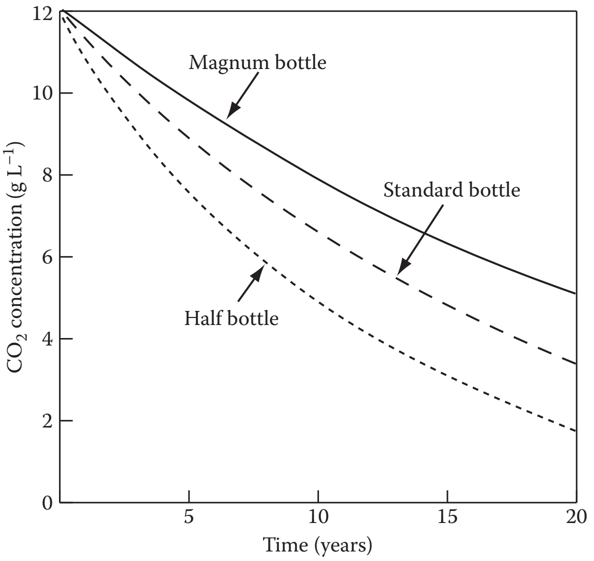

FIGURE 21.6 Theoretical concentrations of dissolved CO_2 in champagne during the aging process (cellar temperature of 12°C) for three distinct bottle types, namely, a magnum bottle (1.5 L), a standard bottle (750 mL) and a half bottle (375 mL). (From Liger-Belair, G. and Villaume, S., *J. Agric. Food Chem.*, 59, 4051, 2011.)

21.8.5.2 Plastics

21.8.5.2.1 Bag-in-Box

The most significant change in the packaging of wine (especially white wine) resulted from the development of the bag-in-box (BIB) package, a flexible, collapsible, fully sealed bag made from one or more plies of synthetic films, a closure and tubular spout through which the contents are filled and dispensed and a rigid outer fiberboard box or container. The bag-in-box concept appeared in the United States in the late 1950s, being introduced into the dairy industry in the form of a disposable, single-ply bag for bulk milk in 1957. By 1962, it had gained acceptance as a replacement for the returnable 19 L can used in institutional bulk milk dispensers (Arch et al., 2009). It also found use in nonfood applications such as the packaging of sulfuric acid to activate dry-charge batteries.

Interest grew during the mid-1960s in Australia, and a PVdC copolymer-coated PA-LDPE laminate inside a fiberboard box entered the market in Melbourne in the 1970s as the first BIB package for wine. Today, five-layer coextruded bags are used that rely on the barrier properties of EVOH copolymer, the strength of PA and the sealability of LLDPE.

Metalized PET can also be used to improve O_2 barrier properties, but it has lower flex resistance. The OTR of multilayer metalized laminates can be as low as 0.0043 mL m^{-2} day^{-1}. The physical strength of the bag is of prime importance, and it must remain intact during distribution and subsequent storage. During transportation, the bag is subjected to vibration which is transmitted to the wine through the materials that flex. Because all flexible materials have a fatigue life, eventually a hole appears and the bag fails. Methods of overcoming this problem include the use of polymers which have high flexure resistance and ensuring that the bag and box volumes are close.

Taps used in BIBs are now typically multicomponent types made from a variety of compounds including PP, LDPE and thermoplastic elastomer resin. Doyon et al. (2005) reported that up to 60% of total O_2 ingress in BIB is through the tap, and it is highly temperature sensitive (Q_{10} = 1.9 between 23°C and 30°C). Published values for OTRs of tap systems are in the range 0.04–0.2 mL tap^{-1} day^{-1}.

Fu et al. (2009) investigated the effects of temperature (22°C, 35°C and 45°C) and storage time (48, 30 and 15 days) on the quality of white wine in BIB. Color, free and total SO_2, total aldehyde and total phenol were monitored and correlated with OTR. The quality changes were significantly affected by OTR of the BIB, and the valve contributed to more than 60% of the OTR of the whole package.

21.8.5.2.2 Bottles

Wine packaged in PET bottles is becoming increasingly accepted as it offers considerable reductions in weight and not insignificant reductions in total volume for the same content volume (Reeves, 2010). For example, an airline can save between 35% and 45% of the total weight currently involved in carrying wine and gain about 15%–20% additional space in a bar cart by replacing glass bottles with PET bottles.

The decrease in quality of red and white wines packaged in 1 L PET bottles with and without an O_2 scavenger was compared to wine packed in glass bottles by Mentana et al. (2009). All bottles were closed with screw caps and stored at 15°C–18°C in the dark for 7 months. Classical enological parameters including the anthocyanin fraction and the volatile fraction were monitored. Wines in the PET bottle with O_2 scavenger were similar to those in glass, particularly for red wines, although some oxidation as well as scalping occurred in the PET bottles. Red wine bottled in PET showed significant losses in most of the volatile compounds, including alcohols, acids and esters, although the concentration of some compounds increased which the authors could not explain. Fewer compounds were scalped by the PET bottles with an O_2 scavenger, and from white wines in both types of PET bottles.

Changes in the chemical and sensory quality of white and red wines packed in glass bottles, monolayer and multilayer (with nylon-MXD6) PET bottles and BIB with EVOH copolymer were assessed by Ghidossi et al. (2012). Commonly used and commercially available package volumes were used (185 and 750 mL for bottles and 3 L for BIB) and the wines were stored for up to 18 months at 20°C in the dark. White wine was noticeably affected after 6 months in PET monolayer bottles. In multilayer PET bottles, as well as in BIB containers, the results were similar to those in glass bottles. No significant differences were detected for red wine. Sensory analysis confirmed the chemical analyses and no differences were observed.

The 10–20 ng g^{-1} of acetaldehyde that may be present in PET bottles prior to filling is not a problem for wine because not only will any free acetaldehyde rapidly react with free SO_2 rendering it non-odorous but the resulting reduction in free SO_2 (about 0.003 mg L^{-1}) will be insignificant. Moreover, acetaldehyde bound to SO_2 is found in wine as a result of normal fermentation (Reeves, 2010).

21.8.5.3 Metal

Wine has been canned in small quantities since the 1960s, using beverage cans made from aluminum or very occasionally tinplate. Although widely accepted for many beverages, cans have not been especially well received as packaging for wine. When packaging still wines in cans, it is necessary to increase the internal pressure in the cans by injection of N_2 or carbonating the wine to an internal pressure of about 170 kPa in order to prevent collapse of the can body. This is because the beverage cans are constructed in such a way that they rely on a significant internal pressure to augment the inherently low strength of the can body itself. The two main requirements for the successful packaging of wine in cans are the nature and integrity of the enamel lining on the inside walls of the can and the O_2 content of the wine at the time of filling. Modern epoxy enamel coatings are claimed to withstand 35 mg L^{-1} free SO_2 and up to 250 mg L^{-1} total SO_2. The O_2 content should be as close to zero as possible to minimize undesirable degradative reactions; this can be achieved by using N_2 gas flow closure. Wine in metal cans may from time to time show problems with sulfur-like odors (Reeves, 2010).

21.8.5.4 Laminated Paperboard Cartons

Since the early 1980s, increasing quantities of popular still wines have been packaged aseptically in plastic-alufoil-paperboard laminated cartons. It is not expected that the wine in cartons would be held by consumers for aging over long periods of time, and thus a shelf life of 6–12 months is all that is required. This can be achieved, as the foil in laminates provides a good O_2 barrier (OTR about 0.02 mL m^{-2} day^{-1}) providing about 12 months' shelf life even with packs as small as 200 mL. As with all other forms of wine packaging, the DO and headspace O_2 would be a significant contributor to loss of initial free SO_2 and hence influence shelf life. Brick-type packs can be formed with zero headspace, and so with good wine handling and filling technology, there is no reason why the initial DO levels in the packed wine would be significantly different to bottled wine (Reeves, 2010).

Buiatti et al. (1997) found that wine in cartons could be stored for up to 24 months, as measured by several quality-related properties, and that this was longer than for PET and BIB packaging. However, recent improvements to the barrier and scavenging properties of PET, as discussed earlier, have improved the performance of this type of package.

Scalping of flavors by plastic in contact with wine could present problems in certain situations. Licciardello et al. (2009) determined the sorption kinetics in LLDPE and CPP of two wine volatiles (ethyloctanoate and linalool) chosen on the basis of their low threshold and high odor activity value from a model solution simulating wine composition. Ethyloctanoate was sorbed more into CPP than LLDPE, and to a much greater extent than linalool, as a consequence of the different polarity of the molecules. The amount of ethyloctanoate lost at steady state led to a significant imbalance in the original aroma composition.

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22 Legislative and Safety Aspects of Food Packaging

22.1 INTRODUCTION

22.1.1 Package Selection Criteria

A number of criteria must be considered when selecting a packaging system for a food. These include the following:

1. The stability of the food with respect to the deteriorative chemical, biochemical and microbiological reactions that can occur. The rates of these reactions depend on both intrinsic (compositional) and extrinsic (environmental) factors.
2. The environmental conditions to which the food will be exposed during distribution and storage. The ambient temperature and humidity are the two most important environmental factors and they dictate the barrier properties required of the package.
3. The compatibility of the package with the method of preservation selected. For example, if the food is being thermally processed after packing, then the packaging must obviously be able to withstand the thermal process. Likewise, if the food is to be stored at freezer temperatures after packing, then the packaging must be able to perform at these temperatures.
4. The nature and composition of the specific packaging material and its potential effect on the intrinsic quality and safety of the packaged food as a consequence of the migration of components from the packaging material into the food.

The latter consideration—namely, the migration of potentially toxic moieties from the packaging material to the food—is of major concern in the selection and use of plastic packaging materials for food packaging. However, the migration of components from the packaging to the food occurs with other packaging materials as well and these will also be discussed in this chapter.

22.1.2 Migration

In food packaging terminology, *migration* is generally used to describe the transfer of substances from the package to the food. Substances that are transferred to the food as a result of contact or interaction between the food and the packaging material are often referred to as *migrants*. However, it is important to note that migration is a two-way process because constituents of the food can also migrate into the packaging material. An example is the “scalping” of flavor compounds from fruit juices by plastics and this was discussed in Chapter 21. In addition, compounds present in the environment that surrounds the packaged food can be sorbed by the packaging and migrate into the food. For example, perfumes from soaps can be picked up by fatty foods under certain circumstances, which depend, among other factors, on the nature of the packaging materials used for the soap and the food, as well as on the proximity of the two products and the time of exposure.

It is important to distinguish between *overall migration* (OM; originally referred to as *global migration*) and *specific migration* (SM). OM is the sum of all (usually unknown) mobile packaging components released per unit area of packaging material under defined test conditions, whereas SM relates to an individual and identifiable compound only. OM is, therefore, a measure of all compounds transferred into the food whether they are of toxicological interest or not, and will include substances that are physiologically harmless. Mass transport by diffusion is one of the most important processes that occur during the shelf life of packaged foods, and legislation to limit the quantity of migrants in foods is discussed later in this chapter.

The migration of molecules from the packaging material into the food is a complex phenomenon, and most mathematical treatments of transport processes are derived initially from a consideration of gaseous diffusion as discussed in Chapter 4. It is worth recalling that diffusion in liquids is approximately one million times slower than in gases, and diffusion in solids about one million times slower than in liquids. In most cases, migration from a polymer package into a food can be described by Fick's second law, which was derived in Chapter 4:

$$\frac{\delta c}{\delta t} = D\frac{\delta^2 c}{\delta x^2} \tag{4.7}$$

This simplified form of Fick's second law of diffusion applies under circumstances where diffusion is limited to the x-direction and D is independent of concentration that is usually true in polymers above their T_{g}. A solution of Equation 4.7 describing the flux J of substance m_{t} migrating into the food in time t across a surface of area A is

$$J = \frac{m_{\mathrm{t}}}{A} = 2c_{\mathrm{P_o}}\left[\frac{\beta}{1+\beta}\right]\left[\frac{D_{\mathrm{p}}t}{\pi}\right]^{1/2} \tag{22.1}$$

where

$$\beta = \frac{1}{K}\left[\frac{D_{\mathrm{F}}}{D_{\mathrm{p}}}\right] \tag{22.2}$$

and c_{Po} is the initial concentration of a migrant in the polymer. Equation 22.2 shows that the magnitudes of the diffusion coefficients (D_{F} and D_{P}) in both the food and the polymer phases, respectively, are important. The partition coefficient K gives the ratio of the concentration of the migrant in the polymer to that in the food at time t. In most cases, D_{F} is orders of magnitude greater than D_{P} so that $\beta >> 1$ (i.e., the concentration gradient of the migrant in the food is negligible), and migration is controlled by the slower diffusion of the migrant in the polymer phase. If, on the other hand, $\beta << 1$ (i.e., because of the poor solubility of the migrant in the food), migration will be dominated by migration in the food as indicated in the following equation:

$$\frac{m_{\mathrm{t}}}{A} = \frac{2c_{\mathrm{Po}}}{K}\left[\frac{D_{\mathrm{p}}t}{\pi}\right]^{1/2} \tag{22.3}$$

Equation 22.1 shows that m_{t} is proportional to the square root of time. This is a common result in the initial stages when up to 60% of the migrant is lost from a polymer to a food. Mathematical solutions of Fick's second law for cases involving different volumes, types of food phases, fixed or agitated systems, or with boundary layers can be found in Crank (1975). Detailed aspects of migration have been discussed by other authors (e.g., Piringer, 2007; Mercea and Piringer, 2008; De Meulenaer, 2009) and should be consulted for further details.

There is a general consensus about the usefulness of mathematical modeling of migration to limit laboratory tests that are tedious and costly, and there is now the possibility to use mathematical modeling in order to prove compliance with legislation in both the EU and the United States.

Poças et al. (2012) analyzed mathematical models to describe migration from packaging into food using two approaches: Fick's second law and a kinetic model based on the Weibull distribution function. Results indicated that the Weibull model can be used to describe the migration from packaging to foods with the advantage of significant simplicity of calculation compared to Fick's second law. The model can also be applied to packaging systems with mass transfer processes more complex than those described by simple diffusional phenomena. In addition, this simple model can potentially be used in probabilistic approaches for exposure assessments of consumers to migrants originating from packaging materials.

22.2 REGULATORY CONSIDERATIONS

22.2.1 General Requirements

Concern about the wholesomeness and safety of foods has increased dramatically over the last century, particularly in those countries where food security is not a problem. An increasing understanding of, and interest in, technological matters on the part of consumers and organized consumer groups, coupled with a recognition that neither government nor industry can guarantee the safety of food, has lent support to this concern.

Safety is an emotive issue, and because everyone must consume food to live, the safety of food is especially emotive. Most concern usually focuses on food additives, both those added intentionally to the food and those ending up in the food from, for example, the packaging material or processing equipment. A detailed discussion of food safety is outside the scope of this book but the basic concepts will be presented to put the discussion that follows into perspective.

It is worth repeating the oft-quoted saying of the sixteenth-century Swiss alchemist and physician (and the patron saint of toxicology) Paracelsus (also known as Auroleus Phillipus Theophrastus Bombastus von Hohenheim) that "all substances are poisons; there is none that is not a poison; the dose differentiates a poison and a remedy." The last phrase is particularly important; only the dose makes the difference. Attempts to determine what a "safe" dose is lie at the heart of the problem faced by legislators and regulatory authorities.

Because food safety is a subject of intense study by a large group of highly sophisticated scientists, many consumers think that food safety determination can be solely a scientific process. That this is not so has been pointed out by several authors including one (Zeckhauser, 1979) who stated that

1. There is no known way to demonstrate absence of risk
2. Controlled experiments, the most reliable means for assessing risk levels, cannot ethically be applied to humans
3. Retrospective studies are unreliable
4. Reliance must, therefore, be placed principally on animal studies
5. Unfortunately, the mechanisms for extrapolating from risks to animals at high concentrations to risks to humans at low concentrations are unreliable

It follows from the preceding paragraph that absence of evidence of harm is not evidence of absence of harm. It is important to note that it is not the toxicity of the chemical at the concentrations at which it is present in the packaging material that is at issue here, but rather the toxicity of the chemical at the concentration at which it is present in the food after migrating from the packaging material.

The various terms used in toxicology need to be defined. The *toxicity* of a substance is its inherent capacity to produce injury when tested by itself. Almost any chemical substance can be shown to be toxic if tested at some sufficiently high level of consumption in experimental animals. Thus, a chemical may be toxic (i.e., inherently capable of producing injury when tested by itself) without being a *hazard* (i.e., likely to produce injury under the conditions of exposure as in a diet).

The concern, therefore, is not directly with the intrinsic toxicity of a particular chemical component of a food, but rather with the potential hazard of that material when the foods in which it is present are consumed.

Underlying the idea of food safety is the risk/benefit concept. *Benefit* can be defined as something that contributes to an improvement in condition or promotes well-being, while *risk* is the possibility of an adverse event occurring such as loss, injury, disadvantage or destruction and can be subdivided into two categories: vital and nonvital. A *vital risk* is one necessary or essential to life, while a *nonvital risk* does not usually involve a threat to life but may lead to injury, loss or damage. Although the difference between vital and nonvital risks is not always clear-cut, the categories of risks are different. The terms risk and benefit are not opposites, because risk always and explicitly includes the element of chance; benefit does not (IFT Expert Report, 2009).

Risks can also be subdivided into voluntary and involuntary risks. An example of a *voluntary risk* is cigarette smoking, where the risk of lung cancer is likely but no one is compelled to smoke (passive smoking is an *involuntary risk*). Another example of an involuntary risk would be a food additive in a staple item of the diet, if the additive had been shown from animal tests to be carcinogenic. In this situation, consumers would have difficulty avoiding the risk since the food was a staple item. An investigation of consumer attitudes toward technological risk concluded that the public's willingness to accept voluntary risks is approximately a thousand times greater than that for involuntary risks, and the risk of death from disease appears to be a psychological yardstick for establishing the acceptability of other risks. The consumption of a chemical that had migrated from a packaging material into a food would be classified as an involuntary risk, even if the chemical had regulatory approval.

The toxicity assessment of food additives usually follows a decision-tree approach. Acute, subchronic and chronic toxicity tests are normally required. The final phase of toxicologic evaluation involves an assessment of the potential risk to humans, and, in particular, the extrapolation of high-dose experiments with animals to low-dose risk assessments of humans. The maximum dose at which there are no observed effects is called the no observed effect level (NOEL). Sometimes the term no observed adverse effect level (NOAEL) is used instead of NOEL to distinguish between an observed effect that is adverse and an effect that is not.

Acceptable daily intake (ADI) is generally used for substances intentionally added to food. Tolerable daily intake (TDI) is generally used for substances appearing in food but not deliberately or intentionally added, for example, chemicals migrating from packaging material into the food. The ADI or TDI is defined as the amount of a chemical, expressed on a body weight basis (using standard body mass of 60 kg) that can be ingested daily over a lifetime without appreciable risk to health. A TDI for a chemical is generally calculated by dividing the lowest NOAEL revealed by toxicity tests by a factor, usually 100, known as a safety factor or uncertainty factor (UF). The incorporation of a safety factor or UF gives an additional margin of reassurance to take account of the possibility that humans may be more sensitive than animals, and that among humans, some may be more sensitive than others. Thus, a TDI errs on the safe side, producing a conservative estimate of the intake of a food chemical likely to be without risk for humans.

Various mathematical models have been proposed for the relationship between dose and response, and much debate has resulted, particularly over the appropriateness or otherwise of a linear extrapolation. In connection with carcinogens, debate has centered over whether or not it is possible to have a "no-effect" or threshold level of a carcinogen in a food. Different approaches to evaluating the nature of the low end of the dose–response curve and the possible existence of thresholds for toxic agents has been discussed by Boobis et al. (2009).

Returning to the risk/benefit concept, the evaluation of the benefit arising from the presence of a particular chemical in a food is also fraught with difficulties and is ultimately a subjective decision. Manufacturers package foods in a variety of packaging materials to achieve certain benefits such as extending the shelf life of the food, or making its storage and preparation for consumption more convenient, or reducing the cost of the food compared to its cost if another type of packaging material were used. The fact that a component of the packaging material may migrate into the food and pose a risk to the consumer requires that the benefits arising from the use of the particular packaging material be balanced against the risk arising from consumption of the component. Attempting to quantify the risks and benefits and then arrive at a decision that a certain packaging material should be permitted for use because the benefits outweigh the risks is extraordinarily complex, and because it is ultimately subjective, there will always be some consumers (and manufacturers) who will disagree with the final decision.

The ways in which decisions are made about the migration of components from packaging materials into foods differ to varying degrees in various countries around the world and are detailed in a recent book (Rijk and Veraart, 2010). Rather than describe the situation in each country, the legislation adopted by the United States and the EU will be discussed because, between them, they account for a large proportion of packaging materials used with foods, and many other countries have modeled their own legislation on one or the other of these approaches (Heckman, 2005).

It is worth noting that there have not been any documented cases of deaths arising from the consumption of food containing food contact substances that have migrated from packaging. This is in contrast to the many deaths each year resulting from microbial contamination of food.

22.2.2 United States of America

The 1906 Food and Drugs Act was the first time that the U.S. Government exercised the principle that it has a duty to protect public health by controlling the adulteration of food. Although adulterated food became less common, the provisions of the legislation were clearly inadequate to insure that public health was protected.

In 1938, the federal Food, Drug and Cosmetic Act (FDCA) was introduced. Among other provisions, it prohibited foods dangerous to health; prohibited unsanitary packages; established the Food and Drug Administration (FDA); established fines for unauthorized practices; and gave the FDA the authority to close plants and to issue injunctions. However, it did not control food additives, except where such additives were already known to be poisonous substances. While this legislation provided an improvement over the previous legislation, the laws regarding toxic additives were handled in an ad hoc fashion and only those additives with a long toxic history were acted upon.

In 1958, congress passed the Food Additives Amendment to the 1938 Act. This amendment required the manufacturer to establish the safety of any product about to be marketed and the government had the responsibility to check the evidence of safety supplied. The shift in the burden of proof of safety from government to industry meant that manufacturers were required to demonstrate the safety of additives before they would be allowed to be used. The FDA generally defines “safe” as requiring “a reasonable certainty in the minds of competent scientists that the substance is not harmful under the intended conditions of use” (§ 170.3(i)). It is not altogether clear what a “reasonable certainty” is, which experts are qualified or even expert, and how the intended conditions of use are to be defined (Heckman, 1992).

§ 348(c)(3)(A) of the amendment (often referred to generally as the “Delaney clause” after New York congressman James J. Delaney who was Chairman of the House Rules Committee) states in part:

> ….no additive shall be deemed to be safe if it is found to induce cancer when ingested by man or animal, or if it is found, after tests which are appropriate for the evaluation of the safety of food additives, to induce cancer in man or animal.…

At the same time, congress provided for the approval of commonly used food ingredients by defining Generally Recognized As Safe (GRAS) substances as well as prior-sanctioned food ingredients (i.e., those approved before September 6, 1958). The latter category contains certain substances employed in the manufacture of food packaging materials (§ 181.22). Such substances are excluded from the definition of a food additive, provided that they are of good commercial grade, are suitable for association with food, and are used in accordance with good manufacturing practice.

U.S. legal requirements are published in the Code of Federal Regulations (CFR). The Code is divided into 50 titles or broad areas subject to federal control and includes nearly 1900 sections and 1200 pages. Title 21 is made up of seven volumes and contains general regulations for enforcement of the Food, Drug and Cosmetic Act and the Fair Packaging and Labeling Act. However, these CFR provisions do not even begin to tell the whole picture, since thousands of substances are addressed through nonrule actions by FDA or are not reviewed by the FDA at all (Neltner et al., 2011).

The most important provisions relating to packaging materials can be found in Volume II, Parts 100–199, including lists of specific antioxidants, plasticizers, release agents, stabilizers, and so on, as well as copolymers and resins. Material composition is controlled by specifying the amount of additive that can be used, as well as the types of polymer to which it can be added. Other regulations contain specifications for the residual monomer content and minimum molecular mass, and many of them limit OM from the polymer or the final food contact article. The regulations contain time–temperature–solvent conditions for short-term migration simulations. Selection of extractability conditions depends on the type of food and the conditions of use and, in particular, the thermal treatment applied to the package after filling with food.

Subpart E § 110–80(h) states the following:

> Packaging processes and materials shall not transmit contaminants or objectionable substances to the products, shall conform to any applicable food additive regulation (Parts 170 to 189) and should provide adequate protection from contamination.

The definition of a *food additive* can be found in § 201(s):

> Any substance the intended use of which results or may reasonably be expected to result, directly or indirectly, in its becoming a component or otherwise affecting the characteristics of any food (including any substance intended for use in … packing, … packaging, … or holding food …).

A *food contact substance* (FCS) is specified in § 348(h)(6) as

> Any substance that is intended for use as a component of materials used in manufacturing, packing, packaging, transporting, or holding food if such use of the substance is not intended to have any technical effect in the food.

The FDA identifies any FCS that is reasonably expected to migrate to food under conditions of intended use to be a food additive in § 170.3, which includes the following statements:

> A material used in the production of containers and packages is subject to the definition [of a food additive] if it may reasonably be expected to become a component, or to affect the characteristics, directly or indirectly, of food packed in the container.
>
> If there is no migration of a packaging component from the package to the food, it does not become a component of the food and thus is not a food additive.

In addition to the inherent toxicity of the packaging material components, it is the extent of migration that comprises the parameters of risk assessment of packaging materials (Munro et al., 2002). While the FDA has not provided definitive criteria for determining at what point a substance may reasonably be expected to become a component of food, guidance has been provided by a 1979 U.S. Court of Appeals opinion in *Monsanto v. Kennedy* (Monsanto, 1979), which was concerned with migration of acrylonitrile monomer into food. In this case, the court essentially said that the FDA was required to determine with a fair degree of confidence that a substance migrates to food in more than insignificant amounts for the substance to be classified as a food additive. This case has been cited as authority for the FDA's adoption of what has come to be called the de minimis policy (Middlekauf, 1985). The words de minimis refer to the legal maxim de minimis non curat lex, which is commonly interpreted as meaning that the law does not care for, or take notice of, very small or trifling matters. Under this policy, the FDA has permitted substances that contain low levels of carcinogenic impurities to remain on the market when the amounts expected to become a component of food have been found to be of no toxicological significance or de minimis (Heckman, 1992).

Since migration is the principal mechanism by which components of packaging materials enter food, the focus of the premarket safety evaluation by FDA is a prediction of the amount and nature of the migrants from the packaging material under the proposed conditions of use. These predicted levels of migration are then translated into an ADI derived by dividing the NOEL by an applicable safety factor, generally 1000 for 90-day studies and 100 for chronic data.

Unlike food additives, human exposure to components of packaging materials that have migrated into foods (FCSs) is typically very small. Because complete toxicological data sets are not always available for such migrants, the FDA developed a process in the 1990s to make the evaluation of packaging materials more efficient, instead of relying on the extensive review normally required for food additives. This process is used to determine "when the likelihood or extent of migration to food of a substance used in a food contact article is so trivial as not to require regulation of the substance as a food additive." This trivial level, also known as the *threshold of regulation* (TOR), was based on a large database of carcinogenic potencies. The basic concept is that, because the toxic hazard arising from a substance varies with dose, then for every substance, there must be a level below which the hazard is so low that there is no need for it to be controlled by specific legislation.

The TOR applies when the overall dietary concentration of a packaging material migrant is <0.5 ppb, which equates to an intake of 1.5 μg day^{-1} if it is assumed that the total daily intake of food and drink is 3 kg per person. Substances that are below the threshold value are considered by the FDA to be exempted from regulation as food additives (Munro et al., 2002). The exemption is applicable provided the substance does not contain any carcinogenic constituents or impurities with a TD$_{50}$ (the dose that causes cancer in 50% of the test subjects) of less than 6.25 mg kg^{-1} body weight day^{-1}. Complete details concerning the criteria to be followed in seeking TOR exemption can be found in § 170.39 and in the Federal Register.

FDA's Center for Food Safety and Applied Nutrition (CFSAN) has accepted the concept of "functional barrier" as a subset of the "no migration" exclusion in the definition of food additive (§ 170.3(e)). An exception to the requirement for assessing the migration of materials used in food packaging is made when there is a determination that the material is not reasonably expected to migrate to the food above the TOR, or at least not above a safe limit based on the toxicity of the material in question. If the food contact materials are determined to form a layer that prevents the migration of materials from the outer layers, then a functional barrier is presumed to exist and materials outside the functional barrier are presumed to be unable to migrate into the food. Safety of the materials in the outer layers then requires less scrutiny.

No formal definition for functional barrier exists in the FDCA or in FDA regulations. The concept, however, is addressed in CFSAN guidances regarding recycled plastics and premarket submission for FCSs. An example of a functional barrier is metal foil or a polymeric material of sufficient thickness and impermeability. An example of an exterior layer material is printing ink or adhesive.

As a result of the FDA Modernization Act of 1997 (specifically § 309), the FDA implemented from January 2000 the *Food Contact Notification* (FCN) system as the primary means to regulate FCSs. The FCN system is applicable to all FCSs and represents a radically new approach to their regulation. Under the FCN system, manufacturers can file an FCN instead of a *Food Additive Petition* (FAP) with the FDA, and unless formal substantive objections are made by the FDA, the FCS may be marketed 120 days after filing of the FCN. This compares with an average time of 2–4 years for the FDA to publish a formal food additive regulation when an FAP is filed.

The requirements for an FCN are substantially similar to those for an FAP and will not be detailed here. Note that substances evaluated by the FDA under the FCN process are only allowed to be used in special applications and concentrations that are mentioned in their authorization processes (FCN). To use these substances in other applications, a new FCN has to be submitted to the FDA. In contrast, petition approval results in a "generic" listing in the CFR allowing widespread use. Also, a TOR exemption is effective for any manufacturer/supplier of the FCS. Under all three processes, the submitter bears the burden of demonstrating that the intended use of the FCS is safe.

Within CFSAN, the Office of Food Additive Safety (OFAS) is responsible for premarket evaluation of food and color additives submitted in petitions and notifications, and for the evaluation of GRAS notifications. If the FCS is a polymer, OFAS recommends toxicity testing on the low-molecular weight oligomers (LMWOs; typically 61,000 Da with exceptions for fluorinated compounds) but not on the polymer itself, as the oligomers are expected to be the primary migrants to food from the use of the FCS (Nelson et al., 2011).

The calculation methods used by the FDA to estimate probable exposure will not be described here except for two aspects. One is the "consumption factor" (CF), which describes the fraction of the daily diet expected to contact specific packaging materials. The CF represents the ratio of the weight of all food contacting a specific packaging material to the weight of all food packaged. CF values for packaging categories (e.g., metal, glass, polymer and paper) and specific food contact polymers are summarized in Table 22.1. These values were derived by the FDA using information on the types of food consumed, the types of food contacting each packaging surface, the number of food-packaging units in each food-packaging category, the distribution of container sizes and the ratio of the weight of food packaged to the weight of the package.

They were initially developed from market survey data collected around 1980 and have been periodically revised as newer market data became available.

When the FDA computes exposure to an FCS, it assumes that the FCS will capture the entire market for which it is intended for use. This approach reflects both uncertainties about likely market penetration as well as limitations in the data surveyed. Thus, if a company proposes the use of an antioxidant in PS, then it is assumed that the antioxidant will be used in all PS manufactured for food contact. In certain cases where an adjuvant is intended for use in only a part of a packaging or resin category, a lower CF representing the coverage that is sought may be used. For example, if a stabilizer is intended for use only in rigid and semirigid PVC, then a CF of 0.05 rather than 0.1 could be used in estimating exposure since only about 50% of all food contact PVC could contain the stabilizer.

When new products are introduced, they are initially treated as replacement items for existing technology. FDA generally makes estimates based on the assumption that the new product will capture the entire market. For example, the retortable pouch was initially treated as a replacement for metal cans and was assigned a CF of 0.17. As additional information on actual use of the retortable pouch became available, the CF was lowered to 0.05. In certain cases, the submission of resin or packaging market data may lead to the use of a lower CF.

Before migration levels can be combined with CF values to derive estimates of probable consumption, the nature of the food that will likely contact the food contact article containing the FCS must be known. To account for the variable nature of the food contacting each food contact article, the FDA has calculated "food-type distribution factors" (f_T) for each packaging material to reflect the fraction of all food contacting each material that is aqueous, acidic,

TABLE 22.1
Fraction of Daily Diet in the United States Expected to Contact Specific Packaging Materials, that is, CFs

Package Category	CF	Package Category	CF
A. General			
Glass	0.1	Adhesives	0.14
Metal–polymer coated	0.17	Retort pouch	0.0004
Metal uncoated	0.03	Microwave susceptor	0.001
Paper uncoated and clay coated	0.1	Polymer	0.4
		All polymers[a]	0.8
B. Polymer			
Polyolefins	0.35	PVC	0.1
LDPE	0.12	Rigid/semirigid	0.05
LLDPE	0.06	Plasticized	0.05
HDPE	0.13	PET[b]	0.16
PP	0.04	Other polyesters	0.05
Polystyrene	0.14	RCF	0.01
EVA	0.02	PA	0.02
Acrylics, phenolics, etc.	0.15	All others[c]	0.05

Source: From Guidance for Industry: Preparation of Premarket Submissions for Food Contact Substances: Chemistry Recom-mendations. 2007. U.S. Food and Drug Administration. Available at www.fda.gov/Food/GuidanceComplianceRegulatory Information/GuidanceDocuments/FoodIngredientsandPackaging/ucm081818.htm

[a] Originates from adding CFs for metal–polymer coated, paper–polymer coated and polymer (0.17 + 0.2 + 0.4 = 0.8).

[b] A CF of 0.05 is used for recycled PET applications.

[c] A minimum CF of 0.05 is used initially for all exposure estimates.

alcoholic and fatty. Appropriate f_T values for both packaging categories and polymer types are shown in Table 22.2.

For calculating the concentration of the FCS in the daily diet, the concentration of the FCS in the food contacting the food contact article, <M>, is derived by multiplying the appropriate f_T values by the migration values, M_i, for simulants representing the four food types. This effectively scales the migration value from each simulant according to the actual fraction of food of each type that will contact the food contact article. The estimated daily intake (EDI) is then determined by multiplying the dietary concentration by the total weight of food consumed by an individual per day. The FDA assumes that an individual consumes 3 kg of food (solid and liquid) per day:

$$\text{EDI} = 3\,\text{kg}\,\text{food}\,\text{person}^{-1}\,\text{day}^{-1} \times < \text{M} > \times \text{CF}$$

So a concentration in the daily diet of 1 ppm (1 mg kg^{-1}) corresponds to an EDI of 1 mg FCS kg^{-1} food × 3 kg food person^{-1} day^{-1} = 3 mg FCS person^{-1} day^{-1}. The cumulative estimated daily intake (CEDI) is estimated by considering all sources of exposure, and represents a conservative estimate of the dietary intake of the FCS because it is based on the assumption that the FCS will always migrate at the maximum level found in extraction studies, and that all food contact materials of

TABLE 22.2
Food-Type Distribution Factors (f_T) in the United States for Each Packaging Material to Reflect the Fraction of All Food Contacting Each Material That Is Aqueous, Acidic, Alcoholic and Fatty

	Food-Type Distribution Factors (f_T)			
Package Category	**Aqueous**[a]	**Acidic**[a]	**Alcoholic**	**Fatty**
A. General				
Glass	0.08	0.36	0.47	0.09
Metal–polymer coated	0.16	0.35	0.40	0.09
Metal uncoated	0.54	0.25	0.01[b]	0.20
Paper–polymer coated	0.55	0.04	0.01[b]	0.40
Paper uncoated and clay coated	0.57	0.01[b]	0.01[b]	0.41
Polymer	0.4	0.16	0.01[b]	0.34
B. Polymer				
Polyolefins	0.67	0.01[b]	0.01[b]	0.31
Polystyrene	0.67	0.01[b]	0.01[b]	0.31
Impact	0.85	0.01[b]	0.04	0.10
Nonimpact	0.51	0.01	0.01	0.47
Acrylics, phenolics, etc.	0.17	0.40	0.31	0.12
PVC	0.01[b]	0.23	0.27	0.49
Polyacrylonitrile, ionomers, PVdC	0.01[b]	0.01[b]	0.01[b]	0.97
Polycarbonates	0.97	0.01[b]	0.01[b]	0.01[b]
Polyesters	0.01[b]	0.97	0.01[b]	0.01[b]
Polyamides (nylons)	0.10	0.10	0.05	0.75
EVA	0.30	0.28	0.28	0.14
Wax	0.47	0.01[b]	0.01[b]	0.51
RCF	0.05	0.01[b]	0.01[b]	0.93

Source: From Guidance for Industry: Preparation of Premarket Submissions for Food Contact Substances: Chemistry Recom-mendations. 2007. U.S. Food and Drug Administration. Available at www.fda.gov/Food/GuidanceComplianceRegulatory Information/GuidanceDocuments/FoodIngredientsandPackaging/ucm081818.htm

[a] For 10% ethanol as the food simulant for aqueous and acidic foods, the food-type distribution factors should summed.

[b] 1% or less.

a given type will be made using the FCS (Baughan and Attwood, 2010). The simulants for use in migration studies with various types of foods are listed in Table 22.3.

The default FDA contact ratio is 10 g food in.$^{-2}$ FCM, which is equivalent to 10 g food 6.45 cm^{-2} (0.0645 dm^2) FCM or 1 kg food 6.45 dm^{-2} FCM. If 10 g of food are in contact with 1 in.^{2} of FCM, a migration of 0.01 mg in.$^{-2}$ corresponds to a concentration in the food of 1 mg kg^{-1} (1 ppm). For specialized food contact applications where an assumed ratio of 10 g food in^{-2} is not appropriate, such as in dual-ovenable trays and microwave susceptor applications, the lowest ratio from the actual food contact applications is used, provided that justification can be given for the ratio selected.

TABLE 22.3
Classification of Food Types and Recommended Food Simulants for Food Contact Articles in the United States

Type	Description	Classification
I	Nonacid, aqueous products; may contain salt, sugar or both (pH >5)	Aqueous
II	Acid, aqueous products; may contain salt, sugar or both, and including oil-in-water emulsions of low- or high-fat content	Acidic
III	Aqueous, acid or nonacid products containing free oil or fat; may contain salt, and including water-in-oil emulsions of low- or high-fat content	Fatty
IV	Dairy products and modifications	
	A. Water-in-oil emulsions, high- or low-fat	Fatty
	B. Oil-in-water emulsions, high- or low-fat	Aqueous
V	Low moisture fats and oils	Fatty
VI	Beverages	
	A. Containing up to 8% alcohol	Low alcohol
	B. Nonalcoholic	Aqueous
	C. Containing more than 8% alcohol	High alcohol
VII	Bakery products (other than those under types VIII or IX)	
	A. Moist bakery products with surface containing free fat or oil	Fatty
	B. Moist bakery products with surface containing no free fat or oil	Aqueous
VIII	Dry solids with the surface containing no free fat or oil	Dry
IX	Dry solids with the surface containing free fat or oil	Fatty

Food Types I, II, IVB, VIB and VIIB: 10% ethanol, for aqueous and acidic foods;

Food Types VIA, VIC: 10% or 50% ethanol (actual ethanol concentration may be substituted), for low- and high-alcoholic foods;

Food Types III, IVA, V, VIIA, IX: Food oil (e.g., corn oil), HB307, Miglyol 812, or others (HB307 is a mixture of synthetic triglycerides; Miglyol 812 is derived from coconut oil), for fatty foods.

More refined exposure estimates may be possible with additional information provided in an FCN or FAP. For instance, subdividing packaging or resin categories could reduce the calculated exposure by lowering the CF for the category. The division of PVC into rigid and plasticized categories is one example; another is the division of polymer coatings for paper into subcategories such as PVA coatings, styrene–butadiene coatings, and so on. If an FCS is to be used solely in styrene–butadiene coatings for paper, use of the CF for polymer-coated paper (0.2) would be a gross exaggeration.

Migration levels in food are typically estimated based on the results of migration testing under the anticipated conditions of use or, in certain cases, under the assumption of 100% migration of the FCS to food. A third alternative accepted by the FDA involves migration modeling. If this approach is taken, then the source of any material constants used in migration modeling should be appropriately referenced, whether the source is the FDA migration database or the open literature. Semiempirical methods have been developed to determine migration levels with limited or, in certain cases, no migration data. These diffusion models rely on estimation of diffusion coefficients based on the nature of the migrant and the physical properties of the polymer. The FDA considers that such models may be useful substitutes for, or additions to, experimental data under limited circumstances but has several caveats that should be considered in the application of such diffusion models.

The FDA Food Safety Modernization Act (FSMA), is the most sweeping reform of food safety laws in more than 70 years, and was signed into law in January 2011. It aims to ensure that the U.S. food supply is safe by shifting the focus from responding to contamination to preventing it. However, no changes have been made to the FDCA or FDA regulations related to FCSs.

22.2.3 EUROPEAN UNION

22.2.3.1 Background

The Treaty of Rome was signed in 1956 and the European Economic Community (renamed the European Community [EC] in 1993) was born. After the entry into force of the Treaty of Lisbon in 2009, the EC was transferred to the newly consolidated European Union (EU). One of the original objectives in 1956 was to set up a common market so that goods could be moved as freely within the Community as within national borders. The European Commission (hereinafter referred to as the Commission) is the executive body of the EU and is responsible for proposing legislation, implementing decisions, upholding the Union's treaties and the general day-to-day running of the EU, while the Council of the European Communities (hereinafter referred to as the Council) is the decision-making body of the EU representing the executives of member states, the other legislative body being the European Parliament.

Because different regulations in member states in the EU could constitute a nontariff barrier to trade, it is valid under the Treaty of Rome and the Single European Act for directives to be promulgated that harmonize such legislation. Harmonization of food legislation is usually classified into *vertical directives* (concerned with a specific group of similar products, e.g., coffee extracts) and *horizontal directives* (concerned with subjects of general application to all foods, e.g., additives, materials intended to come into contact with foods, methods of control, and so on). To assist in the free movement of goods, the Commission has given priority to harmonization work in the horizontal sectors.

Directives do not immediately become Community law; rather, they are instructions to governments of member states to bring their own legislation into line within a certain period (typically, 12 months). There is a detailed process of consultation, study and preparation leading up to the promulgation of a directive, and although the resultant legislation is intended to represent a consensus, the views of the Commission carry considerable weight. In contrast, a regulation is automatically converted into the national law of all EU countries 20 days after publication.

The Scientific Committee for Food (SCF) was an advisory body set up by the Commission in 1974. It consisted of individuals nominated by member countries in the fields of toxicology, metabolism, mutagenicity and so on. The SCF constituted an ad hoc working committee in the area of packaging materials. The main task of the Scientific Committee was the preparation of scientific advice in the area of new and harmonized approaches for risk assessment of food and feed. It has now been superseded by the European Food Safety Authority (EFSA). The EFSA is the keystone of EU risk assessment regarding food and feed safety and works in close collaboration with national authorities to provide independent scientific advice and clear communication on existing and emerging risks; however, risk management decisions are made by the Commission.

22.2.3.2 Directives

The Commission initially drew up a framework directive in order to establish general principles for all materials and articles, and criteria and procedures to be followed in drafting specific directives; that is, directives concerning individual sectors to be regulated (e.g., plastics, ceramics, and so on) or individual substances (e.g., vinyl chloride). The framework Directive 76/893/EEC of 26 November 1976 (superseded by 89/109/EEC of 21 December 1988) established two general principles:

1. The principle of the "inertness" of the material and the "purity" of the food, whereby the materials and articles must not transfer to foods any of their constituents in quantities that could "endanger human health and bring about an unacceptable change in the composition of the foodstuffs or a deterioration in the organoleptic characteristics thereof." This regulation applied not only to packaging, but to all articles whose surface could come into contact with food at any stage of production, storage, transport or consumption. For practical reasons, covers and coatings, potable water distribution systems and antiques were excluded.

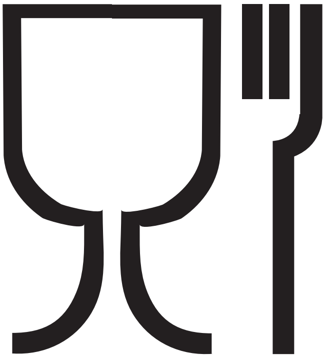

FIGURE 22.1 Symbol that may accompany materials and articles intended to come into contact with food in the EU.

2. The principle of “positive labeling” whereby materials and articles intended to come into contact with foods must be accompanied by the words “for food” or an appropriate symbol, described in Directive 80/590/EEC and shown in Figure 22.1. At the retail stage, Member States have the option not to insist on marking where articles are “by their nature clearly intended to come into contact with foodstuffs.”

In 1989, the framework directive was replaced by Directive 89/109/EEC, which laid down the sectors in which the Commission is asked to establish Community rules and the criteria and procedures to be followed in the drafting of specific directives. Having defined the general framework, the Commission began to study three of the principal materials to be dealt with at Community level, these being regenerated cellulose film (RCF), ceramics and plastics. The most important of these is plastics and is discussed later.

In 1980, the Commission began to draw up rules for what is undoubtedly the most complex and economically important area of packaging, namely plastic materials and articles intended to come into contact with food. Directive 82/711/EEC (amended by Directive 2004/19/EC) laid down test methodology, in particular, simulants and test conditions for plastics, including laminates, where the plastic is in direct contact with the food. RCF, elastomers, rubbers, adhesives, paper and paperboard impregnated with plastic materials were all excluded. Directive 82/711/EEC listed conditions of time and temperature that simulate actual product use conditions. The migration of substances under these simulating conditions should not exceed the limits given in the positive list. Directive 85/572/EEC established the list of simulants to be used in migration tests and included a table of correlations between food groups and their food-simulating liquids.

The overall migration limit (OML) is a measure of the inertness of the material and prevents an unacceptable change in the composition of the food. Moreover, it reduces the need for a large number of specific migration limits (SMLs) or other restrictions, thus giving effective control.

The EU assumes an intake of 1 kg of food in contact with a particular packaging material per 60 kg person per day, which equates to 16.7 g kg^{-1} body weight. A food packaging surface area:volume ratio of 6 dm^2 kg^{-1} is assumed, equivalent to 0.1 dm^2 kg^{-1} of body weight. Directive 90/128/EEC set the OML at a level of 10 mg dm^{-2} of food contact surface area of material or article. The assumption is that 1 kg of food is exposed to 6 dm^2 surface area of packaging material, that is, it forms a 1 kg cube with a food contact surface area:volume ratio of 6 dm^2 L^{-1} or kg^{-1}, the same as a 1 dm (10 cm) cube as shown in Figure 22.2. If each face of the cube releases 10 mg into the food, then an OML of 10 mg dm^{-2} of contact area becomes 60 mg L^{-1} or kg^{-1}. Recall that the default FDA contact ratio is 10 g food $in.^{-2}$ FCM, which is equivalent to 10 g food 6.45 cm^{-2} (0.0645 dm^2) FCM, or 1 kg food 6.45 dm^{-2} FCM, which is close to the EU ratio of 1 kg food 6.0 dm^{-2} FCM except that the FDA assumes 3 kg rather than 1 kg food $person^{-1}$ day^{-1}. In reality, there are very few packages on the

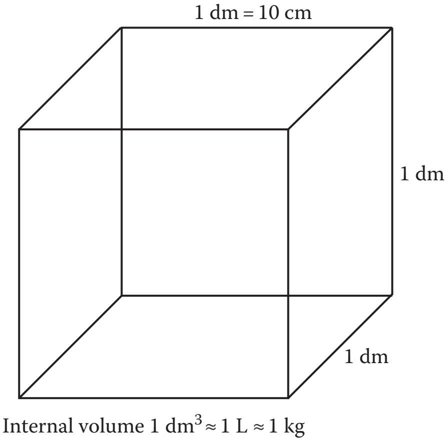

FIGURE 22.2 EU legislation assumes that for packages with a capacity of 0.5–10 L, 1 kg of food is exposed to 6 dm^2 surface area of packaging material, that is, it forms a 1 kg cube with a food contact surface area:volume ratio of 6 dm^2 L^{-1} or kg^{-1}, the same as a 1 dm (10 cm) cube.

market with these dimensions. In most foods, the contact surface area per unit weight of food is substantially larger. For example, in metal cans, the surface area to weight ranges from 8 to 17 dm^2 kg^{-1}. For metal closures, the ratio is 0.2–1.2 dm^2 kg^{-1}. Therefore, the tolerated migration in terms of concentration in the food is higher.

The OML of 60 mg kg^{-1} of food is for articles that are containers or are comparable to containers or that can be filled with a capacity of 0.5–10 L. For smaller containers, the limits apply as migration per surface area. For sheet, film or other materials that cannot be filled or for which it is impractical to estimate the surface area in contact with food, and for caps, gaskets, stoppers or similar devices for sealing, the limits always apply as migration per unit surface area in contact with the food, that is, as mg dm^{-2}. This means that for the majority of packs, the limits apply as amounts per contact surface area and, thus, the conversion factor of 6 dm^2 kg^{-1} is used, which is why this conversion factor is so important. It also means that SMLs are not really based on the consumption of 1 kg of food, but on the amount of food that is in contact with 6 dm^2, which is mostly far less than 1 kg in real life. Grob et al. (2007) suggested that the legal limits in terms of concentration in food should be converted to migration per contact surface area by a ratio that no longer focuses on the 1 L cube but on the current smaller packs. They proposed 20 dm^2 contact surface area L^{-1}, that is, the OML of 60 mg kg^{-1} should correspond to 3 mg dm^{-2}.

In contrast to the United States, no consumption or food-type distribution factors are used in the EU. Oldring (2008) quoted some “pseudo” food CFs that suggested that the food contact area for all packaging in the EU was 20.1 dm^2 person^{-1} day^{-1} of which plastic accounted for 62% or 12.4 dm^2 person^{-1} day^{-1}, which is significantly higher than the EU assumption of 6 dm^2 person^{-1} day^{-1}. However, if the FDA assumption of 3 kg rather than 1 kg food person^{-1} day^{-1} is used, there is much better agreement (18 dm^2 vs. 20.1 dm^2 person^{-1} day^{-1}). Given the diversity of consumption within the EU (use of polyethylene in Benelux and Ireland is quoted as about 10 dm^2 person^{-1} day^{-1} compared to just over 4 for Spain, Portugal and Greece), it would be difficult to derive any meaningful pan-European factors for exposure to migrants from FCMs.

Recently, Foster et al. (2010) suggested that children might be at increased risk to exposure from migrants as they have higher intakes of food per kg body weight compared with adults. In addition, much of the food marketed for/to children is in small portions and, therefore, the FCM surface area:volume ratio is relatively high. In a field study of 297 U.K. children aged 0–6 years, they found that these children, on average, consumed 1.6 times (ages 0–1), 2 times (ages 4–6) and 3 times (ages 1–4) as much food packaged in plastic as estimated by the current EU approach. The mean area of packaging in contact with the food consumed daily per kg body weight was 0.65 dm^2 kg^{-1} for the infants under 1 year, 0.81 $dm^2\ kg^{-1}$ for the 1–4 year olds and 0.66 $dm^2\ kg^{-1}$ for the 4–6 year olds. All 297 children had intakes that exceeded 0.1 $dm^2\ kg^{-1}$ of body weight.

In addition, the directive contained two lists of substances (1340 in total of which 540 are monomers and 800 additives) used in the preparation of plastics for foods. The first, so-called Community list contains substances on which the SCF had delivered an opinion and which are, therefore, authorized and harmonized at Community level. The second, so-called optional national list contained substances on which the SCF had not yet been able to deliver a final opinion for lack of data and which, therefore, did not have Community recognition. Thus, the current list of additives was incomplete because it did not contain all the substances that were currently accepted in one or more member states. Accordingly, these substances continued to be regulated by national laws pending a decision on inclusion in the Community list. The European inventory list of chemicals used to make plastics intended for food contact contains more than 1500 listed substances, and inventory lists of a similar length exist for chemicals used to make paper, can enamels, inks and adhesives (Castle, 2001).

As migration experiments are time consuming, expensive and often complicated to carry out, the use of "generally recognized diffusion models" based on experimental data was approved in the sixth amendment of Directive 90/128/EEC (2001) for estimating the migration level of substances in certain types of plastics as an alternative test method.

The Framework Regulation (EC 1935/2004) is the basic Community legislation covering all FCMs and articles. It defines FCMs and articles and sets basic requirements for them:

1. Shall not endanger human health
2. Shall not change composition of the food in an unacceptable way
3. Shall not change taste, texture or odor of food
4. Shall be manufactured according to GMP

The authorization of substances is divided into a risk assessment performed by EFSA and a risk-management decision by the Commission. Until recently, this authorization procedure applied only to substances used in plastic FCMs or in RCF that were regulated by a specific measure. Since the promulgation of Regulation 10/2011 Plastics Implementing Measure in May 2011, plastics are now covered and the Plastics Directive 2002/72/EC has been repealed. Many of its specific provisions will be implemented over a 4-year period to allow industry additional time to comply with them, for example, use of additives others than plasticizers for plastic layers or plastic coatings in caps and closures. In addition to consolidating all of the EU's directives and regulations on plastic FCMs, this regulation introduced a number of significant changes including expansion of EU plastic legislation to include plastic layers in multimaterial articles (unless they are separated from the food by a functional barrier—see below) and changes in the simulants to be used for migration testing (see Table 22.4). As mentioned earlier, for very small and very large containers, the real surface area:volume ratio of packaged food varies a lot from the conventional assumption. Therefore, Regulation 10/2011 specifies that their surface area should be normalized before comparing testing results with migration limits.

TABLE 22.4
Simulants for Use With Plastic Food Contact Materials in the EU

Simulant A:	10% ethanol, mimicking aqueous foods pH >4.5
Simulant B:	3% acetic acid, mimicking acidic foods with pH <4.5
Simulant C:	20% ethanol, mimicking alcoholic foods
Simulant D1:	50% ethanol: for alcoholic foods with >20% alcohol and for oil in water emulsions including milk
Simulant D2:	Vegetable oil for foods that contain free fats at the surface
Simulant E:	Poly(2,6-diphenyl-*p*-phenylene oxide) also known as Tenax® for dry foods

A correction factor has been established to correct for overestimation in fatty foods: the fat reduction factor (FRF). The conventional assumption is that a 60 kg person consumes 1 kg of food daily. However, the consumption of fat is at most 200 g on a daily basis, and so for lipophilic substances that only migrate into fat, this should be taken into consideration.

No rules have yet been set out for the risk assessment of the use of colorants in plastics and, therefore, their use remains subject to national law. Although all plastics can be coated and printed, coatings, printing inks and adhesives are presently covered by national legislation but not yet by specific EU legislation; therefore, they not subject to the requirement of a declaration of compliance.

A functional barrier is defined as a barrier consisting of one or more layers of any type of material that ensures that the final material or article complies with Regulation 1935/2004 and 10/2011. Nonauthorized substances may be used behind a functional barrier, provided they fulfill certain criteria and their migration remains below a given detection limit (0.01 mg kg^{-1}). Substances that are mutagenic, carcinogenic or toxic to reproduction are not covered by the functional barrier concept. A functional barrier is not necessarily an absolute barrier but a function of the given food packaging application. In the specific case of PET bottles or sheets, an outer and inner layer of virgin PET acts as a functional barrier, while in the core layer some conventionally recycled PET is used. Another functional barrier technology is the application of a SiO_x coating on the inner surface of PET bottles (Welle and Franz, 2008). Cruz et al. (2006) showed the feasibility of employing a functional barrier made from amorphous carbon film deposited by the PECVD process on the inner surface of recycled PET bottles.

22.3 PLASTICS PACKAGING

22.3.1 Vinyl Chloride Monomer

PVC is used for food contact applications, not only for bottle and film applications but also for other uses including liners and sealing gaskets. Vinyl chloride (boiling point −13.9°C) is a colorless gas at ordinary temperatures and pressures but, in industry, it is usually handled as a liquid under pressure in steel cylinders. The acute toxic effects of vinyl chloride have been known since the 1930s when it was rejected as an anesthetic because it was found to be a cardiac irritant. An investigation in the United Kingdom in 1970/1971 into the tainting of spirits packaged in miniature PVC bottles for use in aircraft traced the cause to vinyl chloride monomer (VCM). However, the chronic effects were not made public until January 1974 when the B.F. Goodrich Co. voluntarily revealed to federal and state regulatory officials that, since 1971, three workers at its PVC polymerization plant in Louisville, Kentucky had died of angiosarcoma of the liver. This form of cancer is extremely rare, and workers who were in contact with PVC only and not VCM were apparently unaffected, suggesting that VCM was the culprit. By May 1974, a cause-and-effect relationship between VCM and human angiosarcoma was generally accepted, and confirmed cases of cancer in workers at PVC plants had risen to 19, 17 of whom were already dead.

In 1973, it was discovered that VCM in PVC packaging material could migrate into foods. Reported levels of VCM found in bottles, rigid film and some foods in the period 1974–1977 showed a marked reduction, and this change was also reflected in the levels found in foods such as fruit drink, cooking oil, butter and margarine. EU directive 78/142/EEC laid down the maximum permitted quantity of VCM in plastic materials and articles as 1 mg kg^{-1}, and stated that the quantity of VCM released to the food should not be detectable by a method of analysis with a detection limit of 0.01 mg kg^{-1} (10 ppb). Directives 80/766/EEC and 81/432/EEC established the methods of analysis for VCM in the finished article and in foods, respectively, and were repealed in Regulation 10/2011.

In the United States, the prior sanctions and the food additive regulations for PVC were all promulgated prior to the discovery that VCM caused liver tumors in humans, and, thus, there were no limitations on the residual VCM level in PVC. In response to the findings regarding the toxicology of VCM, the FDA published a series of proposals designed to control the potential exposure to VCM from food contact materials. FDA did not propose to ban or otherwise limit use of PVC per se, however, because there was no evidence that PVC itself is a carcinogen.

In general, the FDA proposed to limit residual VCM levels to 10 ppb in rigid PVC food contact articles and 5 ppb in plasticized, flexible PVC. The FDA also proposed to issue new regulations that would have codified some of the prior sanctions for PVC polymers, as well as to establish a new regulation for rigid and semirigid PVC articles, and establish limits on the residual level of VCM permitted in these articles. This new regulation would have established a 10 ppb limit on the residual level of VCM in these articles. However, the FDA proposals were never finalized because of difficulties encountered in preparing an environmental impact statement for the proposed actions. PVC continues to be used in food contact applications in the United States subject to the limitations provided in the 1986 proposal. A practical result of the proposal was the removal of PVC liquor bottles from commercial use. Today, most rigid PVC applications have been replaced by PET, largely because of cost.

22.3.2 STYRENE MONOMER

Styrene monomer (boiling point 145°C) is metabolized to styrene oxide, which is a potent mutagen in a number of test systems; further metabolism produces hippuric acid. The most frequently observed changes from the toxic effects of styrene in humans are of a neurological and psychological nature: styrene acts as a depressant on the central nervous system, has a toxic effect on the liver and causes neurological impairment.

Vitrac and Leblanc (2007) estimated that median household exposure to styrene from yogurt pots in France ranged between 1 and 35 μg person^{-1} day^{-1} (5th and 95th percentiles) with a likely value of 12 μg person^{-1} day^{-1} (50th percentile). They found that exposure did not vary independently with the average consumption rate and contact times. Thus, falsely assuming a uniform contact time equal to the sell-by-date for all yogurts overestimated significantly the daily exposure (5th and 95th percentiles of 2 and 110 μg person^{-1} day^{-1}, respectively) because consumers with a high consumption showed quicker turnover of stock.

Between 1991 and 1999, the FDA's Total Diet Study analyzed 320 different foods and found styrene residues in 49 of them. In 258 samples containing styrene, the mean concentrations for individual food items varied between 10 μg kg^{-1} for eggs and 274 μg kg^{-1} for strawberries. The median concentration for the 49 foods was 21 μg kg^{-1}.

A TDI of 7.7 μg kg^{-1} body weight day^{-1} was set by the Joint FAO/WHO Expert Committee on Food Additives. A cigarette contains 20–48 μg of styrene.

Styrene contamination of foods is generally apparent as a characteristic, unpleasant, plastic-like chemical odor or taste and is discussed further in Section 22.7.2.

22.3.3 ACRYLONITRILE MONOMER

Acrylonitrile (AN) (boiling point 77.5°C) is a component of several polymers used as food packaging materials, the basic terpolymer material containing as much as 70% AN in conjunction with styrene and/or butadiene.

The FDA began to examine PAN containers in 1974 when a polymer manufacturer submitted test results that indicated that there was the potential for significant migration from PAN containers. In 1975, the commissioner published a regulation that limited residual AN monomer levels to 80 ppm in the wall of the container and stipulated that monomer migration into the food could not be greater than 0.3 ppm.

In 1976, the FDA established an interim regulation limiting AN extraction in food-simulating solvents to 0.3 ppm and making the continued use of AN copolymers in food applications conditional on additional toxicological testing. The following year, the FDA stayed the interim regulations permitting the use of AN copolymers in beverage containers and proposed a reduction of the extraction limit in other food applications from 0.3 to 0.05 ppm. The 1977 action was based in part on proliferative brain lesions observed in rats at 300 and 100 ppm of AN in drinking water after 13 months of a 2 year study. The 1977 ban on the use of AN copolymers for beverage bottles was removed in 1984 on the proviso that the level of residual AN in the container was less than 0.1 ppm. By this time, PET had become firmly established for the packaging of carbonated beverages, and even though AN has a significantly higher melting point and, thus, can be hot filled, it has never gained significant market share for beverage packaging. AN copolymers were not approved for alcoholic drinks.

Acrylonitrile–butadiene–styrene (ABS) resins are used in many food contact applications, where the levels of the three monomers in the polymer are varied to obtain the different properties desired. The correlation of residual AN monomer concentration in AN-containing polymers with AN migration into food simulants is of interest because the FDA regulates the use of these polymers on the basis of the amount of AN that may migrate into food simulants.

22.3.4 PLASTICIZERS

A *plasticizer* is a substance that is incorporated into a material (usually a plastic or elastomer) to increase its flexibility and processability. The vast majority of plasticizers are esters of phthalic acid (phthalates) with a wide variety of long-chain alcohols containing up to 13 carbon atoms; next in importance are those based on adipic acid. About 90% of all plasticizers were used to convert PVC into a soft, elastic material. However, copolymers of PVC and PVdC are plasticized with up to 5% of acetyltributyl citrate (ATBC), and such films used to find widespread use in microwave cooking. They have now largely been replaced by LLDPE films that do not contain any plasticizers.

22.3.4.1 Phthalate and Adipate Esters

Surveys carried out in a number of countries have indicated that, over the last few decades, there has been a fall in the quantity and quality of male sperm, although the effects appear to be variable. There is also evidence that, in some countries, there has been an increase in testicular cancer. Much of the concern focuses on synthetic—and mainly organic—chemicals as highlighted in the book *Our Stolen Future* (Colborn et al., 1997). *Endocrine disrupting chemicals* (EDCs) enter the body from the external environment and mimic or interfere with the human endocrine system. Chemicals that mimic the female hormone estrogen or act as antiestrogens are suggested as being responsible for some observed effects on wildlife such as the feminization of fish. It has been further suggested that these same chemicals may be responsible for the aforementioned male human health problems. A recent book gives details of endocrine-disrupting compounds in foods (Nollet, 2011), and a recent review focuses on phthalate esters in foods (Cao, 2010). An updated review of exposure, effect and risk assessment of EDCs was presented by Muncke (2011).

Phthalates are among the chemicals that have been labeled as xenoestrogens. Of the phthalic acid esters, di-2-ethylhexyl phthalate (DEHP) was the most widely used. DEHP is also known as dioctyl phthalate (DOP), the terms dioctyl and di-2-ethyl being synonymous. Other phthalates include di-isononyl phthalate (DiNP), dibutyl phthalate (DBP) and di-isodecyl phthalate (DiDP). Adipates, such as di-2-ethylhexyl adipate (DEHA), dioctyl adipate (DOA) and di-isononyl adipate (DiNA), are also used frequently as plasticizers in PVC products as replacements for phthalates. Because they are not chemically bound to plastics, phthalates, and to a lesser extent adipates, have become ubiquitous environmental contaminants due to volatilization and leaching from their widespread applications, and are now commonly detected in the environment where they persist. The determination of phthalates is not an easy task, and often they cause "blank" problems when analyzed at low concentrations. Because of their widespread presence in the laboratory environment, including air, vinyl floor coverings, electrical cables, glassware and reagents, false-positive readings can result.

DEHP, together with diethyl phthalate (DEP) and di-isooctyl phthalate (DIOP) have been granted prior sanction by the FDA as plasticizers in the manufacture of food packaging materials for food of high water content only, and are listed in § 181.27 of the CFR. Other phthalate esters have been cleared as plasticizers under § 178.3740 of the CFR for various food contact uses. Today, the majority of PVC used for food packaging does not contain phthalate plasticizers, and many PVC packaging materials are rigid and unplasticized. Minor uses of phthalates in food packaging include use as plasticizers in cap liners made from PVC plastisols.

The EU SML values for DBP, DEHP and DEHA are 0.3, 1.5 and 18 mg kg^{-1}, respectively. A useful review of recent EFSA toxicological evaluations of phthalates used in FCMs has been presented by Lhuguenot (2009).

Zhang et al. (2008) determined DBP in 110 domestic and imported paper packages and foods sold in U.S. marketplaces. The concentration of DBP ranged from 0.14 to 55 mg kg^{-1}, with most lower than 20 mg kg^{-1}, suggesting that migration into food would be very low or undetectable. DBP was only detected in two domestic and four imported food samples with concentrations ranging from 50.01 to 0.81 mg kg^{-1}. In many paper packages, DBP is associated with printing inks and may become a component of food via "set-off," which refers to the process whereby the nonprinted (inner) surface of packages contacts with the printed (outer) surface such as occurs when printed packaging material is stored as rolls or printed containers are stacked or "nested" within each other.

Recently, Cirillo et al. (2011) reported that 92% of foods employed in school meal preparation in Naples contained DEHP, and 76% of them DBP, at detectable levels. The meals were packed in plastic-coated alufoil, and the DEHP median values ranged from 127.0 to 253.3 ng g^{-1}, and DBP median values varied from 44.1 to 80.5 ng g^{-1}. The mean increases of median concentrations of DEHP and DBP in cooked foods before and after packaging were 113% and 125%, respectively. For nursery and primary schoolchildren, DEHP intake via school meals can raise on average the respective EFSA TDI by 18% and 12% and that of DBP by 50% and 30%.

Although plasticizers are not used in PET bottles, a number of studies have reported various phthalates in mineral water bottled in PET. Phthalates may come from bottling lines, cap-sealing resins or water treatment facilities. Background pollution in the laboratory analyzing phthalates may also be a source. A recent literature review showed that contradictory results for PET-bottled water can be explained by the wide variety of analytical methods, bioassays and exposure conditions employed (Bach et al., 2012). It was concluded that more investigations are needed to improve the accuracy of the analytical methods and to clarify the entry pathways of plasticizers in the bottling line.

Glass jars with metal twist closures are widely used for a broad range of foods such as infant foods, pickled herrings, vegetables in oil or water, sauces, peanut butter, milk products, soft cheese products, pesto and so on. Many of these products are intended for storage up to 2 years, and in order to ensure a long shelf life, a plasticized PVC gasket is placed inside the closures to form an airtight seal against the rim of the jar. A lid typically contains 1 g of gasket material of which 250–350 mg is in direct food contact. As PVC gaskets contain 35–45% plasticizer, more than 100 mg plasticizer is exposed to the food. Phthalates are the main plasticizers in some 25% of these gaskets, and in oily foods, phthalate concentrations up to 1000 mg kg^{-1} have been reported.

Plasticizers (predominantly phthalates) are also used in printing inks where they assist adhesion of the ink to the packaging material and improve the ink's flexibility. They can migrate into food either as a result of set-off or by migration through the packaging material.

22.3.4.2 Acetyltributyl Citrate

ATBC (tri-*n*-butyl acetyl citrate) is a plasticizer formed by the esterification of citric acid. It is considered a "prior sanctioned food ingredient" and is not classified as a food additive by the U.S. FDA. It is the most widely used plasticizer in PVdC copolymer films at levels of up to 4.8% w/w. The EFSA has given ATBC a TDI of 1.0 mg kg^{-1} body weight.

ATBC migrates into a variety of foods when plasticized film is used for normal domestic applications including cooking or reheating of meals in a microwave oven. The highest levels of migration would be expected where the film was used in direct contact with a fatty food surface. Zygoura et al.

(2011) reported ATBC migration into cod fillets of 11.1–12.8 mg kg^{-1} (0.11–0.13 mg dm^{-2}) and herring fillets of 32.4–33.4 mg kg^{-1} (0.32–0.33 mg dm^{-2}). The film surface area:weight of fish was ca. 89:1, in contrast to the generally agreed relationship of 6 dm^2 kg^{-1} food (6:1). Fish samples were stored at 4°C and analyzed for ATBC content at time intervals between 12 h and 240 h of contact. Electron beam (EB) radiation at pasteurizing doses did not significantly affect the SM characteristics of the films.

22.3.4.3 Epoxidized Soy Bean Oil

Epoxidized seed and vegetable oils such as epoxidized soy bean oil (ESBO) are widely used in a range of FCMs to serve as multifunctional additives exhibiting plasticizer, lubricant and heat stabilizer properties. ESBO is produced by the controlled epoxidation of soy bean oil in which the C=C double bonds are largely converted to epoxy groups. PVC gaskets used in the lids of glass jars can contain ESBO levels up to 30%, while other materials such as PVdC copolymer and PS used to contain epoxidized oils but at lower levels. ESBO was also employed as a component of enamels and, therefore, was present in the food contact surface of certain metal cans but its use for this purpose appears to have ceased. The use of ESBO, as well as some low molar mass plasticizers such as ATBC and DOA, has increased in recent years as an alternative to phthalates.

ESBO has an SML of 60 mg kg^{-1} food simulant, which corresponds to the OML. In 2007, the SML was lowered to 30 mg kg^{-1} for infant food because the TDI of 1 mg kg^{-1} body weight was often exceeded. Bueno-Ferrer et al. (2010) reported the migration of several plasticizers from commercial lids into the fat simulants 95% ethanol and iso-octane, neither of which are approved simulants in the EU. The results (Table 22.5) revealed that the highest amounts of plasticizers were found when 95% ethanol was used as a simulant. All plasticizers migrated in amounts higher than the current EU legal migration limits. Two of them showed high levels of ESBO and, in the case of the pâté lid, even above the transitional limit of 300 mg kg^{-1}. The pesto sauce showed high levels of ATBC.

22.3.5 ANTIOXIDANTS

Antioxidants are used to prevent the degradation of the polymer as a result of its reaction with atmospheric O_2 during molding operations at high temperature, or when used in contact with hot foods. They are also used to prevent embrittlement during storage. A simple primary antioxidant is butylhydroxytoluene (BHT: 3,5-di-*tert*-butyl-4-hydroxytoluene), a lipophilic compound that is primarily used as an antioxidant food additive (E number E321). However, its use in FCMs has recently declined

TABLE 22.5
Migration of Plasticizers from Commercial Lids to Food Simulants

		Mean Value (mg kg^{-1} Food Simulant)		
Plasticizer	**Simulant**	**Pâté**	**Pesto Sauce**	**Mayonnaise**
ESBO	95% Ethanol[a]	676 ± 282	18 ± 18	71 ± 24
	Iso-Octane[b]	94 ± 49	<LOQ	<LOQ
ATBC	95% Ethanol[a]	22 ± 19	285 ± 12	ND
	Iso-Octane[b]	8 ± 2	19 ± 3	ND
DOA	95% Ethanol[a]	ND	ND	0.23 ± 0.01
	Iso-Octane[b]	0.23 ± 0.05	0.23 ± 0.01	0.53 ± 0.04

Source: Bueno-Ferrer, C. et al., *Food Addit. Contam.,* 27, 1469, 2010.

LOQ, Limit of Quantification; ND, Nondetectable.

[a] After 10 days at 40°C.

[b] After 2 days at 20°C.

TABLE 22.6
BHT Migration into Semisolid and Solid Foods

Food	Temperature (°C)	Duration (days)	Food Mass/ HDPE Surface Area (g dm^{-2})	Migration µg dm^{-2}	Migration %
Margarine	4	4	70	0.5	0.2
		45	130	1.6	0.5
		99	130	2.4	0.8
Whipped topping	4	7	130	0.9	0.4
		14	130	0.9	0.4
		21	130	0.9	0.4
Mayonnaise	21	2	70	4.7	1.8
		8	130	7.4	2.3
		45	130	26.4	8.5
		89	130	36.2	11.3
Vegetable shortening	21	2	70	6.3	2.5
		91	130	58.6	18.4
		206	130	59.2	18.6
Dry milk	21	100	130	17	5.1
Chicken soup mix	21	99	130	50	16.3

Source: Till, D.E. et al., *Ind. Eng. Chem. Prod Res. Dev*., 21, 106, 1982.

somewhat as it has a low SML of 3 mg kg^{-1} and a relatively high migration into fatty food compared to its higher MW alternatives (Cooper, 2008). Secondary antioxidants such as tris(2,4-di-*tert*-butylphenyl)phosphite (known as Irgafos 168) decompose hydroperoxides and remove peroxide radicals as they are formed. Use of both primary and secondary antioxidants usually provides a synergistic effect.

A study (Till et al., 1982) of the migration of BHT from HDPE to foods (skim and whole milk, margarine and mayonnaise) and food simulants found no accumulation of BHT in the aqueous phase. However, when corn oil was the simulant, all the BHT migrated during the 50 day test period. Migration at 4°C to skim and whole milk was less than for corn oil but greater than for migration to water. It was felt that some ingredients from milk could penetrate the HDPE even at such a low temperature, and modify the migration propensity of the BHT. A summary of the results is given in Table 22.6. The mechanism for BHT transfer would appear to be evaporation from the film surface with vapor phase diffusion from the HDPE and adsorption onto the powder.

Cereals packaged in HDPE impregnated with BHT have an extended shelf life, due to adsorption by the cereal of BHT from the package. Lee et al. (2004) evaluated the rate of loss of BHT from a co-extruded HDPE pouch with a heat seal layer of ionomer-EVA impregnated with BHT (0.1137% w/w). The BHT-impregnated pouch showed a notable effectiveness in retarding lipid oxidation of a freeze-dried model food at 45°C and 50% RH as a function of storage time. After 6 days, no BHT was detected in the pouch material.

22.4 METAL PACKAGING

22.4.1 TIN

When tinplate was first used to make containers for food over 200 years ago, many cases of food poisoning, apparently due to ingestion of excessive amounts of metal, occurred. A congress of physicians held in Heidelberg in Germany even went so far as to recommend that "tinplate should be forbidden for the making of vessels in which articles of food are to be preserved" (Reilly, 2007). The quality of tinplate has been greatly improved since those days, and foods that are likely to attack tin are packaged in tinplate containers with an appropriate enamel coating (see Chapter 7). Despite considerable research, it has not yet been demonstrated that tin is an essential element in the diet of humans, although a WHO report suggested that tin deficiency can be produced in rats (Murphy and Amberg-Müller, 1996).

The provisional tolerable weekly intake for tin is 14 mg kg^{-1} body weight and the recommended maximum permissible levels of tin in food are typically 250 mg kg^{-1} for solid foods and 150 mg kg^{-1} for beverages. Although no long-term health effects are associated with consuming tin, a review of published data concluded that there appears to be a small amount of evidence suggesting that the consumption of food or beverages containing tin at concentrations at or below 200 mg kg^{-1} has caused adverse gastrointestinal effects in an unknown but possibly small proportion of those exposed (Blunden and Wallace, 2003). At its 55th meeting, the FAO/WHO Joint Expert Committee on Food Additives (JECFA) assessed the available evidence on the acute toxicity of tin, and concluded that it was insufficient to establish an acute reference dose or to derive maximum permissible levels in canned foods and beverages. However, they reiterated their previously stated opinion that the limited human data available indicate that concentrations of 150 mg kg^{-1} in canned beverages or 250 mg kg^{-1} in other canned foods may produce acute manifestations of gastric irritation in certain individuals.

22.4.2 LEAD

The toxicity of lead, especially to the neonate, is a matter of great concern to regulatory authorities. Abundant evidence supports the fact that during early life, human infants are particularly susceptible to lead exposure, with a greater portion of the retained lead being distributed to bone and brain in infants than in adults. Subacute ingestion of lead by children results in encephalopathy, convulsions and mental retardation. The JECFA has recommended that for adults, the weekly dietary intake of lead should not exceed 50 μg kg^{-1} body weight, and for infants and young children, it should not exceed 25 μg kg^{-1} body weight.

For many years, the side seams of three-piece tinplate cans were soldered with a lead/tin (98:2) solder, resulting in some lead being taken up by the food depending on the amount of solder exposed to the food, the acidity of the food and the time the food had been in the can. Some lead contamination may also originate from the tin coating, which contains a small but finite proportion of lead at levels around 500 mg kg^{-1} (Murphy and Amberg-Müller, 1996). Regulatory limits for lead in most countries are now 2 mg kg^{-1} in canned foods generally, but only 0.5 mg kg^{-1} for baby foods and 0.2 mg kg^{-1} for soft drinks. EC Regulation 466/2001 limits lead in cows' milk and infant formulae to 0.02 mg kg^{-1} and 0.05 mg kg^{-1} in fruit juices. In Europe, EC Regulation 242/2004 limited lead in canned solid foods to 200 mg kg^{-1} and 100 mg kg^{-1} in canned beverages, with levels in canned foods for infants and young children being limited to 50 mg kg^{-1}.

U.S. canners voluntarily stopped using lead solder in 1991. Despite this and a 1995 FDA ban on lead-soldered cans, requiring their removal from shelves by June 1996, this source of lead in the diet has not been fully eliminated. A few countries still use lead-soldered cans for food, and these food items may still occasionally be imported, albeit illegally, into the United States.

To obtain the lower lead levels in baby foods, it was common to use a pure tin solder, which was considerably more expensive than the conventional solder. The newer welded cans have eliminated solder altogether, which has done much to reduce the lead intake from canned foods, typically to about one-tenth.

22.4.3 ALUMINUM

Although aluminum is a nonessential metal to which humans are frequently exposed, it has a long history of safe usage in connection with food and food packaging, and is deemed to be GRAS by the U.S. FDA. Aluminum-containing food ingredients are used mainly as preservatives, coloring agents, leavening agents, anticaking agents and so on.

Although aluminum forms an oxide layer very quickly on exposure to air after manufacture, it can still be attacked by certain foods, especially those containing acids and/or salts. As was discussed in Chapter 7, pure aluminum is not used as a food packaging material. Instead, to provide strength, improve formability and increase corrosion resistance, various alloying elements are added, including iron, copper, zinc, manganese and chromium. These metals, as well as aluminum itself, may migrate into the food if corrosion takes place. Published data on aluminum migration from food contact materials are sparse.

In one study, carbonated, nonalcoholic beverages had aluminum contents of 107–2084 ppb with an average of 830 ppb; carbonated, alcoholic beverages had aluminum contents of 67–1727 ppb. Beer in aluminum cans averaged 300 ppb, which is not much more aluminum than that in beverages in the same class; carbonated wines and wine coolers averaged 970 ppb of aluminum (Schenk et al., 1989).

Aluminum soft drink cans enameled on the inner surface were fairly resistant to acidic cola drinks for storage periods of 30–120 days, with the aluminum content of various batches ranging from 15 to 250 ppb; there was considerable variability between batches. High aluminum concentrations of 400–800 ppb were detected in these beverages after storage periods >400 days, while low aluminum levels of 15–20 ppb were found in colas stored in bottles made of glass or PET. Inconsistent quality of the protective stove lacquering in aluminum cans was suggested as being responsible for the observed effects (Murphy and Amberg-Müller, 1996).

22.4.4 Chromium

Chromium is an essential element for humans and is present in the diet mainly as Cr(III). It has a role in carbohydrate, lipid and protein metabolism related to improving the action of insulin. Cr(III) is much less toxic than the hexavalent form; some Cr (VI) compounds can be carcinogenic. As discussed in Chapter 7, the tin layer in tinplate cans undergoes a chromium treatment known as *passivation* in order to make it more resistant to oxidation and to improve enamel adherence. The chromium deposition on the tinplate after passivation can amount to $0.5\,\mu g\ cm^{-2}$, and if all this chromium were to dissolve in the food, this would result in the contamination of the contents of a 454 g can with about $0.4\ mg\ kg^{-1}$ (Jorhem and Slorach, 1987). In their study of canned fruit and vegetables, the mean level of chromium in enamel cans was $0.018\ mg\ kg^{-1}$, and in plain cans $0.090\ mg\ kg^{-1}$. This compares with levels in fresh foods of the same type of $0.009\ mg\ kg^{-1}$. No cases of intoxication have emerged, and it appears that the level of chromium present in tinplate is probably not enough to cause either toxic or adverse organoleptic effects (Murphy and Amberg-Müller, 1996).

The whole surface of ECCS cans consist of chromium oxide, but since it is only about 1/30 of the thickness of the tin layer on tinplate, it is always enameled prior to use. Although some Italian studies indicated that the absence of a thin layer renders ECCS less suitable for acid fruit packs, this is only likely to be a problem if a major loss of enamel occurred, which is unlikely since ECCS displays excellent enamel adhesion properties (Murphy and Amberg-Müller, 1996).

22.4.5 Silver

Silver nanoparticles (Ag NPs) are widely used for their antibacterial, antimicrobial, antibiotic, antifungal and partial antiviral activity, and nanocomposite packaging containing Ag NPs is being used to extend the shelf life of fresh foods. The increasing use of antimicrobial Ag NPs has been the subject of concern regarding environmental and health issues. Several reports have indicated that Ag NPs are toxic to cells and can alter the normal function of mitochondria, increase membrane permeability and generate reactive O_2 species. The main risk of consumer exposure to NPs from food packaging is likely to be through the potential migration of NPs into food and drink, as found for other heavy metals. Song et al. (2011) determined the migration of Ag from nanosilver–polyethylene food packaging film into food simulants at different temperatures and migration times.

Results indicated that the maximum migration ratios were 1.70%, 3.00% and 5.60% for 3% (w/v) aqueous acetic acid at 20°C, 40°C and 70°C, respectively, while for 95% (v/v) aqueous ethanol, the maximum migration ratios were 0.24%, 0.23% and 0.22% at 20°C, 40°C and 70°C. A more general discussion on the toxicology of nanomaterials in food can be found in Magnuson and Bouwmeester (2011).

22.4.6 EPOXY RESIN COATINGS

Epoxy resins are thermosetting resins that contain two or more epoxide (oxirane) groups per molecule and are obtained by the condensation of epichlorohydrin and bisphenol A (BPA), which yields bisphenol A diglycidyl ethers (BADGEs) of varying degrees of condensation (n), depending on the reaction conditions and the mole ratio of the reactants (Biles et al., 1999). While high MW ($n = 9$–11) epoxy resins are used as can enamels, many commercial epoxy resins are BADGE ($n = 0$) free (Simal-Gándara et al., 1998).

It is well established that because a residual amount of monomer remains after the polymerization process, BPA and other components migrate, at very low concentrations (ppb), from the epoxy coatings into the can contents during processing and storage. Powder formulations of high MW epoxies are used mainly to coat the internal surfaces of two-piece DRD food cans, while UV-curable coatings based on low viscosity aromatic, aliphatic and cyclo-aliphatic epoxy resins are used to coat the exterior and ends of cans. The success of epoxies as coatings for food cans is a result of their desirable flavor-retaining characteristics, their excellent chemical resistance and their outstanding mechanical properties. BPA is also used in the manufacture of polycarbonates and as an antioxidant and an inhibitor of end polymerization in PVC.

Noonan et al. (2011) quantified BPA concentrations in 78 canned and two frozen food products representing 16 different food types from the U.S. market. BPA was detected in 71 of the 78 canned food samples but was not detected in either of the two frozen food samples. Detectable BPA concentrations across all foods ranged from 2.6 to 730 ng g^{-1}. Large variations in BPA concentrations were found between different products of the same food type, and between different lots of the same product. Given the large concentration ranges, the only distinguishable trend was that fruits and tuna showed the lowest BPA concentrations.

A report into the mechanisms involved in the migration of BPA from can enamels into drinks found that it was necessary to heat the can to a temperature above the T_g of the epoxy resin (105°C) in order for the compound to be mobilized (Kawamura et al., 2001).

In the mid-1990s, the U.S. FDA and the SCF in Europe began investigating human exposure to BPA and BADGE in order to ascertain whether the use of certain epoxy resins might be exposing consumers to estrogenic xenobiotics. The FDA concluded that there was no public health concern regarding these chemicals. Several risk assessment reports have been prepared in recent years by authorities in Europe, Canada and the United States to assess the risk to consumers emerging from regular exposure to BPA. These assessments draw different conclusions regarding the potential risk of BPA, based mainly on the interpretation of the toxicity data. For example, Beronius et al. (2010) scrutinized 10 risk assessments and found that differences in conclusions were mainly influenced by the evaluation of low-dose effects and the uncertainties surrounding the significance of these data for health risk assessment. The results illustrate the impact of differences in risk assessment policy and expert judgment on the risk assessment process and highlight the importance of transparency in this process. A useful opinion piece by Sharpe (2010) commented on many of the controversies surrounding scientific studies on BPA that have entered the wider media.

Current BPA food contact uses in the United States were approved in 1963 when BPA was classified as an indirect food additive and GRAS. Today, there exist hundreds of different formulations for BPA-containing epoxy linings, which have varying characteristics. As currently regulated, manufacturers are not required to disclose to FDA the existence or nature of these formulations.

In 2006, EFSA set the TDI for BPA at 0.05 mg BPA kg^{-1} body weight day^{-1} based on the NOAEL of 5 mg kg^{-1} body weight day^{-1} that had been identified in two multigeneration reproductive toxicity studies in rodents, where the critical effects were changes in body and organ weights in adult and offspring rats and liver effects in adult mice, respectively. In 2008, EFSA reaffirmed this TDI, concluding that age-dependent toxicokinetic differences of BPA in animals and humans would have no implication for the default uncertainty factor (UF) of 100 and in turn for the TDI. In 2010, after reviewing hundreds of recent studies, EFSA concluded that the current TDI should remain unchanged.

EU Regulation 1895/2005 established a TDI of 0.15 mg kg^{-1} body weight for BADGE and its hydrolysis products, and a corresponding SML of 9 mg kg^{-1} in food and food simulants or 9 mg 6 dm^{-2}. The use of BFDGE and NOGE was prohibited from 2005 and 2003 respectively.

BPA is also used in the manufacture of polycarbonate. Recently, the release of BPA from polycarbonate baby bottles into food and food simulants was reviewed from the perspective of the current intensive discussions on possible risks arising from such migration (Hoekstra and Simoneau, in press).

22.5 PAPER PACKAGING

Paper and board are natural products made up of a large number of organic molecules (>700) and the toxicity of all of these substances, individually and in combination, is not known. Paper and board for food contact use are inhomogeneous materials, and can be composed of virgin or recycled pulp, additives like fillers, sizes, starch, starch derivatives, wet strength sizing agents and pigment or polymer coatings. Although paper and board food packaging materials are not currently subject to any specific legislation at EU level, like all FCMs, they should meet the general requirements laid down in Framework Regulation (EC) No. 1935/2004. Article 3 states that materials and articles shall not, under normal or foreseeable conditions of use, transfer their constituents to food in quantities that could endanger human health. Some examples of contaminants that have migrated from paper and board into food are now discussed.

22.5.1 Dioxins

Dioxin is the generic name for members of the family of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The different amounts and locations of the chlorine substituents in these molecules give rise to 75 possible isomers of PCDDs and 135 of PCDFs; these related compounds are known as congeners. There is an enormous body of toxicological information available, although it relates almost entirely to the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin isomer (2,3,7,8-TCDD), the most toxic isomer. In the case of the other isomers, their toxicity is related back to that of 2,3,7,8-TCDD to give the *toxic equivalent* (TEQ) to aid risk assessment. Toxicological and biological data are used to generate a series of weighting factors called *toxic equivalency factors* (TEFs), each of which expresses the toxicity of a "dioxin-like" compound in terms of the equivalent amount of TCCD. Multiplication of the concentration of a compound by its TEF gives a TEQ (Harrison, 2001).

Concern about trace amounts of dioxins in bleached paperboard packaging and the possible migration of the dioxins into milk packaged in paperboard cartons surfaced in North America in 1987. The dioxins arise during the bleaching process to delignify the pulp when chlorine is used. Although reported levels of dioxin in paperboard were extremely low and in the order of 4–5 pg kg^{-1} (ppt), concentrations in whole milk packaged in chlorine-bleached paperboard cartons were typically 0.1 ppt, with the concentration in the fat phase being around 3 ppt; the corresponding figures for milk packaged in glass containers were 0.005 and 0.15 ppt. In 1990, an expert group convened by the WHO recommended a TDI of 10 pg TCDD equivalents kg^{-1} bodyweight; in 1999 this was reduced to 1–4 pg kg^{-1} bodyweight, the lower end of the range being seen as a target (Harrison, 2001). EU Regulation 1881/2006 set maximum levels for dioxins and PCBs in food; for example, the sum of dioxins in milk and dairy products should not exceed 3.0 pg g^{-1} fat.

Despite the extremely low risk presented by dioxins in milk, suppliers of bleached paperboard adopted bleaching processes which reduced or avoided the production of dioxins in paper and paperboard. These processes included improving the washing of unbleached pulp to reduce dioxin precursors prior to the bleaching process; avoiding the use of elemental chlorine in the bleaching process by replacing chlorine with chlorine dioxide and/or oxygen compounds; and implementing an O_2 and/or extended delignification process prior to the bleaching process.

Dioxin continues to contaminate foods but the source is dioxin-contaminated animal feed rather than packaging. Recent incidents include Irish pork products and eggs in the Netherlands where animals had been exposed to feed contaminated with dioxin.

22.5.2 BENZOPHENONE

Over the past 30 years, there has been a move away from solvent-based inks toward those that are cured by UV radiation or (less commonly) EBs. This move has been driven, in part, by the increasing legislative focus in developed countries on VOCs (volatile organic compounds) of which the solvents used in printing are a major source. Another reason for the widespread use of UV-cured inks for printing cardboard and labels is because the fast cure permits online cutting and folding, enabling rapid production of finished packaging.

Benzophenone (BP) is widely used as a photoinitiator for inks and varnishes/lacquers that are cured with UV light. In addition to being a drying catalyst, BP is an excellent wetting agent for pigments and acts as a reactive solvent, increasing the flow of inks. Such inks typically contain 5%–10% photoinitiator. Because only a small portion of the initiator is used up during the curing process, BP can remain in the printed material and migrate through the open structure of carton board into the packaged food as it is not irreversibly bound into the print film layer. It may also be present if the carton board is made from recycled fibers recovered from printed material (Anderson and Castle, 2003).

In an extensive analysis of 350 retail samples in carton board food packaging, 41% had significant (>0.05 mg dm^{-2}) BP with 22% in the range 0.8–3.3 mg dm^{-2}. The highest level was 7.3 mg dm^{-2} found in a high-fat chocolate confectionery product packaged in direct contact with carton board. When the mass fraction of BP migration was calculated for different contact and storage regimes, there was a 6-fold reduction in migration for indirect contact compared with direct contact, a 6-fold reduction for chilled/frozen storage compared with ambient storage, and a 40-fold reduction for the two contact conditions combined (Anderson and Castle, 2003).

Studies of the migration of BP from printed carton board have been carried out at freezer temperature and during microwave heating (Johns et al., 2000). BP was found to migrate to the packaged food, even from LDPE-coated board. After 1 week at −20°C, migration was readily apparent, with BP being detected in the carton board of four out of seven samples at levels of 0.4–3.0 mg dm^{-2}. BP was also detected in three foods at levels of 0.6–2.9 mg kg^{-1}, which corresponded to a 1%–2% transfer from the printed board.

In 2009, German authorities reported a high migration of 4-methylbenzophenone (4-MBP) from carton board packaging into cereals. Although an SML exists for BP of 0.6 mg kg^{-1} for its use as an additive in plastics, there is no specific European legislation covering cardboard boxes and printing inks for food contact use. However, due to the high levels detected, EFSA recommended a limit of 0.6 mg kg^{-1} for the sum of BP and 4-MBP. BP and 4-MBP are not usually present in the same packaging, but rather seem to replace one another (Koivikko et al., 2010).

The aforementioned studies emphasize that the potential for migration to dry and frozen foods cannot be ignored. Although the inks were applied to the outside of the carton board, the board itself presented little if any barrier to migration. UHT milk packaged in HDPE bottles in Australia was recalled due to the presence of BP (10 ppb) and benzaldehyde (25 ppb) that had migrated into the milk from the UV-cured ink used to print the labels, giving rise to a metallic taint and many consumer complaints. The strong odor and taste of the offending chemicals prevented their ingestion by consumers.

22.5.3 ISOPROPYLTHIOXANTHONE

Isopropylthioxanthone (ITX) is another photoinitiator used in UV-cured offset printing inks and is always mixed with a co-photoinitiator (mainly 2-ethylhexyl-4-dimethylamino benzoate (EHDAB)). In September 2005, Nestlé undertook a recall of over 30 million cartons in four European countries of UHT milk for babies packaged in Tetra Brik Aseptic cartons, following the discovery by Italian food safety authorities of the presence of the ITX and EHDAB. The level of ITX ranged from 120 to 305 ppb for baby milk and from 74 to 445 ppb in milk for babies aged 12 months and over; ITX was found at 600 ppb in a single sample of flavored milk tested. ITX was also found in chocolate and cocoa milk products sourced from Austria; in grapefruit juice and pineapple juice produced within Italy, and in milk and cocoa beverages from Germany.

Since then, German researchers detected ITX in 36 of 137 packages (26%) not limited to multilayer laminate cartons (e.g., it was found in sausage skins and plastic cups), and significant migration occurred in 75% of the packaging materials that tested positive (Rothenbacher et al., 2007). The levels of ITX ranged up to 357 ppb in orange juice. The authors concluded that industry should utilize other, less-migrating photoinitiators, and that the implementation of legislative standards for GMP with a positive list for printing inks and maximum migration limits, especially for substances with incomplete toxicological assessment, is essential.

ITX is not prohibited for use in food packaging by the EU; it is also not listed on the WHO's prohibited list. According to EFSA, the scientific evidence indicates that the presence of the chemical in packaged foods does not pose a health risk. Tetra Pak has stated publicly that it is no longer using ITX in its printing inks. ITX differs from BP in that there is no obvious off-taste or odor to alert consumers to its presence in food.

In response to the ITX recall, the printing ink industry has developed new low-migration printing inks based on a novel fatty acid ester (FAE) consisting of a quaternary alcohol esterified with short fatty acids as the solvent. Richter et al. (2009) reported migration of the FAE from printed cardboard packaging into simulants and meat, chocolate and sweets. Levels of contamination of these foods were between 5 and 80 µg FAE kg^{-1}, with higher levels in the simulants.

22.5.4 MINERAL OIL SATURATED HYDROCARBONS

Since 1997, there has been an increasing number of reports of contamination of powdered baby milk and other dry foods packed in cardboard cartons with mineral oil saturated hydrocarbons (MOSH). The migration into dry foods proceeds by evaporation from the box and recondensation in the food, possibly with an intermediate passage through the wall of an internal bag. Internal paper bags with a plastic layer did not stop the migration.

There are two potential sources of mineral oil: offset printing inks applied to the package and recycled fibers (primarily from newspapers) contaminated by inks containing mineral oils. Conventional offset printing inks usually contain 20%–30% mineral oil as solvents. These oils range from about the n-alkane C_{13} to about n-C_{20}, and consist of MOSH as well as typically 5%–20% mineral oil aromatic hydrocarbons (MOAH). These inks "dry" by the solvent being sucked into the paperboard, where it largely remains.

At present, no regulatory authority has established legal limits for MOSH and MOAH. However, in 2002, JECFA specified a "temporary" ADI of 0–0.01 mg kg^{-1} body weight. Assuming 60 kg body weight and 1 kg of food contaminated with the given substance being consumed daily, the SML for these oils can be calculated as 0.6 mg kg^{-1} food. The JECFA evaluation was based on white mineral oils, refined to eliminate MOAH, whereas the mineral oils in recycled board and most printing inks are of technical grade and, thus, also contain MOAH.

Biedermann et al. (2011) investigated the migration of MOSH into taglioline (fine noodles with a large surface area, 4.1% fat and a shelf life of 2 years) packaged in a printed paperboard box overwrapped with LDPE; the box was glued together with an adhesive containing less than 1000 mg kg^{-1} MOSH. After 65 days, bottom packs in contact with the corrugated fiberboard transport package (estimated MOSH of 158 mg kg^{-1} at time of packing) contained 6.1 mg kg^{-1} MOSH and had the potential to contaminate all the packs on average at about 10 mg kg^{-1} after 2 years. Second, the migration from an improved recycled paperboard with five times less mineral oil than average amounted to 4.9 mg kg^{-1}. Third, a printing ink containing 3 g kg^{-1} MOSH (about 100 times less than conventional offset inks) contaminated the taglioline with 0.6 mg kg^{-1} MOSH. Finally, the taglioline were already contaminated with 2.5 mg kg^{-1} MOSH and <0.2 mg kg^{-1} MOAH before packing, illustrating that there are other as yet unidentified sources of mineral oil.

One way to minimize the migration of contaminants from packaging materials into food is to use a functional barrier. Fiselier and Grob (in press) determined the breakthrough periods of MOSH through various potential functional barriers. Polyethylene films showed breakthrough periods of only a few hours, whereas those of PP were roughly a month. Even thin layers of PA and PET were characterized by breakthrough periods of more than 6.9 years at 25°C, well beyond that needed to protect foods stored at room temperatures.

Recently, Biedermann-Brem et al. (2012) reported the confusion that exists between MOSH and POSH (polyolefin oligomeric saturated hydrocarbons). POSH consist largely of branched hydrocarbons such as the oligomers released by polyolefins and, thus, are comparable to MOSH; both could accumulate in the human body. Difficulties can arise in the analysis of MOSH as a result of interference from POSH because both POSH and MOSH consists largely of highly isomerized, branched and possibly cyclic hydrocarbons. No adequate data set is available to draw conclusions about the significance of POSH concentrations in foods currently on the market. Table 22.7 details levels of POSH and MOSH detected in powdered infant formula.

22.5.5 MISCELLANEOUS

The manufacturing process of paperboard food packaging can produce small quantities of 3-monochloropropane-1,2-diol (3-MCPD) when wet-strength resins containing epichlorohydrin are used. 3-MCPD is from the same family as 1,3-dichloro-2-propanol (1,3-DCP), which is known to cause cancer in animals. 3-MCPD has been found in paperboard for food contact.

TABLE 22.7
POSH and MOSH in Powdered Infant Formula by Molecular Mass Ranges of the *n*-Alkanes (POSH + MOSH Extracts from the Internal Surface of the Packaging Material)

	Food POSH + MOSH (mg kg^{-1})			Packaging (Internal Side) POSH + MOSH (μg dm^{-2})		
Packaging Type	**<C16**	**C16–C24**	**C24–C35**	**<C16**	**C16–C24**	**C24–C35**
Paperboard box with internal heat sealable alufoil bag	0.6	1.5	3.4	12	92	383
Same as above	1.4	3.5	5.1	5	24	309
Paperboard box with internal metallized and heat sealable bag	0.3	1.2	1.9	2	20	66
Paperboard box lined with alufoil/polyolefin	0.7	1.5	1.4	26	79	240

Source: Biedermann-Brem, S. et al., *Food Addit. Contam.*, 29(3), 449, 2012.

Pace and Hartman (2010) demonstrated that although 3-MCPD was present at concentrations up to 9.9 mg kg^{-1} within the paperboard matrix, it does not migrate through polyethylene extrusion-coated paperboard beverage cartons into food simulants. Also, no significant amount of 3-MCPD migrates through the unskived edges on the inside seam of the paperboard structure.

With the increasing use of microwave-interactive packaging, there is the possibility of degradation products that might adulterate the foods they contact. The high temperatures attained by packaging using susceptor technology may result in (1) the formation of significant numbers of volatile chemicals from the susceptor components and (2) the loss of barrier properties of FCMs, leading to rapid transfer of nonvolatile adjuvants to foods. Studies by the FDA with hot vegetable oil in contact with a susceptor, have shown that the susceptor materials liberate volatile chemicals that may be retained in the oil at ppb levels. The FDA recommends the use of the protocol outlined by McNeal and Hollifield (1993) for the identification and quantification of volatiles from susceptors.

The possible migration of diisopropylnaphthalenes (DIPNs) from recycled paper and paperboard used for food contact applications has raised health concerns since it was first detected in FCMs in 1994. DIPNs are widely used for ink-jet printers and as solvents in the preparation of specialty papers such as carbonless and thermal copy paper. As not all DIPNs are removed during the recycling process, some may be present in the finished board and, under certain circumstances, migrate into food via direct contact or gas phase transport. The concentration of DIPN in food and paper packaging materials from the U.S. marketplace ranged from 0.09 to 20 mg kg^{-1} (Zhang et al., 2008). DIPNs have been detected in U.K. takeaway food packaging materials (paperboard rings around hamburgers) at levels ranging from 0.06 to 0.17 ppm in the food after a contact time of less than 10 min.

Trimethyldiphenylmethanes (TMDPMs), used as solvents in carbonless copy paper, have also been found in solid foods such as egg pasta and rice packed in paperboard containing recycled fibers. Maximum levels of TMDPM in the paperboard were 998 ppb and in egg pasta 34 ppb; DIPN was present at 72.9 ppb in the paperboard and 0.9 ppb in rice.

Perfluorochemicals are biopersistent and widely used in the manufacturing and processing of a vast array of consumer goods, including electrical wiring, clothing, household and automotive products. Furthermore, relatively small quantities are also used to coat paper and make it oil and moisture resistant. In 2005, there were reports that fluoropolymers used in the manufacture of grease-resistant packaging for candy, pizza, microwave popcorn and hundreds of other foods are absorbed by fatty foods and then broken down by the body into perfluorooctanoic acid (PFOA). PFOA was labeled a “likely” human carcinogen by the EPA in January 2006.

Begley et al. (2008) reported that fluorochemical paper additives migrated to food during actual package use. For example, microwave popcorn contained 3.2 mg fluorochemical kg^{-1} popcorn after popping, and butter contained 0.1 mg kg^{-1} after 40 days at 4°C. Tests also indicated that common food-simulating liquids for migration testing might not provide an accurate indication of the amount of fluorochemical that actually migrates; oil containing small amounts of an emulsifier significantly enhanced migration of a fluorochemical from paper. The average and high U.K. adult dietary intakes of PFOA from the diet in 2007 were estimated at 0.01 and 0.02 μg kg^{-1} body weight day^{-1} respectively, well below the TDI recently set by the EFSA of 1.5 μg kg^{-1} body weight day^{-1}.

In a study on the capability of a PP film barrier to prevent the migration of residual contaminants from recycled paperboard into food simulants, benzophenone, anthracene, methyl stearate and pentachlorophenol were chosen as chemical surrogates (Song et al., 2003). Although the concentrations of the surrogates in the food simulants decreased with an increase in PP film thickness, they were still high and generally resulted in dietary concentrations >0.5 μg kg^{-1}, the level that the FDA would equate with negligible risk for a contaminant migrating from food packaging. It was concluded that, for an extended time at 100°C, PP would not be an acceptable barrier to migration of contaminants that are expected to be in post consumer paper and paperboard.

22.6 GLASS PACKAGING

Chemically, glass is highly resistant to attack from water, aqueous solutions and organic compounds. Water and acids have very little effect on silica, although they attack some other constituents of the glass. Standard tests have been developed in which glass containers are autoclaved with various test liquids under defined conditions and the liquid analyzed for components present in the glass. Silica and alkali are the main components leached from the glass, and as the initial rate of solution varies approximately with the square root of time, a diffusion mechanism of leaching is suggested. The main chemicals extracted into aqueous solutions (i.e., silica and sodium oxide) are unlikely to have any significant effect on the organoleptic properties of foods. The danger of contamination by leaching of lead and cadmium from glass into food is remote since these two metals seldom occur in glasses used in food contact applications.

22.7 TAINTS AND OFF-FLAVORS

A *taint* is a taste or odor foreign to the product (i.e., derived from an external source such as packaging); an off-flavor is defined as an atypical flavor or odor usually associated with deterioration (e.g., microbial spoilage or lipid oxidation). Both are generally unpleasant. Although the compounds responsible for taints and off-flavors in food are frequently only present at trace levels (ppt) and thus rarely present a health risk to the consumer, they are perceived by the human senses, and consumers seldom distinguish between the two, particularly when making complaints (Ridgway et al., 2010).

The odor or taste threshold of a taint is defined as the lowest concentration of a compound detectable by a certain proportion (usually 50%) of a given group of people.

The threshold is not an inherent property of the compound, because the threshold for any substance will vary with the medium in which it is present (i.e., the food or drink) and between different people. The wide range of human thresholds to chemical stimuli is a major reason for the difficulties in preventing food taints and in positively identifying the causes of taints. The threshold concentration difference between the most sensitive 5% and the least sensitive 5% is typically 2000-fold. This is why most complaints about taint arise from only a small proportion of those purchasing a particular batch of tainted product, because in most cases only the more sensitive detect it as a taint.

Because of the complex structure and chemical composition of packaging materials, a variety of chemical reactions can occur during package manufacture and use. These reactions occur between some packaging components, with other components acting as catalysts, resulting in the formation of compounds with low odor thresholds. These compounds then migrate through the material during storage and slowly diffuse into the product or package headspace. Identification and analysis of these compounds is very difficult, and usually many isolation and concentration steps are required because the odor thresholds are lower than analytically detectable. Resolving sensory issues related to food packaging involves knowledge provided by sensory scientists, materials scientists, packaging manufacturers, food processors and consumers (Duncan and Webster, 2009).

22.7.1 SOLVENTS

During the printing of plastic and paper packaging materials, many inks were applied dissolved or dispersed in organic solvents, which were subsequently removed by evaporation, usually in specially designed ovens. Today, water-based or UV-cured inks have replaced organic solvents to a large extent. However, if organic solvents are used, then a certain amount of residual solvent can remain. The solvents may be low MW organic compounds consisting of hydrocarbons, alcohols, glycol ethers, ketones and esters, which can then migrate into the foods by direct contact or via the free space inside the package. Fortunately, the human senses of smell and taste often show very high sensitivity to the presence of such volatiles, and, in most cases, the threshold for sensory detection of the solvents used in ink and adhesive formulations is considerably below the toxicologically significant level. The sensory thresholds for toluene, ethyl acetate, various aldehydes and ketones range from the ppm to ppb level. Toluene and xylene, which are aromatic compounds, should be avoided in the printing of food packages. The regulatory problem is mitigated by the potential for economic damage from off-taste and odor in packaged foods. The migration of alkylbenzenes (used as solvents in offset inks) into food at a level of 2 ppm have been reported (Aurela and Söderhjelm, 2007).

22.7.2 Residual Monomers

Residual styrene monomer in PS packaging has been associated with tainting problems in different foods. The taste recognition threshold of styrene monomer in water is 22 ppb, while thresholds in foods range from 0.2 to 0.3 ppm for orange fruit juice drink, a 3% oil-in-water emulsion, and skim milk (0% fat), 1–3 ppm for whole milk and greater than 3 ppm for condensed milk (10% fat), butter, and cream (33% fat) (Baner, 2000). The taste recognition threshold in yogurt ranges from 36 ppb in 0.1% fat yogurt to 171 ppb in 3% fat yogurt.

Coffee creamers and condensed milk packaged in thermoformed PS single serve (5–10 g product) portion packs have demonstrated styrene taint problems (Baner, 2000). These products are typically packaged aseptically and stored at ambient temperature, which increases the potential for styrene taint and substantially decreases shelf life because of tainting issues. The estimated styrene concentration migrating into creamers was 23–31 ppm, far exceeding the sensory threshold of 0.1–3 ppm in cream and potentially creating a sensory impact when the cream is diluted into tea or coffee. The large surface area:volume ratio of single serve portion packs contributes to this high concentration, as does the high fat content of cream.

Monomers used in PET packaging, although not particularly odorous, can form degradation products during the manufacturing process, which can cause taints in beverages. The major significant volatile compound in PET is acetaldehyde (AA), and it was discussed in Section 20.2.3.

Although residual monomers present in polyolefins are not generally responsible for odors, oxidation compounds such as 1-heptene-3-one and 1-nonenal have been identified and these can lead to taints (Piringer and Rüter, 2000).

22.7.3 Organohalogens

The major organohalogens (organic compounds containing chlorine, bromine or iodine) of interest to the food industry are the halophenols and haloanisoles, and the structure of two of the most common are shown in Figure 22.3. Numerous cases of tainting and off-flavors in foods from contamination by organohalogens originating from packaging materials have been reported and documented in the literature. These substances have very low sensory thresholds, with the taste threshold in water for 2,4,6-trichlorophenol (TCP; described as disinfectant) being 2 ppt and the odor threshold for 2,4,6-trichloroanisole (TCA; described as musty) being 3×10^{-8} ppm. Chlorophenols have been

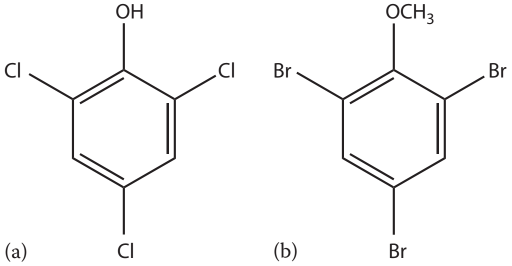

FIGURE 22.3 Structure of two of the most common organohalogen compounds: (a) 2,4,6-trichlorophenol and (b) 2,4,6-tribromoanisole.

used industrially as fungicides, biocides and herbicide intermediates, and tribromophenols (TBP) and their derivatives have been used as fire retardants as well as wood preservatives and general fungicides in leather, textiles, paint, plastics, paper and pulp. Chloro- and bromoanisoles are produced by fungal methylation of the parent halophenols under humid and warm conditions (xerophilic fungi require a moisture content between 12% and 16% and a temperature between 25°C and 35°C for germination and growth). They impart "musty" and "moldy" taints to foods at extremely low (often ppt) concentrations.

Chloroanisole-induced mustiness in dried fruit exported from Australia was found to be due to methylation of chlorophenols from virgin and recycled fiberboard cartons by fungi, with the concentration increasing with increasing RH. The total chlorophenol content in virgin kraft fiberboard was 66 ppb, and in fiberboard prepared from recycled waste paper 1375 ppb; local newsprint made up the bulk of the recovered waste used in the recycling process. The chloroanisole readily migrated through the LDPE liner into the dried fruit, producing the musty taint. Similar experiences have been recorded with multiwall paper sacks implicated in the tainting of cocoa powder, and jute sacks used to package cereal grains and flour.

Shipping containers have been responsible for many food tainting incidents with some shipping container wooden floors having concentrations of chlorophenols >15 ppb. The chlorophenols could originate from previous cargoes such as leather hides, or pretreatment of the timber floor with a chlorophenol-based preservative. Alternatively, it has been shown that when wood is treated with 5% sodium hypochlorite solution, trichlorophenols at the ppm level are formed.

Organohalogens are responsible for taints in wine, and a musty or corked character in wines (referred to as cork taint) has long been associated with 2,4,6-TCA. Around 5%–10% of corked wines are affected, and TCA is capable of producing an off-flavor in wines at levels as low as 10 ppt. The source of the TCA and other chlorinated compounds was presumed to be from chlorination of lignin-related compounds during chlorine bleaching of the corks.

Chatonnet et al. (2004) first identified 2,4,6-TBA in wines, resulting in pungent, musty odors in the absence of chloroanisoles. The TBA came from the precursor TBP, and both derived mainly from environmental pollution in wineries where the atmosphere was contaminated with TBA coming from TBP used recently to treat wood, or originating from much older structural elements of the winery or from used wooden containers. In certain cases, although the initial source had been eliminated, residual pollution adsorbed on walls or found in old barrels could be sufficient to make a building unsuitable for storing wines or sensitive materials (including corks and glass bottles) intended for direct contact with wine. Bromoanisoles have also been identified as the cause of musty odor and chemical taste in packaging where, previously, it resulted from the presence of chloroanisoles. The source of these compounds was traced to phenol-based wood preservatives used on wooden pallets and freight container floors, and, in particular, 2,4,6-TBP, which is converted to 2,4,6-TBA.

Case Study I

HDPE resin was imported into Australia in a shipping container with an LDPE liner supported by fiberboard walls and floor. The resin spent approximately 6 weeks inside the container until it was unloaded and blow molded into bottles, which were then filled with pasteurized milk. Consumer complaints resulted in a product recall and subsequent analysis of the resin and the affected milk revealed the presence of a range of organohalogens as shown in Table 22.8.

With the exception of 4-bromophenol and 2,4-dibromophenol, all the halophenols detected in the contaminated HDPE resin exceeded their taste thresholds in water; six also exceeded their odor thresholds. In the milk, five compounds (2-chlorophenol; 2,4-dichlorophenol; 2,6-dichlorophenol; 2-bromophenol and 2,4,6-tribromophenol) all exceeded their odor and taste thresholds in water. No anisoles were detected, indicating that the container floor was probably quite dry. To avoid repeat incidents, rigorous container inspection procedures prior to loading have been introduced by the resin supplier, and a plastic–alufoil laminate sheet is used to cover the container floor. In addition, sensory testing methods of incoming resin prior to unloading into silos at the blow molding site have been upgraded.

TABLE 22.8
Concentrations of Organohalogens Detected in HDPE Resin and Milk[a]

Organohalogen	Odor Taste Thresholds µg/L (ppb)		Resin	Milk
2-Chlorophenol	0.4	0.1	0.4	0.9–3.36
4-Chlorophenol	20	39		n/d–1.88[b]
2,4-Dichlorophenol	0.4	0.3	2.1	1.14–12.59
2,6-Dichlorophenol	3.5	0.0062	9.6	n/d–29.16
2,4,6-Trichlorophenol	300	2	3.0	n/d–0.42[b]
2-Bromophenol	0.1	0.03	0.7	0.28–1.07
4-Bromophenol	4	23	3.0	n/d–0.01[b]
2,4-Dibromophenol	0.5	4	1.3	n/d
2,6-Dibromophenol	0.1	0.0005	0.7	n/d
2,4,6-Tribromophenol	0.1	0.6	33.9	1.09–272

[a] Twelve different samples that gave rise to consumer complaints.

[b] Below odor and taste threshold concentrations in water.

Case Study II

Consumer feedback cited a musty aroma in freshly canned beer and subsequent analysis identified TBA as the primary entity at levels of 10–40 ppt. Further investigations in the brewery identified the same musty taint in an unbroached pallet of empty can bodies. The can bodies were transported to the brewery by sea freight—a journey lasting 10 days. Climatic conditions during transport and production periods were warm and humid (>30°C and often >60% RH over 14 consecutive days).

An audit of the production facilities found no evidence of atmospheric TBA contamination within the packaging operations of the brewery. However, the floor of the shipping container used to transport the can bodies was found to contain TBA at very high levels (15 g kg^{-1}) and this was the most likely origin of the TBA taint.

Conclusions and Recommendations

Although the mechanism of organohalogen tainting has been studied since the 1960s and the scientific literature is considerable, they continue to be a major source of concern to the food industry and of annoyance to consumers. While there are seldom health concerns arising from taints, the tainting is very objectionable and the threshold levels are extraordinarily low. The food industry has experienced (and continues to experience) many cases of organohalogen tainting resulting in serious losses. Tainting of any component within the ingredient and packaging supply chain may lead to a taint in the packaged food. Most of these incidents are avoidable if the following recommendations are implemented:

1. TBP used either as a preservative, fungicide or fire retardant poses ongoing risks to food contamination and should not be used where it may transfer to food packaging materials.
2. Recycled timber, paperboard products and polymer plastics provide a source of potential taint compounds.
3. Timber pallets and the floors in shipping containers should be closely assessed for taints and, where necessary, covered with a plastic–alufoil laminate barrier as a precaution.
4. Environmental taint potential should be assessed adopting Hazop protocols within a production facility.
5. TCP and TBP levels within the material supply chain should be managed to defined levels within a QA program.

22.7.4 MISCELLANEOUS

The development of a "catty" odor (described elsewhere as *ribes* [blackcurrant leaves from the botanical name *Ribes nigrum* for blackcurrant] or tomcat urine) has been identified in many foods as a result of interactions between food and migrants from packaging. Such odors have been attributed to a sulfur-containing compound 4-methyl-4-mercaptopentan-2-one, which is a hydrogen sulfide adduct of mesityl oxide and has an odor threshold of 10 ppt. Investigations into catty odor in two different "cook-in-the-bag" ham products demonstrated that the mesityl oxide originated from diacetone alcohol (DAA), which was present as a residual printing ink solvent (Franz et al., 1990). Formation of the mesityl oxide was thought to have arisen from dehydration of the DAA, promoted by some property of the ethylene ionomer sealing layer in the multilayer packaging film. Mesityl oxide can also be formed from acetone, which is sometimes used as a solvent in coatings and adhesives. Avoiding the use of mesityl oxide precursors such as DAA in packaging materials can prevent the occurrence of catty odor in sulfur-rich foods. Mesityl oxide is not a true oxide and was assigned this name at an early date because of an erroneous conception of its chemical nature. It is, in fact, an α,β-unsaturated ketone with the formula $(CH_3)_2C{=}CHCOCH_3$ and has a peppermint-like odor (Tice, 1996).

Off-flavor in two-piece cans was shown to be caused by the lubricant used in their production. Fatty acids and esters (normal constituents of the lubricants) are easily oxidized and can contaminate the packaged beer, causing stale, rancid, woody or cardboard-like flavors. A potent flavor constituent of mineral oil (used to aid forming of the cans), which appeared to be naphthenic in nature, has also been found. To eliminate this problem, additional washings were included employing cleaning materials specifically effective at removing fatty acids, esters and mineral oil.

Beer is particularly sensitive to the pickup of off-flavors from metal packaging. If the enamel coating is disrupted in a steel can, a metallic flavor will develop as iron migrates into the beer. With aluminum cans, the off-flavor that develops is sulfury rather than metallic because of galvanic reactions.

22.8 TRACEABILITY

One of the consequences of globalization is that it has become more difficult to trace the origin of our foods and the packaging that surrounds them. Regulatory authorities simply cannot analyze every package on the market for the thousands of possible contaminants that may be present in the packaging material, the adhesives, the ink or the food itself.

Traceability has become an integral requirement of modern quality management systems. In the EU, Article 17 of Regulation 1935/2004/EC requires FCMs or articles to be unequivocally identified when they are shipped to the next operator in the value chain. For materials or articles sourced from outside the EU, traceability extends back to the importer responsible for putting them on the EU market for the intended food contact application. Just how successfully the importer could trace back the origin of the material is unknown.

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23 Food Packaging and Sustainability

23.1 INTRODUCTION

All those involved in the design, development, production or use of packaging and packaging materials must be aware of the environmental demands now placed on them. These demands arise as a consequence of both the materials and processes that are used, and the packaging that is produced, utilized and recovered or discarded.

When the public think about packaging, they equate it to waste in their garbage bin, litter in the streets (waste in the wrong place) and excessive or deceptive packaging; these dominate the public perceptions of packaging. Public perceptions of packaging are created partly by personal experience of its use, partly by personal attitudes to environmental issues and partly by media coverage (Levy, 2000). The fact that food packaging has almost fulfilled its various functions by the time the public consumes the food product partly explains why their perceptions are so negative.

In an attempt to understand the attitudes that have led to the way in which packaging is perceived today, Levy (2000) usefully defined myths, facts and realities. *Myths* are fictitious; *facts*, by definition, can be measured and quantified; and *perceptions* are often a mix of myths and facts. A sense of reality is sometimes hard to come by because it can easily be lost in the emotional persuasiveness of perceptions. Realities often relate more to the myths than the facts. Myths persevere because the known facts (quantified data) are sparse or incomplete. Where facts do exist, many incorrect perceptions are perpetrated by those who do not wish to face up to them for whatever reason.

While not all public perceptions of packaging are mythical, most of them tend to be negative and ignore the key benefits and functions of packaging. The most commonly cited myths and perceptions about packaging are as follows (Levy, 2000):

- It is an unnecessary indulgence on the part of affluent societies.
- It fills the garbage bin and the amount of waste is growing.
- It is the greatest single cause of unrecoverable waste.
- It is disposed of by methods which harm the environment.
- It wastes scarce materials and energy.
- It is not recycled and reused enough.
- It should be returnable for reuse.
- It is a cause of litter.
- It is excessive and products are overpackaged.
- It is deceptive.
- It is only used to promote and help sell the product it contains.
- It should be biodegradable.
- It contributes to pollution.

Rather than rebut each of these myths and perceptions individually, the remainder of this chapter will describe how packaging waste can be, and is being, managed. It discusses how the environmental impacts of packaging can be assessed, the policies on packaging and the environment in the United States and Europe and the key issues concerning packaging and sustainability.

23.1.1 What Is Waste?

Municipal solid waste (MSW)—more commonly known as trash, garbage, refuse or rubbish—is simply what is left of the products that have been used and are no longer needed. MSW is defined by the EPA to include wastes from residential, multifamily, commercial and institutional (e.g., schools, government offices) sources. This definition excludes many materials that are frequently disposed of with MSW in landfills including combustion ash, water and wastewater treatment residuals, construction and demolition waste and nonhazardous industrial process wastes. MSW consists of everyday items such as product packaging, grass clippings, furniture, clothing, bottles, food scraps, newspapers, appliances, paint and batteries.

Waste is an inevitable product of society and has been described as the "effluence of affluence." Waste generation is directly linked to the economic structure of a country, with MSW being closely linked to demography, urban or rural location and culture. The United States and the EU countries contain about one sixth of the world's population, produce and consume more per person than the global average and generate almost one-fourth of the world's MSW. However, developing countries produce more waste from a given amount of production and per dollar of GDP. Although they account for less than one half of the world's GDP, they produce nearly three quarters of its MSW. Paper is the largest component (by weight) in high-income countries, while food waste predominates in low-income countries.

The world at large, and the United States in particular, uses vast amounts of materials and those amounts are rapidly increasing (EPA, 2009). In the past 50 years, humans have consumed more resources than in all previous history. The United States consumed 57% more materials in the year 2000 than in 1975; the global increase was even higher. With less than 5% of the world's population, the United States was responsible for about one third of the world's total material consumption from 1970 to 1995. In 1900, 41% of the materials used in the United States were renewable (e.g., agricultural, fishery and forestry products); by 1995, only 6% of materials consumed were renewable. The majority of materials now consumed in the United States are nonrenewable, including metals, minerals and products derived from fossil fuel. This rapid rise in material use has led to serious environmental effects such as habitat destruction, biodiversity loss, overly stressed fisheries and desertification.

In the United States in 2010, about 250 million tonnes of MSW were generated, which is approximately 2.0 kg of waste person^{-1} day^{-1}, up from 1.66 kg person^{-1} day^{-1} in 1980 (EPA, 2011). The packaging fraction of MSW was 75.64 million tonnes (0.61 kg person^{-1} day^{-1}) or approximately 30% w/w, a percentage that has remained relatively constant over the last 50 years. However, there have been significant shifts in the composition of packaging during this time. Glass packaging has declined from a peak of 9.8% in 1970 to 3.7% in 2010, while plastics packaging has increased from just 0.1% in 1960 to 5.5% in 2010. Corrugated boxes have also increased from 8.3% in 1960 to 11.6% in 2010. Steel cans have declined from 5.0% in 1960 to 0.9% in 2010. These numbers reflect many interesting changes in packaging design and development, materials substitution and light weighting or source reduction.

If secondary packaging such as corrugated boxes and wooden packaging is excluded, then primary packaging made up 36.3 million tonnes (0.29 kg person^{-1} day^{-1}) or 14.7% of MSW. It consisted (w/w) of 37.7% plastics; 25.6% glass; 23.8% paper and paperboard and 12.7% metals. Food scraps were 13.9% of total MSW in 2010 (34.8 million tonnes) compared to 13.8% in 1960. Yard trimmings declined from 22.7% in 1960 to 13.4% in 2010. The recovery rate increased from 9.6% of MSW generated in 1980 to 34% in 2010. Disposal of MSW to landfill decreased from 89% of the amount generated in 1980 to about 54% in 2010.

In the EU, per capita consumption data needs to be treated with caution, as the 27 Member States do not all use the same methodology to calculate packaging placed on the market, meaning that per capita estimates for different countries are not necessarily comparable. In the EU, just over 17 million tonnes of packaging were sent for final disposal (i.e., landfill or incineration without energy recovery) in 2008; this compares with the estimated 89 million tonnes of food wasted per year (Europen, 2011). Per capita consumption of non-wood packaging in the core 15 EU countries increased by 4.8% between 1998 and 2008—an average annual growth rate of just 0.46%; however, per capita non-wood packaging sent for final disposal varied widely, from 0.22 kg $person^{-1}$ day^{-1} in Ireland to 0.025 kg in Germany.

In a detailed analysis of the composition of MSW in 10 cities located in eight EU countries, it was found that packaging varied between 20% and 36% by weight of MSW. The relative quantities of the different packaging materials also varied: paper from 15% to 42%; glass from 5% to 17%; metal from 2% to 11%; and plastics from 5% to 14%, with the organic fraction varying from 19% to 50%. MSW in a specific city varied depending on the season, the housing type (less MSW in high-rise compared to low-rise housing) and the day of the week (Fonteyne, 2000).

Materials that do not go for so-called *final disposal* but instead are recycled, composted or incinerated with energy recovery are often classified as "recovered" or "diverted" and, in the EU, the application of these processes to packaging is referred to as "valorization."

On a per person basis, modern household waste production may not be much higher than early last century, when coal ash and horse manure were significant sources of waste in cities. Coal ash production alone created an estimated 1.5 kg of waste $person^{-1}$ day^{-1} in Manhattan in the early 1900s. It should always be remembered that nineteenth-century cities were hardly pristine, with trash and human waste routinely dumped into local waterways or primitive sewers that flowed into harbors, creating "foul air" as the tide came in, particularly on warm summer nights. The same is still true today in the large cities of many developing countries.

23.2 WASTE MANAGEMENT OPTIONS

23.2.1 Hierarchy of Waste Management

In its 1989 report entitled *The Solid Waste Dilemma: Agenda for Action*, the EPA outlined what is referred to as a hierarchy of waste management options, with reuse, reduction and recycling at its apex and landfilling and incineration at its base. Several variations of the hierarchy are currently in circulation and one that is widely used is shown in Figure 23.1. It is important to note that the hierarchy is not the result of any scientific study of waste management options. It makes no attempt to measure the impacts of individual options or of the overall system. Despite these shortcomings, the hierarchy has become accepted as dogma in some countries and among some policymakers, politicians and environmentalists who insist, for example, that reuse is always preferable to recycling, despite the realities in a specific geographical location (e.g., the distance that refillable bottles might have to travel to be refilled).

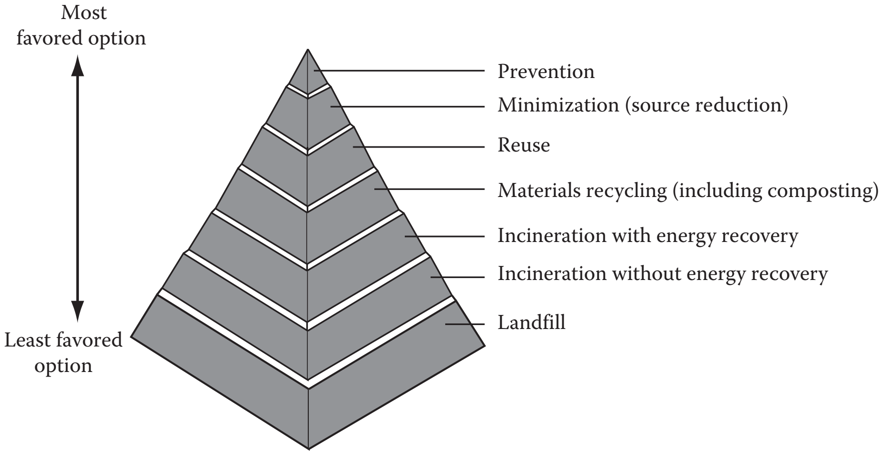

FIGURE 23.1 A hierarchy of solid waste management.

Several MSW management practices, such as source reduction, recycling and composting, prevent or divert materials from the waste stream. Source reduction involves altering the design, manufacture or use of products and materials to reduce the amount of material used. Recycling diverts items such as paper, glass, plastics and metals from the waste stream. These materials are sorted, collected and processed and then manufactured, sold and bought as new products. Composting involves microbial decomposition of organic waste such as food scraps and yard trimmings, as well as uncoated paper and other biodegradable packaging materials, to produce a humus-like substance.

Other practices address those materials that require disposal. Landfills are engineered areas where waste is placed into the earth. Landfills usually have liner systems and other safeguards to prevent groundwater contamination. Combustion is another MSW practice that has helped reduce the amount of landfill space needed. Combustion facilities burn MSW at a high temperature, reducing waste volume and, in many cases, generating electricity from the waste heat.

Given the wide variability in MSW composition, it follows that there can be no single, global solution to the issue of packaging recovery. Specific technical approaches for each waste management program are required, reflecting geographical differences in both composition and the quantities of waste generated, as well as differences in the availability of some disposal options (e.g., MSW incinerators are rare in many countries). The economic costs of using different waste management options also show large variations between and within countries (e.g., the costs for sorting collected postconsumer packaging).

Since the mid-1990s, the concept of integrated solid waste management (ISWM) has begun to replace the hierarchy as a more useful, organizing framework for thinking holistically about waste management. It recognizes that all disposal options have a role to play in integrated waste management and stresses the interrelationships between the options. Today, a mix of waste management options is employed depending on the specific local conditions, the objective being to optimize the whole system rather than its parts, making it economically and environmentally sustainable (McDougall et al., 2009).

23.2.2 SOURCE REDUCTION

Source reduction (also referred to as *resource conservation* or *lightweighting*) is just below prevention (is that packaging really necessary?) at the top of the waste management hierarchy and for a very good reason: source reduction translates into less total material use and, consequently, less "waste" at the end. Lighter packages also require less energy for transportation, thus reducing the environmental impacts from energy production and use.

There have been dramatic reductions in the weight of basic food packages over the last 40 years, driven largely for economic rather than environment reasons (packaging is an extremely cost-competitive industry). An alternative approach to lightweighting is material substitution and this has become very common with, for example, PET being substituted for glass and retort pouches for metal cans. Some examples showing the dramatic reductions in package weight are presented in Table 23.1.

While the potential merits of source reduction are widely acknowledged, less well understood are the potential trade-offs between source reduction and recycling in certain circumstances. The U.S. Office of Technology Assessment report describes the modern snack chip bag to illustrate this point (*Green Products by Design: Choices for a Cleaner Environment*, 1992). These bags are now made of thin laminated layers of nine different lightweight materials, each of which serves a different function in assuring overall product integrity and consumer convenience. Although this multi-layering makes recycling difficult and economically unattractive, the package is much lighter than an equivalent package made of a single recyclable material and provides longer shelf life, resulting in less food waste.

While lightweighting of primary packaging provides an obvious environmental benefit in reduced material use, it is very important to recognize that the key factor is the amount of material used in the total packaging system (i.e., including secondary and tertiary packaging).

TABLE 23.1
Examples of Lightweighting of Packaging

Package Type	Year	Unit (g)	Reduction/Comment
330 mL glass beer bottle	1980	270	
	1999	200	
	2011	150	44% weight reduction
330 mL PET beer bottle	2010	33	
750 mL glass wine bottle	2006	500	
	2011	350	30% reduction
750 mL PET wine bottle	2010	51	
355 mL aluminum beverage can	1970	21.8	
	1980	18.6	
	1990	15.9	
	2000	13.6	
	2010	13.2	39% weight reduction
450 mL steel food can	1974	49	
73 × 110 mm body only	2011	27	45% weight reduction
Paperboard aseptic	1980	34	
beverage carton	2010	26	23% weight reduction
2L HDPE milk jug	1965	120	
	1990	65	
	2011	48	60% weight reduction
2 L PET carbonated beverage bottle	1980	68	Includes PP base cap
	1999	44	Base cap removed
	2010	40	47% weight reduction
500 mL PET water bottle	1989	24	
	2002	15	
	2008	13	
	2011	10	58% weight reduction

Sources: Data obtained from various sources and should be used as indicative only.

23.2.3 RECYCLING

Recycling can be defined as the diversion of materials from the solid waste stream for use as raw materials in the manufacture of new products. All common types of food packaging are technically capable of being recycled. However, whether they actually are recycled depends on where they become waste, the local waste management infrastructure and the availability of recycling/reprocessing capacity.

In 2006, the United States recycled 32.5% (or 81.8 million tonnes) of its waste, up from 31.9% in 2005. This resulted in 49.7 million tonnes of carbon equivalent (MTCE) saved or the emissions equivalent of taking 39.4 million cars off the road for one year. In addition, 1.3 quadrillion BTUs of energy were saved, which is enough energy to power 13% of U.S. residences for one year (EPA, 2007).

23.2.3.1 Closed-Loop Recycling

Closed-loop recycling refers to the recycling of a particular material back into a similar product; for example, the recycling of glass bottles back into new glass bottles. Corrugated boxes and glass bottles are typically recycled in a closed-loop system. Among some sections of the community, closed-loop recycling has taken on a special significance and in their eyes ranks much higher than open-loop recycling. There is no factual basis for this view and the reason is very simple; the physical environment is unconcerned with whether recycling is open or closed loop. What is important are the environmental impacts from the various recycling options, and those options that result in the lowest impacts should be preferred, regardless of whether or not they are open or closed loop.

23.2.3.2 Collection and Sorting

Before any postconsumer packaging material can be recycled, it first has to be collected and sorted so that a clean stream of material can be delivered to the recycler. In an ideal world, households would source separate their various used packaging materials into individual bins, which would then be collected, consolidated and sent for recycling. In reality, no one wants to have 15 individual bins in their home, let alone remember what day each will be collected. In an effort to reduce the variety and quantity of used packaging collected from homes, bring systems have been developed. These are particularly common in many European cities where residents can take their paper and glass to large bins located in their neighborhood for collection and subsequent recycling. However, even where bring systems for paper and glass operate, few cities collect separated used packaging; most run "commingled" systems in which recyclables are collected from the curbside in a single container and sent to a sorting center for separation. Sorting adds significantly to the cost of producing clean streams of materials for recycling.

A sharp increase in the use of one-way, nonreturnable, disposable packaging for beverages began in the 1960s in the United States In 1960, refillables accounted for 95% of soft drink and 53% of beer containers. By 1970, refillable glass bottles accounted for only 49% of soft drinks and 26% of beer containers (Ackerman, 1997). The nonreturnable beverage containers became a highly visible type of litter and the public policy response was to introduce so-called bottle bills in several states (Vermont and Oregon led the way in 1972, being joined later by nine more states). In these states, consumers pay a deposit for each beverage container at the point of purchase, which is redeemed at retail outlets or special centers. Refillable containers (primarily glass bottles) are then returned to bottlers and nonrefillable containers (primarily glass bottles and aluminum cans) are recycled. Deposit systems result in relatively pure streams of used packaging to recyclers.

23.2.3.3 Materials Recovery Facility

Sorting of commingled packaging materials takes place at a materials recovery facility (MRF (pronounced "merf")). The MRF is a relatively recent approach to MSW management, but its utility has become obvious and its popularity is increasing. Although the first MRF was built in New York City in 1898, the first modern MRF was established in the 1980s in Groton, Connecticut (Pitchel, 2005). The design and operation of MRFs varies widely within and between countries, with developed countries installing more automated sorting machinery in an effort to increase efficiency and reduce costs (Worrell and Vesilind, 2012). Generally, the commingled material is sent down a conveyor belt and "pickers" remove specific items by hand, a typical sorting procedure being shown in Figure 23.2. Steel cans can be removed magnetically and aluminum material by the use of eddy currents. Mechanical systems use air classification or perforated revolving drums to separate lighter fractions such as plastic from heavier fractions such as glass. Of course, not all the material which enters an MRF can be recovered for recycling and the unrecyclable residue which is taken to landfills can be as high as 40% in some cases.

23.2.3.4 Benefits

"Why do we recycle?" is a simple question which many consumers, policymakers and industries have asked. The answers are not so simple or unanimous. The speed and spread of recycling programs in the United States in the early 1990s has been attributed to the perception of an imminent landfill crisis. For many consumers, recycling has been a sensible response to the profligate life style that began in the 1960s and the increasing number of global environmental problems which industrialization has created (e.g., depletion of the ozone layer and global warming).

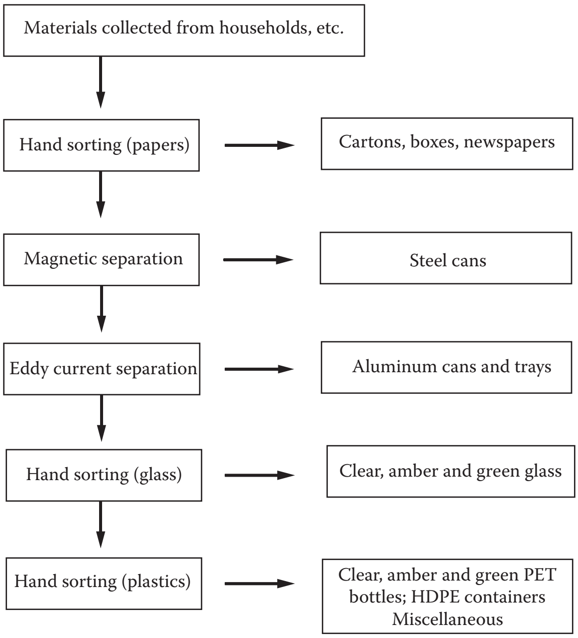

FIGURE 23.2 A typical sorting procedure at an MRF.

The EPA gives the following benefits of waste prevention and recycling (jointly referred to as waste reduction):

- *Reduces methane emissions from landfills.* Waste prevention and recycling (including composting) divert organic wastes from landfills, thereby reducing the methane released when these materials decompose.
- *Reduces emissions from incinerators.* Recycling and waste prevention allow some materials to be diverted from incinerators and thus reduce greenhouse gas (GHG) emissions from the combustion of waste.
- *Reduces emissions from energy consumption.* Recycling saves energy, because manufacturing goods from recycled materials typically requires less energy than producing goods from virgin materials. Waste prevention is even more effective at saving energy, because when people reuse things or when products are made with less material and/or greater durability, less energy is usually needed to extract, transport and process raw materials and to manufacture replacement products. When energy demand decreases, fewer fossil fuels are burned and less CO_2 is emitted to the atmosphere.
- *Increases storage of carbon in trees.* Trees help absorb CO_2 from the atmosphere and store it in wood, in a process called carbon sequestration. Waste prevention and recycling of paper products allow more trees to remain unharvested, where they can continue to remove CO_2 from the atmosphere.

Although recycling enjoys broad popular support, there is no consensus about the benefits it is expected to provide. Some people believe that recycling is saving money for their municipality by reducing the costs of garbage collection and disposal. Analysis of U.S. recycling costs, however, suggests that only the best programs consistently save money for their communities. Average programs save money in some years, but add to municipal costs at other times. Another popular reason for recycling is the perceived lack of landfill space and the fear that there will soon be nowhere left to put garbage.

A scholarly, yet practical, attempt to answer the question "Why do we recycle?" has been provided (Ackerman, 1997). He argued that recycling is a profitable activity only for relatively low-income people (and for a handful of specialized businesses). In the cities of developing countries, countless scavengers pick over the waste found on the streets and in landfills, pulling out anything of value in order to resell it. However, as economies grow and incomes rise, scavenging tends to disappear, displaced by higher-wage occupations. Recycling, as it occurs in developed countries, is a different process, motivated by altruistic concerns for the community, the environment and the future rather than by hope of personal economic gain.

Ackerman (1997) suggested that there is still an important meaning and value to recycling, even in the absence of a landfill crisis or an immediate opportunity for profit. Waste disposal is not the whole story; a stronger case for recycling rests on its benefits in resource use and manufacturing. The products that consumers buy and discard are made by industry, and the process of manufacturing most goods has far greater environmental impacts (e.g., much greater toxic emissions) than disposal of the same things in modern landfills. Recycling is good for the environment because making most things out of recycled materials results in lower industrial emissions than making the same thing out of virgin material. Using less material in the first place (source reduction) is even better for the environment than recycling. Recycling and waste reduction are also important because they minimize the use of nonrenewable resources.

In Ackerman's view, recycling is an attempt to answer at least three questions that the market rarely articulates. First, what new technologies will emerge and become profitable when there is public pressure to reduce, reuse and recycle the material goods that we buy? The techniques of production that are profitable today evolved over the last 150 years in a context of cheap, often publicly subsidized, virgin raw materials. Policies that push industry in the opposite direction will, over time, lead to a different set of production techniques and a different calculation of profitability. Industries based on recycling may come to prosper as well, for similar reasons.

Second, what provision should we make for the material welfare of future generations? Economic techniques such as cost-benefit analysis (CBA) are designed to weigh the interests of people who are alive today. Because our obligation to unborn future generations is not expressed in the market, it is not reflected in current prices, costs and benefits. Yet it is clear that many people care about leaving a livable world for their descendants. Recycling is in part an attempt to conserve materials for the future, even if they appear cheap enough to waste freely at present.

Third, how should the value of nature be described and respected? Air and water pollution, and many other forms of environmental degradation, cause a harm that has no price; they diminish something whose worth was never expressed in monetary terms. Economists have proposed methods for assigning prices to environmental damages, but this has remained largely a theoretical endeavor.

It must be remembered that recycling addresses long-term environmental goals, not an immediate crisis. Thus it is not necessary—nor is it technically feasible—to recycle everything in the municipal waste stream. Some things remain prohibitively expensive to recycle, and efforts should be concentrated elsewhere. Clarity about the goals of recycling should make it possible to set priorities, selecting areas where the greatest quantities of useful materials can be conserved or recovered, and the greatest environmental gains achieved, at the lowest cost. Clarity about the goals of recycling also leads to the conclusion that waste reduction can be an even better route to the same destination. The objectives that motivate recycling can sometimes be best advanced by minimizing material use, rather than by maximizing recycling.

Ackerman concluded that recycling makes a modest but valuable contribution to the creation of an environmentally sustainable future. It is far from being the most urgent environmental policy initiative under discussion today; it is distinguished by being the most accessible step for millions of people to take in the course of their daily lives. Recycling is the answer to several important questions, including, "What can you, personally, do to help the environment?"

Another academic (Thøgersen, 1996) has argued that in affluent industrial societies, environmental behaviors like recycling are typically classified within the domain of morality in people's minds. Attitudes regarding this type of behavior are not based on a thorough calculation, conscious or unconscious, of the balance of costs and benefits. Rather, they are a function of the person's moral beliefs; that is, beliefs in what is right or wrong. If people are provided with proper information and opportunities, then most are willing to carry some costs if it benefits the environment. However, if an economic incentive is offered to compensate for the private costs from behaving in an environmentally friendly fashion, then this may weaken or destroy the moral obligation.

23.2.3.5 Technologies

23.2.3.5.1 Paper

Paper packaging can be divided into three main groups: corrugated boxes, cartons and packaging papers. Corrugated boxes are widely recycled, with their bulk making them easy and cheap to collect. Cartons and packaging papers used as primary food packaging are also recycled but to a lesser extent. Paper is relatively simple to recycle, with the basic process consisting of repulping the fibers by dissolution in water, typically using a hydrapulper (so-called because of the hydraulic forces which are created) as shown in Figure 6.2. Many cartons are coated with a thin layer of LDPE on one or both sides and the paper fibers can also be recovered using a hydrapulper. The process takes from 5 to 20 min and is usually continuous. The recycling process shortens the fibers each time they are processed, and after about five cycles, they lose 10% ~ 30% of their original strength and are too short to stay on the paper-making wire. Unless they can be used as the middle ply in a multi-ply board, they finish up as sludge. Fractionation, the separation of fibers by length and using only the longer and stronger fibers, is one method of ameliorating this degradation. However, a certain fraction of virgin fibers will always be needed (Scott, 2011).

A key step in the recycling of paper packaging is removal of the ink, a process known as *de-inking*. The most common technique used for de-inking consists of flotation where soaps are added to the pulp slurry and air is injected into the base of tank. As the air rises to the surface it carries ink particles in the range of 20–100 μm suspended on the surface of flotation bubbles. The foam which forms on the surface is then removed. Further washing removes fillers, finely divided ink particles and other colloidal materials from the paper fibers (Franz and Welle, 2003).

Although a large quantity of waste paper is recycled worldwide, great care must be taken if the packaging material made from it is used in direct contact with food. The following fractions of recovered paper are considered unsuitable for inclusion in food contact paper and board:

- Contaminated waste paper and board from hospitals
- Recovered paper and board which has been mixed with garbage and subsequently sorted out
- Used stained sacks which have contained, for example, chemicals and foods
- Covering materials, such as paper used for covering furniture during repair and painting work

23.2.3.5.2 Steel

Steel cans are either tin- or chromium-plated (ECCS), and there is no simple way of separating them prior to recycling. Because they are magnetic, steel cans are generally automatically sorted at MRFs from other recyclables using a magnetic conveyor belt. These belts usually feed the steel directly into automatic baling presses, which produce bales that are ready for shipment. The first step of the recycling process for tin cans is "detinning" the cans. The cans are loaded into a large perforated steel drum and dipped into a sodium hydroxide solution that dissolves the tin from the steel. The detinned steel cans are then drained, rinsed and baled to be sold to steel mills and made into new products. Meanwhile, the sodium stannate solution is filtered to remove scraps of paper and garbage and the tin recovered by electrolysis and formed into ingots.

With a drop in tin prices, a declining percentage of tin in the mix and the increasing quantity of ECCS (tin-free steel) cans, detinning has fallen out of favor. The lowering of the tin percentage in scrap cans has also allowed the steel mills to use this metal directly, without it first being detinned. Since the late 1980s, steel mills have directly charged bundled steel cans into their scrap furnaces and markets for tinplate steel cans have developed.

23.2.3.5.3 Aluminum

Aluminum cans were the first food packaging materials to be recycled, and recycling rates as high as 90% have been recorded in some countries, for example, Brazil. The recycling rate in the United States was 58% in 2010. After collection and sorting, the cans are crushed and baled for shipment to a recycling plant where they are shredded into small pieces and passed through a magnetic separator to remove any steel present. The ink and enamel coatings are burnt off in a decoating process, where the emissions from this process are recirculated and burned with more fuel to preheat further batches of shredded cans, thus improving energy efficiency and reducing emissions. The hot shreds of aluminum then pass into melting furnaces where, depending on the intended end use, alloying metals are added and the aluminum is then cast into ingots (Page and White, 2000).

Very little aluminum foil is used in the unlaminated state; of the aluminum foil used, very little is recovered for recycling. When aluminum foil is laminated to plastics, it can be recovered either by pyrolysis in the absence of $O_{2,}$ where the energy in the plastic is captured and used, or by dissolving the plastic in a solvent. In both processes, the aluminum foil is recovered in a clean condition but its light weight, coupled with the high cost of separating it at MRFs, has limited the establishment of commercial recycling plants.

Aluminum foil used in liquid paperboard cartons (see Chapter 13 for details of the structure) can be recovered as part of the recycling process. The aluminum is sandwiched between layers of LDPE, and after hydrapulping, the combined foil/plastic material is separated from the paper fibers using a simple rotary screen. The combined material can be used "as is" and extruded or injection molded to make a variety of products, or it can be used as fuel. Alternatively, the foil can be separated using pyrolysis or solvents but this approach is not widespread. Another option is to shred the whole cartons and then compress them under heat and pressure to form a high-strength panel (Ayrilmis et al., 2008). No additives such as adhesives are necessary because the cartons contain 20% LDPE that melts and binds the fibers and alufoil pieces together.

23.2.3.5.4 Glass

Traditionally, glassworks have used 15%–20% of *cullet* (broken or used glass) in their raw material mix, but since the widespread increase in recycling in many countries, the proportion of cullet has increased to 65% or more in many cases, with green glass in Switzerland being manufactured entirely from cullet (Page and White, 2000). Glass for recycling is typically contaminated with a variety of materials including labels, metals, cork and plastics. The glass is crushed in a hammer mill, passed under a magnetic separator and then screened using an air classifier which removes lightweight material such as paper and plastics.

The key challenge to successful glass recycling is separation of the various colored containers into flint (clear), amber and green. The color distribution of glass in MSW averages 65% flint, 20% amber and 15% green in the United States (Borchardt, 2009). Color separation is generally done by hand at the MRF, although automated processes based on transmittance or reflectance of visible light are used where large quantities of collected glass containers are available. Used glass containers of mixed colors can only be recycled to make amber glass for which there is a finite demand. A major barrier to recycling glass in the United Kingdom is the shortage of clear cullet. While the United Kingdom produces plenty of clear glass, much of it is exported as bottles for spirits. By comparison, a large amount of green glass, principally as wine bottles, is imported and collected for recycling. The imbalance in the supply and demand for green glass is of particular concern, with the waste stream containing almost 1 million tonnes of green glass annually, yet the U.K.'s container furnaces produce just 400,000 tonnes.

A study for the U.S. Department of Energy addressing the question of whether glass container recycling actually saves energy concluded that it does not save much energy or valuable raw material and does not reduce air or water pollution significantly (Gaines and Mintz, 1994). The most important impacts are the small reduction of waste sent to landfill and increased production rates at glass plants. If used glass containers have to be transported more than 160 km (100 miles) to an MRF, then, according to this study, a break-even point is reached and recycling saves no energy. When there is insufficient demand for cullet of a specific color and grade for glass container production, open-loop recycling, for example, using cullet as a substrate in road construction, is an option (Butler and Hooper, 2011).

23.2.3.5.5 Plastics

Plastics packaging is lightweight and functional, and its use in food packaging has increased dramatically over the past 50 years, replacing many of the traditional materials such as glass and metals. Today, plastic account for up to 50% of primary food packaging. Despite the widespread use of plastic films, it is mainly the rigid plastic packaging materials that are recycled, with PET providing the greatest tonnage, followed by HDPE and PP.

Sorting is the critical step in plastic packaging recovery, determining the purity and ultimately the value of the secondary raw materials. The plastics stream, as received from households, consists mainly of films, foamed trays, thermoformed cups and sheets and bottles, which have been used to package food, together with containers for detergents, shampoos and other personal care products. The large majority of the bottles as well as parts of foamed trays and thermoformed materials consist of PET; containers for milk as well as various detergents are composed mainly of HDPE, while LDPE and LLDPE are the main film constituents. Other foamed trays, cups and thermoformed products consist of PP, PS and PVC, the latter also composing a small fraction of beverage bottles.

Most sorting of plastics is still done manually at an MRF as shown in Figure 23.2, although there are large variations between and within countries. The result is a postconsumer recycled (PCR) PET fraction that may or may not consist of bottles of the same color; an HDPE fraction that may be further subdivided into food and nonfood containers (the latter category is subject to heavy odor contamination); and a mixed plastics fraction containing films, trays and other rigid plastic materials. The mixed plastics fraction is typically used for energy recovery, although it can be recycled if a compatibilizer (a rubber-based compound that acts as a binder) is added. One problem with products made from mixed plastics is that they can have variable properties because of the variation in the constituents. The product can be used for fence posts and as a wood substitute (Page and White, 2000). There is now an increasing range of automatic machinery available to perform part, or even all, of the sorting operation. It is based on a variety of technologies which make use of differences in density, optical properties and shape.

After sorting, PCR PET is washed, ground to produce flakes of 4–20 mm in size and then washed again. The presence of small quantities of LDPE and PP (mainly from closures) is undesirable and so a separation technique based on flotation in the presence of surfactants is employed. Drying is the final operation, after which the PCR PET flakes are ready to be recycled. In the production of flakes, closures, labels and so on are removed which leads to a loss of 18% w/w of the in-coming material (Welle, 2011).

Three types of recycling processes are used for PCR PET flakes: mechanical methods, including melt reprocessing, chemical recycling involving depolymerization, followed by purification and repolymerization, and multilayer extrusion.

Mechanical recycling is defined as reprocessing the PCR PET without changing its chemical structure. It involves washing using a detergent or caustic alkali promoter at temperatures of up to 80°C, depending on the degree of contamination or prior contents of the containers. This is followed by separation involving large tanks or hydrocyclones to remove lower density materials such as PP, LDPE and HDPE, which all have densities <1.0 (PET and PVC have densities >1.33 and cannot be separated from each other using this method). After a final wash in clean water, the flakes are dried and then subjected to a final sort to remove black specks and so on. The flakes may be given a secondary treatment involving further drying (to avoid hydrolytic degradation on melting), followed by extrusion (to remove absorbed volatile organics) and melt filtration to remove nonmelting, particulate solids and degraded particles. Finally, the PCR PET is extruded and cut into pellets (Matthews, 2002). A major recycling application for PCR PET flakes is the fiber industry, which normally requires lower MW resin than do bottle manufacturers. Typical end-products include fiberfill and carpets for automobiles.

Chemical recycling (also known as *solvolysis*) is much more complicated and energy intensive than mechanical recycling. It involves breaking down the polymer chains by treatment with chemicals and two technologies are used commercially: methanolysis and glycolysis. Both cleave the ester linkages in the polymer to form monomers with glycolysis (using an excess of EG at 240°C) having some significant advantages over methanolysis (using methanol at 250°C) (Matthews, 2002). Very small quantities of PCR PET are recycled using the aforementioned processes. A third chemical recycling process is hydrolysis using mineral acids or sodium hydroxide to produce TPA and EG. However, the subsequent purification steps are very costly and the hydrolysis process is no longer commercial (Borchardt, 2009).

A possible use of PCR PET is in the multilayer extrusion of beverage bottles where the PCR PET middle layer is surrounded on both sides by virgin PET. In 1993, the FDA granted a "no objection letter" for multilayer PET containers, provided there was a 0.025 mm thick inner virgin PET layer to prevent food contact by the PCR PET layer. Today, the use of functional barriers in multilayer PET bottles plays a minor role, because the preform manufacturing process is too expensive and too slow for modern production lines. For PET sheets, however, multilayer structures with conventionally recycled PET in the core layer of the sheets are widely used (Welle, 2011).

So-called "super-clean" processes for PET bottle-to-bottle recycling use further deep-cleansing steps to clean-up conventionally recycled PET flakes and reduce contamination levels similar to those of virgin PET pellets. Although there are many different technologies commercially available, a typical deep-cleansing process involves heating to 200°C so contaminants can diffuse to the surface of the pellet or flake, vacuum or inert gas treatment to remove contaminants from the surface, and treatment with nonhazardous chemicals such as NaOH to remove part of the surface or EG to swell the polymer matrix so contaminants will diffuse faster to the surface (Welle, 2011). A typical process for the super-clean recycling process is shown in Figure 23.3.

The steps involved in recycling HDPE comprise size reduction by grinding, followed by washing (with detergents frequently being used to aid label removal), rinsing and drying. During the rinse cycle, PET and PVC contaminants sink to the bottom of the bath and can be separated from the HDPE. The clean and dry HDPE flakes can be recycled into a number of nonfood applications.

23.2.4 COMPOSTING

With the exception of plastics, rubber and leather components, the organic fraction of most MSW is composed of proteins, amino acids, lipids, carbohydrates, cellulose, lignin and ash. If these organic materials are subjected to aerobic, microbial decomposition, the end product remaining is a humus material commonly known as *compost*. During the composting process, the organic material is broken down into CO_2, CH_4 and water vapor. In moving from wet biowaste to normal compost, the weight loss is generally around 50% (McDougall et al., 2009).

The compostable fraction of MSW is the paper, paperboard and wood, since steel, aluminum and glass are totally noncompostable, inorganic materials. Although plastics are organic, they are generally resistant to microbial attack and are therefore noncompostable. However, biodegradable plastics (see Chapter 3) are compostable but at present make up a negligible part of MSW. The major food and beverage manufacturers are focusing on recyclable rather than biodegradable plastic packaging, and attempting to replace nonrenewable with renewable resources. The reason is because it makes better sense from both an environmental and economic perspective to capture the raw material and energy contained in a plastic bottle and use it again and again, instead of losing it as

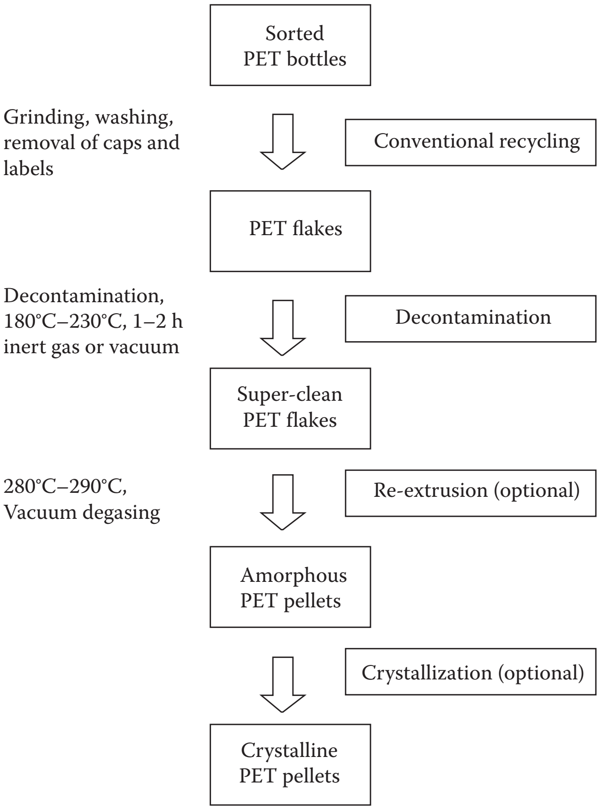

FIGURE 23.3 A typical process for the super-clean recycling process. (From Welle, F., *Resour. Conserv. Recy.*, 55, 865, 2011.)

it degrades. Converting a solid package into a gas during composting should be a last resort option and it is much better to "keep the molecules in play" through recycling.

In theory, about one third of MSW in the United States could be composted: yard trimmings (13.4% of MSW), food scraps (13.9%) and mixed paper waste that appears uneconomical to recycle (16.2%). Although paper and paperboard products make up 28.5% of MSW, many are readily recovered through recycling programs that yield a higher-value product than compost. In 2010, over 19 million tonnes of yard trimmings were composted, representing almost a fivefold increase since 1990.

EU Directive 94/62/EC specified that composting of packaging waste is a form of recycling, owing to the fact that the original product (the package) is transformed into a new product (the compost).

23.2.5 Thermal Treatment

Thermal treatment of solid waste within an integrated waste management system can include at least two distinct processes. The most common is mass burning or incineration of mixed MSW in large incinerator plants, either with or without energy recovery. The other involves separating combustible fractions from MSW to form refuse-derived fuel (RDF) and burning them as fuel.

Incinerating MSW reduces the volume of solid waste to be disposed of by, on average, 90% and the weight by around 70% (McDougall et al., 2009). Incineration also stabilizes the waste by oxidizing the organic component, making the ash relatively inert and significantly reducing landfill gas and leachate production.

Energy can be recovered from the hot flue gases during the incineration process and used to generate steam for use in electricity generation or district heating schemes (particularly common in northern Europe). The thermal efficiency of modern boilers is around 80%, but if the steam is used to generate electricity, the overall recovery efficiency (from calorific content of the MSW to electricity generated) is around 20% (McDougall et al., 2009). Virtually all new incinerators constructed since 1990 employ some form of energy recovery to help offset operating costs and reduce the capital costs of air pollution control equipment.

The energy content of MSW varies according to the country and ranges from 6 to 8 MJ kg^{-1} depending on the proportion of food scraps and green waste. Of the common plastics packaging materials, LDPE has an energy content of 43.6, PS 38.3 and PVC 22.7 MJ kg^{-1}. Beverage cartons (laminates of paperboard, polyethylene and aluminum foil) have an energy content of 21.3 MJ kg^{-1}. By way of comparison, wood chips have an energy content of 8.3, coal 26.0 and oil 41.0 MJ kg^{-1}.

The operation of incinerators results in the production of a variety of gaseous and particulate emissions, many of which are thought to have serious health impacts. In some cases, the cost and complexity of the environmental control system(s) are equal to or even greater than the cost of the combustion facilities (Tchobanoglous et al., 1993).

Several solid residuals are produced by incinerators including bottom ash, fly ash and scrubber product. Bottom ash (about 75% of the total ash produced by an incinerator) is the residue of unburned material from the combustion chamber and is typically disposed of in landfills after magnets remove any ferrous material (including steel cans) for recycling. A primary concern is that bottom ash may, under certain circumstances, leach contaminants into the groundwater (Tchobanoglous et al., 1993). Electrostatic precipitators and cyclones can be used to remove fly ash (particulates from the flue gases), and acid gases (HCl, SO_2 and HF) can be removed using scrubbers and CaO or NaOH solutions.

Of major concern has been the emission of dioxins from incinerators. Provided that the incineration process is run efficiently (residence time after last air injection of at least 2 s at 850°C at $\geq 6\%$ O_2), most of the organic pollutants in the incoming waste will be broken down. Although dioxins can be produced *de novo* in the flue gas, the levels of dioxins emitted from a MSW incinerator are considerably less than the levels in the input (McDougall et al., 2009). To meet the latest stringent emission controls for dioxin, further treatment of the flue gases is necessary.

23.2.6 LANDFILL

Landfills are the physical facilities used for the disposal of residual solid wastes in the surface soils of the earth. A *sanitary landfill* refers to an engineered facility for the disposal of MSW designed and operated to minimize public health and environmental impacts (Tchobanoglous et al., 1993). The modern sanitary landfill had its origins in Great Britain in the 1920s and was introduced a decade later in the United States.

A popular reason often advanced in support of recycling is the perceived lack of landfill space and the fear that there will soon be nowhere left to put MSW. In the late 1980s, many believed the United States faced a landfill crisis, a perception fueled in part by an EPA study, which focused on the number of landfills (many were closing and few were opening) rather than their capacity (which was growing rapidly), and in part by the publicity surrounding the New York garbage barge Mobro 4000, which had nowhere to unload its cargo of 3000 tonnes of trash. The trash had been headed for a landfill in North Carolina but was rejected due to rumors that it contained toxic hospital waste. It traveled to several southern states and Caribbean ports trying unsuccessfully to unload its garbage before returning to New York, where it remained for many weeks before the garbage was unloaded and incinerated.

The great science fiction author Issac Asimov added to the false perception in a 1991 book about environmental issues facing the world claiming that "almost all the existing landfills are reaching their maximum capacity, and we are running out of places to put new ones" (Asimov and Pohl, 1991).

The future of traditional waste management was generally agreed to be bleak. However, in most of the United Sates a landfill crisis never arrived, apart from some densely populated parts where a shortage of landfill space is a reality. The same is true for many other countries. Disposal of waste to landfill in the United States has decreased from 89% of the amount generated in 1980 to about 54% of MSW (136 million tonnes) in 2010. Since 1990, the total amount of MSW going to U.S. landfills dropped by almost 10 million tonnes, from 145.3 to 135.7 million tonnes in 2010.

It has been calculated that if Americans landfilled 110 million tonnes of garbage each year, a century of such waste would occupy a landfill only 22.5 km^2 and 33 m high (Lomborg, 2001). While this suggests that the United States will not become inundated with garbage, it does not imply that landfills will be easy to site since nobody wants to be live close to a landfill (which illustrates the "NIMBY" (not in my backyard) phenomena). Thus, although landfilling of garbage may be a political problem, it is not a problem of physical space in the United States.

It is important to put packaging waste into context. Packaging may account for up to one third of the volume of what goes into landfills. In analyzing data from landfill digs for the years from 1978 through 1988, it was found that in *per capita* terms, the amount of packaging in MSW in the United States experienced a gradual but real decline (Rathje and Murphy, 1992). In comparison, a year's worth of the *New York Times* newspaper weighs 236 kg and occupies 1.15 cm^3 in a landfill. This is equivalent in weight to 17,180 aluminum cans which is nearly a century's worth of beer and soft drink consumption by an individual (Benjamin, 2003).

Landfill regulations in many countries generally include requirements that all landfills have liners, leachate collection and treatment systems, groundwater monitoring, CH_4 control and prefunding of postclosure activities. In addition, these regulations place restrictions on landfill siting. Such regulations have influenced landfill costs in two ways: (1) they have resulted in the closure of a number of existing, noncompliant landfills, thereby reducing available landfill capacity, with the expected upward impact on "price" in the form of tipping fees; and (2) they have increased actual construction and operating costs of landfills.

Landfills are constructed according to detailed engineering specifications. A foundation of at least a meter of dense clay is laid down on the site and covered with thick plastic liners known as *geomembranes*. HDPE, very flexible polyethylene (VFPE) and PVC are materials typically used in the manufacture of geomembranes for solid waste landfills. This membrane is then covered by a meter of gravel or sand. As garbage is placed in the landfill, layers of dirt or other inert materials are used to cover it, generally each day. This serves several purposes including prevention of pollution of the surrounding landscape by lightweight materials such as paper and plastic bags, and discourages birds and vermin from living among the garbage.

All landfills produce leachate that must be dealt with. *Leachate* is liquid that has percolated through the layers of waste material. The chemical quality of leachate varies as a function of a number of factors, including the quantity produced, the original nature of the buried waste materials and the various chemical and biochemical reactions that may occur as the waste materials decompose. Thus, leachate may be composed of liquids that originate from a number of sources, including precipitation, groundwater, consolidation, initial moisture content and reactions associated with decomposition of waste materials. Landfills should be designed to prevent any waste or leachate from ever moving into adjacent areas. A key first step in controlling leachate migration is to limit production by preventing, to the extent feasible, the entry of external water into the waste layers. A second step is to collect any leachate that is produced for subsequent treatment and disposal (Worrell and Vesilind, 2012).

The anaerobic decomposition of organic materials in a MSW landfill will generate a combination of gases (collectively called *landfill gas*) at a rate of approximately 0.002 $\mathrm{m}^3\ \mathrm{kg}^{-1}$ of waste per year. The underground migration of landfill gas can pose serious safety risks in nearby structures when the gas accumulates at concentrated levels. The gas (ca. 50% CH_4 and 50% CO_2) is an excellent energy source. Methane is generally recovered with conventional gas wells and directed to either a gas turbine or internal combustion engine that is used to power an electrical generator. Thus, the energy content of the landfill waste is converted to electricity. As a GHG, CH_4 is 25 times more potent than CO_2. Consequently, burning CH_4 and converting it to CO_2 reduces the potency of landfill gas as a GHG.

There are currently 503 landfills in the United States at which the gas is converted to energy and an estimated additional 545 landfills at which energy recovery is viable. Nonetheless, as a result of gas generated prior to installation of gas collection systems and fugitive emissions, landfills are estimated to be the second largest source of anthropogenic methane emissions in the United States (Levis and Barlaz, 2011).

The most critical factor in determining a landfill's decomposition rate is the moisture content of the waste. Conventional landfills with a tightly sealed cover impede water from entering the waste. Consequently, decomposition is very slow and, in some cases, expected to take up to 1000 years before waste stabilization is completed. Complete stabilization is when the waste material no longer breaks down into by-products that are released into the environment.

Decomposition time can be reduced to a matter of months using solid waste digesters similar to sewage sludge digesters; they can stabilize waste in weeks. These systems, however, have high construction costs and a more practical approach is to modify an existing landfill operation to accelerate decomposition while maintaining the critical, physical elements of the landfill. Therefore, the current approach to bioreactors is to devise a system in which water is introduced into the waste to wet the material as uniformly as possible. The added moisture then accelerates decomposition, which generates large quantities of landfill gas. With a bioreactor landfill, gas generation begins much faster and generation rates are much higher.

One myth concerning landfills is that they are giant composters. While some biodegradation does take place (if it did not, then no CH_4 would be produced), biologically and chemically, a landfill is a much more static structure than is commonly supposed. They have been described as vast mummifiers, with excavations finding that even after two decades of burial, about one third to one half of food and yard waste remains in a recognizable condition, and old newspapers can be easily read (Rathje and Murphy, 2002).

23.3 LIFE CYCLE ASSESSMENT

Life Cycle Assessment (LCA) is an environmental management tool that attempts to consider the resource and energy use, as well as the environmental burdens, over the entire life cycle of a package, product or service, from extraction of the raw materials through manufacture/conversion, distribution and use to recovery or disposal. It is sometimes referred to as "cradle to grave" analysis and typically compares two or more products that provide the same functional use. LCA had its beginnings in the 1960s when concerns over the limitations of raw materials and energy resources sparked interest in finding ways to cumulatively account for energy use and to project future resource supplies and use. The first LCAs were performed on beverage containers in 1972 in the United States and in Japan in 1977 by the Toray Research Institute (Hunt and Franklin, 1996).

LCA can be split into four phases:

- Goal definition and scoping
- Life cycle inventory (LCI)
- Life cycle impact assessment (LCIA)
- Life cycle interpretation

The ISO 14040 series of international standards provide a framework for conducting LCAs and are intended as a non-prescriptive guide because there is no single method or end use for conducting LCAs. The original standards (four in total) were produced in 1997 and updated (and reduced to just two) in 2006. ISO 14040:2006 is entitled *Environmental management. Life cycle assessment.*

Principles and framework. ISO 14044:2006 is entitled *Environmental management. Life cycle assessment. Requirements and guidelines.*

23.3.1 GOAL DEFINITION AND SCOPING

This stage sets the goals for the study and specifies the reason for conducting the study, the intended use of the results, the geographical area for which the results should be valid, the intended audience, functional unit, system boundaries, data requirements and the procedures for handling data and the study limitations.

The functional unit is a key element and is defined as the unit of product that is going to be studied and compared; it provides a reference to which the inputs and outputs can be related. For packaging, it is commonly the packaging required to deliver a given volume of beverage (e.g., 1000 L) or quantity of food (e.g., 1 tonne). Sometimes, only the primary packaging is included; other times all the packaging involved is included.

23.3.2 LIFE CYCLE INVENTORY

LCI involves a materials and energy balance for the entire system; that is, identification and quantification of all the inputs into, and all the outputs from, the system under study as shown in Figure 23.4. The system must be broken down into individual unit operations and a complete breakdown of all inputs and outputs (both material and energy) determined. Material outputs include air, water and solid waste emissions. Difficulties are sometimes experienced in obtaining quality data for each individual unit operation, particularly when these occur in other countries.

Data collection is the most resource consuming part of an LCA. The quality aspect of the data is crucial, and in an ideal world, all the data required would be obtained from the correct sources. In practice, this is seldom possible and therefore generic data has to be used, at least for part of the LCI. In an effort to reduce the amount of work required to complete an LCI, databanks of relevant information have been established. For example, the U.S. Department of Energy National Renewable Energy Laboratory and its partners created the U.S. Life-Cycle Inventory (LCI) Database (www.nrel.gov/lci/).

It is important to note that LCIs are concerned with quantitative physical data. Therefore, any physical effects that cannot be quantified will not be included in the calculations. Thus, effects such as biodiversity, for which there is no recognized measurement, will be absent from the calculations.

Despite the great deal of information provided about energy use and emissions associated with the life cycle of a product or package, the LCI information cannot be generally applied to the product's effect on human health, ecological quality and natural resource depletion. This is because one kilogram of a given emission may provide substantially different effects on human health or the environment than a kilogram of a different emission (Franklin et al., 2009). The next stage of LCIA helps to address this issue.

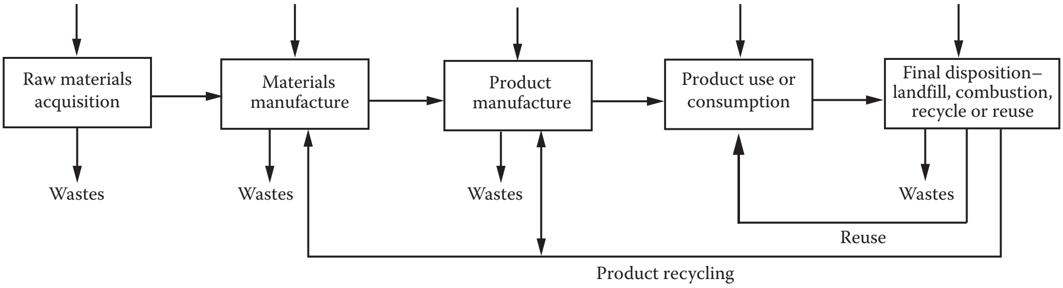

FIGURE 23.4 Inputs and outputs requiring identification and quantification for a life cycle inventory.

23.3.3 LIFE CYCLE IMPACT ASSESSMENT

In this stage, the LCI results are converted into a range of environmental indicators in a two-step process. First, the LCI results are organized according to environmental issues or impact groups such as GHG loading, fossil fuel inputs, ozone depletion potential and nutrient loading. Then, the LCI results for each environmental issue or category are converted using a characterization factor and aggregated into the impact category indicator. The categories chosen for impact assessment should be internationally accepted, scientifically and technically valid and environmentally relevant.

This stage involves considerable value judgments and thus needs to be transparent. It involves the evaluation of the different emissions across all impact groups. The lack of a widely accepted and nonsubjective model for impact assessment limits its applicability to industry and in policymaking.

23.3.4 LIFE CYCLE INTERPRETATION

The aim of the interpretation phase is to reach conclusions and recommendations in accordance with the defined goal and scope of the study. Results from the LCI and LCIA are combined together and reported in order to give a complete and unbiased account of the study. The life cycle interpretation comprises three main elements:

- Identification of the significant issues based on the results of the LCI and LCIA phases
- Evaluation of results, which considers completeness, sensitivity and consistency checks
- Conclusions and recommendations for reducing material use and environmental burdens

ISO 14040 recommends that a critical (peer) review should be performed. In addition, it also states that a critical review must have been conducted in order to disclose the results in public.

23.3.5 LIMITATIONS OF LCA

Despite the increasing popularity of LCAs by both industry and governments, the technique does have significant limitations which are all too often overlooked. The first is that LCAs are not able to assess the actual environmental effects of emissions and wastes from the product or package. This is because the actual effects will depend on when, where and how they are released into the environment. Releasing an emission from a point source will have a very different environmental effect from releasing it continuously over years from many different sources. Other tools such as risk assessment are able to predict the actual effects likely to occur although they do not link the effects to the functional unit.

A second limitation is that LCAs do not consider the various functions which a package has to perform. Thus, when comparing several different packages for the same product, an LCA takes no account of the convenience function such as whether or not the package is reclosable, easy to pour from and so on. Neither do LCAs consider the protection and preservation function of the packages, so that if, for example, one of the packages provides 50% greater shelf life than the other, this is not taken into account. Finally, the communication function is also ignored; this limitation could be significant from a marketing viewpoint, with some packages providing a much greater shelf-facing surface area for branding and so forth than others.

A third limitation is that LCAs take no account of economic factors such as the costs of raw materials, manufacturing, transport and recovery or disposal. In the extremely competitive packaging industry, cost is of prime importance.

A fourth (frequently overlooked) limitation is that the conclusions from LCAs are specific only for the precise system under study. They cannot be extrapolated to provide universal generalizations that one particular package is always better than another in every situation.

A fifth limitation relates to the desire to use LCAs in public policy to determine whether a particular package is good or bad for the environment or whether a particular waste management option is appropriate. EU Directive 94/62/EC on Packaging and Packaging Waste stated that LCAs should be completed as soon as possible to justify a clear hierarchy between reusable, recyclable and recoverable packaging. The problem with, and indeed impossibility of, using LCAs in this way is discussed in the following.

Numerous LCAs have been conducted on the environmental impacts of beverage packaging systems. A recent "meta analysis" of 22 such studies performed over the past 10 years was conducted with the goal of establishing whether it was possible to draw general conclusions regarding the environmental performance of beverage cartons in comparison to alternative packaging systems (von Falkenstein et al., 2010). For climate change, cumulative energy demand/fossil resource consumption and acidification, beverage cartons mostly had the most favorable results, while in terms of land use for forestry, they clearly required the largest area. For summer smog and terrestrial eutrophication, the results pointed toward a favorable picture for beverage cartons, although fewer of the LCA studies provided results for these impact categories. For other environmental aspects, where the results of the analyzed studies varied strongly, no clear pattern could be made out. These results illustrate the impossibility of making a generalization that one packaging material is superior to another.

23.3.6 Uses of LCAs

Despite the limitations described earlier, LCA can be a very useful tool in two major areas. First, package design, development and improvement all benefit from having LCA results available. An LCA can help identify where significant resource use, wastes and emissions are likely to occur and thus suggest where significant changes or improvements can be made. Sometimes, only an LCI is performed and this is used as an initial screening tool when a number of options are being evaluated. In other cases, only life cycle energy is calculated and this is used as a surrogate for environmental impacts. In some situations where a "quick and dirty" comparison is sufficient, only the weight of the competing packages is used because the lightest-weight package almost always has the lowest environmental impacts (PVC would be one exception).

Secondly, LCA can help decision-makers select the product or process that result in the least impacts to the environment. This information can be used with other factors, such as cost and performance data, to select a package or process.

Thirdly, LCA is a useful tool for assessing waste management options. The waste management hierarchy (see Section 23.2.1) has no scientific or technical basis and cannot deal with combinations of treatment options. Instead of relying on a rigid hierarchy, waste planners and managers are turning to LCA tools to help them plan ISWM systems on a case-by-case and regional basis (McDougall et al., 2009).

LCA has emerged as a valuable decision-support tool for both policy makers and industry in assessing the cradle to grave impacts of a product or process. Three forces are driving this evolution. First, government regulations are moving in the direction of life cycle accountability and the concept that a manufacturer is responsible not only for direct production impacts, but also for impacts associated with product inputs, use, transport and disposal. Second, business is participating in voluntary initiatives which contain LCA and product stewardship components. Third, environmental preferability has emerged as a criterion in both consumer markets and government procurement guidelines. Together these developments have placed LCA in a central role as a tool for identifying cradle-to-grave impacts both of products and the materials from which they are made.

In recent years, packaging manufacturers have released the conclusions of LCAs comparing various alternative packaging materials. Regrettably, not all of these LCAs are publicly available and therefore, it is impossible to know what assumptions were made and what data were used.

TABLE 23.2
Total Energy, Solid Waste and Greenhouse Gas Emissions from 10,000 12-oz (355 mL) Soft Drink Containers

Container	Total Energy (GJ)	Solid Waste (Weight) (kg)	Solid Waste (Volume) (m^3)	Greenhouse Gases (CO_2 Equivalents) (kg)
PET bottle	212	251	22.9	946
Aluminum can	203	418	12.6	1378
Glass bottle with steel cap	213–247	1537–1785	28.5–33.0	1670–1930
Glass bottle with aluminum cap	236–270	1581–1829	29.3–33.7	1810–2071

Source: Franklin Associates, *Life Cycle Inventory of Three Single-Serving Soft Drink Containers*, 2009. Downloadable from www.petresin.org/pdf/FranklinLCISodaContainers2009.pdf

One publicly available LCA that follows the ISO 14040 guidelines was conducted by Franklin Associates for the U.S. PET Resin Association (PETRA), and compared total energy, solid waste and GHG emissions for PET and glass bottles and aluminum cans for soft drinks. A summary of the results is shown in Table 23.2. The LCI covered extraction of raw materials through container fabrication, as well as postconsumer disposal and recycling using current U.S. recycling rates. The postconsumer disposal and recycling calculations included transporting to a landfill or incinerator, equipment operations at a landfill and energy recovered by an incinerator, but excluded incinerator and landfill emissions. Post fabrication transportation to the filling site, filling, distribution, storage, retail use and consumer use were excluded. The full report is available at www.petresin.org/pdf/FranklinLCISodaContainers2009.pdf.

A study by Williams and Wikström (2011) highlighted the importance of taking into account food losses when designing packaging and showed that there are obvious potentials to increase customer satisfaction and at the same time decrease the environmental impact of the food packaging system, especially when the packaging design helps to decrease food losses. They found many connections between quality attributes and environmental impacts and suggested that LCAs made to develop new and better packaging ought to include contents and ways to minimize food losses. Most LCAs on packaging do not take contents and consumer behavior into consideration. Additional knowledge about the way packaging design affects food losses, as well as quantification of specific food packaging cases, is needed. They also recommended that the function of the package to preserve its contents should be integrated in future EU directives on packaging and packaging waste, because losses are important in the life cycle of food. Reducing the gross waste of food should take precedence over reducing packaging.

23.3.7 TOOLS FOR LCA

A large number of computer-based tools have been developed to assist in the production of LCAs. Some are more complex and sophisticated than others, making it possible to easily model and analyze complex life cycles in a systematic and transparent way, following the recommendations in ISO 14040 and 14044. Of course, the quality of the input data will determine the value of the results.

23.3.8 CARBON FOOTPRINTING

GHGs naturally blanket the Earth and keep it about 33°C warmer than it would be without these gases in the atmosphere. This is the so-called “Greenhouse Effect,” so named because of a similar effect produced by the glass panes of a greenhouse. Over the past century, the Earth has increased in temperature by about 0.5°C and many scientists believe this is because of an increase in concentration of the main GHGs: CO_2, CH_4, N_2O and fluorocarbons. There is evidence that GHG concentrations due to human activity are the dominant cause of the global warming that has taken place over the last half century. Measurements made since the 1950s show the level of CO_2 rising year on year, from 316 ppm in 1959 to 392 ppm in 2011.

Carbon footprint (CFP) is a term used to describe the amount of GHG emissions caused by a particular activity or entity, and thus a way for organizations and individuals to assess their contribution to global warming and climate change. Understanding these emissions, and where they come from, is necessary in order to reduce them. In this context, manufacturers are asking for the CFP associated with the manufacture, distribution and disposal of products provided to them such as packaging.

The CFP is expressed as CO_2 equivalents (abbreviated CO_2e). Since CO_2 is the reference gas against which other GHGs are measured, it therefore has a Global Warming Potential (GWP) of 1. Examples of GWPs for other GHGs are 25 for CH_4, 298 for N_2O and 22,800 for SF_6.

ISO 14040 and 14044 provide guidance for calculating the GHG associated with a product, and therefore, there is no need to develop a separate method for calculating the CFP. Despite this, a number of ISO standards have been released and more are in development dealing specifically with GHGs (14064 to 14069).

Despite the existence of ISO standards, PAS 2050, a publicly available specification (PAS) for assessing product life cycle GHG emissions, was prepared by the British Standards Institute in 2007 and has become widely accepted globally. PAS 2050:2011 builds on existing methods established through ISO 14040 and 14044 by specifying requirements for the assessment of the life cycle GHG emissions of products. However, CFP results obtained using PAS 2050 differ from those in ISO 14067 because the former does not consider biogenic CO_2 emissions. Another point of difference is the time that emissions from final disposal of packaging are present in the atmosphere; PAS 2050 considers the GWP on the basis of a 100-year time horizon, whereas ISO 14067 does not and consequently the latter CFPs are higher.

Poovarodom et al. (2012) reported the CFPs (calculated according to PAS 2050) of single-serve (85 g) packs of tuna in a two-piece ECCS can with aluminum ring-pull, a PP-alufoil-PA-PP retort pouch and a PP-EVOH-PP retort cup with PET-alufoil-PA-PP lid. The CFPs as CO_2e were 253 g for the retort cup, 280 for the metal can and 322 g for the retort pouch. Package manufacturing constituted 13%–41% of the products' CFP with CO_2e of 33 g for the retort cup, 43 g for the retort pouch and 104 g for the metal can. Recycling of metal cans provided substantial environmental benefits with a credit of 37 g CO_2e; no cups or pouches are recycled and their disposal CFPs were around 2 g CO_2e.

What does it mean for a consumer that a retort pouch of tuna is labeled to have a CFP of 322 g CO_2e? Are they aware, for example, that 2 h of watching television generates 200 g CO_2e or filling of a dishwasher is equivalent to 622 g CO_2e and a flight of 1,000 km would generate 170,000 g CO_2e (Schmidt, 2009)? What sense would it make if a consumer drove to another store to buy tuna in a retort cup and in so doing generated more than the difference in CO_2e saved? Clearly, there needs to be a public education campaign before CFPs are launched to avoid unintended consequences.

In general, the public tend to have a poor understanding of energy (especially embodied energy) as the following example illustrates:

> 1 U.S. gallon (3.79 L) of gasoline comprises about 131.7 MJ of energy. A LCA of plastic water bottles showed that it requires about 92.6 MJ of energy to make the plastic, transport and convert it into one hundred 10 g PET water bottles. Thus, the energy equivalent of 1 gallon of gasoline could potentially create about 142 water bottles. If a car travels 30 miles per gallon, that is the equivalent of about 4.7 bottles per mile.

> When we drive our cars, the exhaust from the burned-up fuel "disappears" out of the tailpipe and we never see it. Ten gallons of gasoline produces about 88 kg of CO_2e, the equivalent footprint of 1940 water bottles. If we had to dispose of, or recycle, 88 kg of material every time we burned 10 gallons of gasoline, many people would think very differently about driving. In theory, the plastic bottles can be recycled to reduce material needed for the next generation of bottles. The burned-up gasoline is lost forever (Amcor Rigid Plastics, 2012).

23.4 PACKAGING AND ENVIRONMENTAL POLICIES

23.4.1 United States

Polls of U.S. citizens in the early 1990s showed them ranking MSW high among their list of environmental concerns, though environmental scientists put solid waste nearly at the bottom of important environmental problems (Levy, 2000). The perception of the solid waste problem was predicated on two beliefs: (1) that disposal capacity could not keep pace with current waste generation rates and (2) that disposal was unsafe, whether in landfills or incinerators. Perceptions of a landfill crisis resulted in legislation in 41 U.S. states to divert waste from landfills.

Examination of the facts confirms that perceptions of a landfill crisis were misplaced. The amount of landfilled MSW in the United States peaked in 1987 at about 82%; 9% was incinerated and the balance (9%) recycled. In 2009, 29.7% of MSW was recovered with 25.2% being recycled and 8.6% composted, 11.9% was incinerated with energy recovery and the remaining 54.3% disposed of in landfills (EPA, 2011). Landfill capacity does not appear to be a problem today, although regional dislocations sometimes occur. The number of landfills in the United States has declined from 8000 in 1988 to 1908 in 2009.

In 1976, the Resource Conservation and Recovery Act (RCRA) gave the EPA broad authority over landfills and incinerators and established national environmental standards for landfills which were made stricter by amendments passed in 1984. A major contribution of the EPA has been issuing statistical reports on the management of solid waste, each report appearing about 11 months after the end of the calendar year (EPA, 2011).

In contrast to Europe, the U.S. federal government has not introduced national packaging goals nor embraced the notion of extended producer responsibility (EPR). The federal government's most visible role in recycling matters has come through federal procurement policy rather than through any comprehensive national legislation. Paper has been the primary target of these efforts to date, with packaging receiving only occasional consideration.

Dr. Winston Porter, the assistant administrator for solid waste at the EPA, established a national goal in 1989 for recycling 25% of the country's MSW, and this nonbinding goal was reached in 1995. Legislation at the state level remains more significant than federal legislation. By 1995, nearly all states had implemented laws requiring or encouraging household and commercial recycling. The number of curbside recycling programs in the United States jumped from a few hundred to over 9000 in the period from 1989 to 2009. Although 11 states have deposit systems for beverage cans and bottles (so-called *bottle bills*), there is very little legislation dictating how postconsumer packaging should be handled. Local municipalities have led the way by introducing curbside collection of recyclables and consumers have generally participated and actively supported these initiatives. It has been calculated that more adults participate in recycling on a regular basis than vote for a President, which led U.S. journalist Jerry Powell to remark in 1992 that recycling is more popular than democracy.

23.4.1.1 Container Deposits

In response to the increase in one-way (nonrefillable) beverage containers from the 1960s, some cities, states and counties have introduced mandatory deposit/refund systems, typically for soft drink and beer containers. However, these systems were not introduced primarily to increase recycling rates, but rather in response to a rising tide of litter in which one-way beverage containers used to feature quite prominently (Ackerman, 1997). Although containers collected under deposit/refund systems appear to achieve higher recycling rates than are achieved in the absence of such programs, they are much more costly than curbside programs, and this additional cost is ultimately paid by the consumer. Today, with the widespread access to curbside recycling programs in many cities, deposit/refund systems are no longer seen as necessary or economically efficient.

23.4.1.2 Extended Product Responsibility

In 1996, the U.S. President's Council on Sustainable Development introduced the term *extended product responsibility* to mean that all participants in the product life cycle (including government, industry with an economic interest in the product, consumers and waste handlers) share responsibility for the environmental effects of products and waste streams. Responsibilities were viewed to shift, depending on which entity most directly generated an environmental impact and had an ability to mitigate that impact. The concept has not found its way into any legislation and has created some confusion with the quite different concept of *extended producer responsibility* (EPR) which is widely applied in the EU (see the following).

23.4.2 EUROPE

Europeans have tended to regard packaging as a form of pollution and applied the "polluter pays" principle (PPP) to packaging manufacturers, requiring them to take back the used packaging at their cost. However, packaging *per se* is not pollution although it may cause environmental impacts if it is littered or otherwise disposed of improperly. In fact, packaging prevents waste by enabling products to be distributed and consumed long distances from their point of manufacture with a minimum of environmental impacts.

23.4.2.1 Producer Responsibility

The idea that producers should be responsible for the total life cycle of the products they manufacture and that responsibility should not be limited to production but extended to the actual products, was first introduced into legislation in Sweden in 1975. Since then, two variations have been introduced: shared producer responsibility, where the producer of the goods may be considered to share responsibility across the life cycle with all the others involved, and EPR, where the producer of the goods alone has responsibility across the life cycle.

EPR is a strategy designed to promote the integration of environmental costs associated with goods throughout their life cycles into the market price of the products. The OECD defines EPR as an environmental policy approach in which a producer's responsibility for a product is extended to the postconsumer stage of a product's life cycle. An EPR policy is characterized by (1) the shifting of responsibility (physically and/or economically; fully or partially) upstream toward the producer and away from municipalities and (2) the provision of incentives to producers to take into account environmental considerations when designing their products. While other policy instruments tend to target a single point in the chain, EPR seeks to integrate signals related to the environmental characteristics of products and production processes throughout the product chain.

A critique of EPR has pointed out that packaging is owned throughout its life cycle from production through sale, consumption, recovery and disposal, though who owns the package or the residue changes as it changes hands (Scarlett, 1998). With ownership come clearly defined rights and responsibilities. As a consequence, all responsibility for subsequently generated environmental impacts passes with ownership; this is the true embodiment of the PPP—not EPR. Relieving consumers of responsibility in the disposal of used packaging and making producers responsible, decouples consumers from the environmental aspects associated with product selection. Under EPR, the producer pays in advance for the pollution created by future owners of the product. However, the EPR concept does not apply to all waste, for example, chicken farmers do not have to pay for the disposal of chicken bones, nor clothing manufacturers for the disposal of used clothing. Despite these criticisms, EPR is an established concept in the EU although today the term *shared responsibility* is also used.

23.4.2.2 German Packaging Ordinance

The first real application of the EPR concept in Europe was the 1991 German Packaging Ordinance where all the costs for managing packaging waste had to be borne by the economic operators who placed goods into the market. This law led to the formation of the Duales System Deutschland GmbH (DSD), which operated a separate but parallel municipal packaging waste management infrastructure financed by the producers and importers of packaged goods. To indicate its participation in the scheme, the DSD licenses a mark known as the *Grüner Punkt* (or *Green Dot*), which is placed on packaging for which the appropriate fee has been paid. The DSD contracts with disposal companies for the collection and separation of packaging using a combination of bring and pick-up systems; recycling is coordinated via guarantors for each material waste stream. The law mandates extremely high recycling targets, and much of the collected and sorted material is sent to other countries in Europe and Asia for recycling. Germany's packaging ordinance has led to the collection and recycling of more than two-thirds of the country's used packaging, albeit at great expense.

Other countries have modified the German approach in the hope of achieving similar results at lower costs. The Green Dot logo is a registered trademark of PRO Europe (Packaging Recovery Organisation Europe: www.pro-e.org/) and is protected in 170 countries. It has been sublicensed to 23 European countries plus Canada and Turkey. Fees vary by country and are based on the packaging material used. Each country has different fees for joining the scheme and ongoing fixed and variable fees. Fees take into account the cost of collection, sorting and recycling methods. The system encourages manufacturers to reduce packaging as this reduces their license fees.

23.4.2.3 Packaging and Packaging Waste Directive

The 1994 EU Directive 94/62/EC on Packaging and Packaging Waste was the first product-specific regulation in the field of EU waste policy. It applied to all packaging placed on the market in the EU and all packaging waste, whether it was used or released at industrial, commercial, office, shop, service, household or any other level, regardless of the material used. The Directive laid down quantitative targets to be met by July 2001 for recovery (i.e., material recycling, incineration with energy recovery and composting) of packaging waste. A substantial increase in the targets was contained in the amendment to the directive (2004/12/EC) released in February 2004. It decreed that by 31 December 2008, 60% as a minimum by weight of packaging waste must be recovered and 55% as a minimum and 80% as a maximum by weight must be recycled, with the following minimum recycling targets for each material (by weight): 60% for glass, paper and board; 50% for metals; 22.5% for plastics (counting exclusively material that is recycled back into plastics); and 15% for wood.

The directive stated that member states shall, where appropriate, encourage energy recovery where it is preferable to material recycling for environmental and cost-benefit reasons. Furthermore, recycling targets for each specific waste material should take account of LCAs and CBAs, which have indicated clear differences both in the costs and in the benefits of recycling.

A comprehensive analysis of packaging and packaging waste statistics in the EU has been provided and should be consulted for specific details about recycling rates and so on (Europen, 2011). Key conclusions were that the amount of packaging being put on the market has been increasing much more slowly than growth in GDP and other indicators, and the amount of used packaging sent for final disposal is declining rapidly, as recovery rates (particularly recycling rates) continue to increase. Recently, Fischer (2011) gave an overview of the set targets, the achieved results and the consequences for GHG emissions of municipal waste management in the EU.

There has long been concern in the EU that so-called packaging waste was being shipped to developing countries (particularly China and India) where much of it was landfilled and not recycled (some shipments also contained hazardous waste). To address this concern, EC Regulation

1013/2006 *Shipments of Waste* and amendment 664/2011 require exporters to check that the destination country is willing to accept that waste type for reprocessing and ensure that each shipment complies with any restrictions. Packaging waste exported out of the EU only counts for the achievement of the obligations and targets if there is sound evidence that the recovery or recycling operation took place under conditions that are broadly equivalent to those prescribed by EU legislation on the matter.

The EU Waste Framework Directive 2008/98/EC stated that when applying the waste hierarchy, member states shall take measures to encourage the options that deliver the best overall environmental outcome. This may require specific waste streams departing from the waste hierarchy where this is justified by life cycle thinking (LCT) on the overall impacts of the generation and management of such waste.

23.5 PACKAGING AND SUSTAINABILITY

23.5.1 Sustainable Development

The concept of sustainability has deep foundations in the history of political and economic thought, with the American statesman Thomas Jefferson writing in 1789 that “the earth belongs in usufruct (defined as the right of enjoying the use and advantages of another’s property short of destruction or waste of its substance) to the living.” In its simplest sense, sustainable means to maintain or keep going continuously, and the word has been used in connection with forest management since the nineteenth century. In 1910, the first Chief of the U.S. Forest Service outlined an approach to resource management that “recognizes fully the right of the present generation to use what it needs ..… of the natural resources now available, but [also] recognizes equally our obligation so to use what we need that our descendants shall not be deprived of what they need.” This approach clearly informed the most widely accepted definition of sustainable development (SD) that appeared in the report of the World Commission on Environment and Development (also known as the “Brundtland Commission”) in 1987 entitled *Our Common Future*:

> …Humanity has the ability to make development sustainable—to ensure that it meets the needs of the present without compromising the ability of future generations to meet their own needs…

Contained within this definition are two key concepts: that of needs, and in particular the essential needs of the world’s poor to which overriding priority should be given, and the idea of limitations imposed by the state of technology and social organization on the environment’s ability to meet present and future needs. In other words, SD is the level of human consumption and activity that can continue into the foreseeable future, so that the systems which provide goods and services to humans persist indefinitely. The practical implications of this definition are diverse, ranging from the consumption of resources with respect to their rate of renewal, to the efficiency of resource use and the equity of their use across societies and generations.

The Brundtland Commission also stated that, “.… Sustainable development ..… is not a new name for environmental protection: it is a new concept of economic growth.”

Imagine being in London 150 years ago and discussing SD. Concerns would have centered on whether there would be sufficient straw to feed the increasing number of horses in the city or enough whale oil to keep the lamps burning. The subsequent invention of the motor car put paid to concerns about straw production and electricity replaced oil lamps. These two examples aptly illustrate the difficulty, and indeed the impossibility, of predicting with any certainty what resources future generations may or may not require to enjoy a standard of living at least equal to that which is enjoyed today. However, leaving future generations a “clean” or unpolluted environment is not conceptually difficult to conceive, although in practice it is a huge challenge to achieve.

Despite these limitations, the term SD has been the underlying principle informing the debate first at the Rio Earth Summit of 1992 and the Johannesburg summit of 2002. The derivative words sustainable and sustainability have also achieved widespread usage but their meaning has been stretched so far as to become nearly meaningless.

It is now accepted that sustainability has three dimensions or pillars: economic, environmental and social. These three dimensions are also referred to as the triple bottom line or profits, planet and people. Sustainable business practices integrate environmental concerns with social and economic ones. The metrics used for the measurement of sustainability are evolving and include indicators, benchmarks, standards and certification systems. Those proposed for packaging are discussed later.

Sustainable production involves creating goods by using processes and systems that are non-polluting, conserve energy and natural resources in economically viable, safe and healthy ways for employees, communities and consumers and are socially and creatively rewarding for all stakeholders in the short- and long-term. However, strategies relying on a mere improvement of resource productivity and ecoefficiency of processes and products are not able to fully address the environmental impacts resulting from increasing consumption. What is required is a move away from a material-intensive consumer culture to a society with less materialistic aspirations, that is, toward sustainable consumption. Although food packaging sits right in the centre of this material-intensive consumer culture, there is a noticeable lack of strategies and debate on how societies might move toward sustainable consumption.

The worldwide per capita consumption of Coca-Cola (based on 8 U.S. fluid ounces (237 mL) of finished beverage) has increased from 43 in 1990 to 89 in 2010. Highest consumption is in Mexico (675) with China at 34 and India at 11. What is sustainable consumption of Coca-Cola and how could it possibly be controlled? There is no simple answer to this question which is an issue faced by all food and beverage companies.

23.5.2 SUSTAINABLE PACKAGING

In 2005, the U.S.-based Sustainable Packaging Coalition (SPC) defined sustainable packaging by listing eight criteria that relate to the activities of the packaging value chain and define the areas in which it actively seeks to encourage transformation, innovation and optimization; the latest version is presented in Table 23.3 and discussed by Johnson (2009). It is intended as a "target vision" for companies to strive toward through continuous improvement and will evolve over time with new materials and technologies, leading to more sustainable packaging systems. The SPC claims quite correctly that their criteria blend broad sustainability objectives with business considerations and strategies that address the environmental concerns related to the life cycle of packaging and the activities of the SPC membership. The SPC members believe that by successfully addressing these criteria, packaging can be transformed into a closed loop of packaging materials in a system that is economically robust and provides benefits throughout the life cycle—a sustainable packaging system.

TABLE 23.3
Sustainable Packaging Criteria[a]

Is beneficial, safe and healthy for individuals and communities throughout its life cycle
Meets market criteria for performance and cost
Is sourced, manufactured, transported and recycled using renewable energy
Optimizes the use of renewable or recycled source materials
Is manufactured using clean production technologies and best practices
Is made from materials healthy throughout the life cycle
Is physically designed to optimize materials and energy
Is effectively recovered and utilized in biological and/or industrial closed loop cycles

Source: Sustainable Packaging Coalition, 2011. www.sustainablepackaging.org/

[a] No ranking is implied by the SPC in the order of criteria.

A detailed critique of the SPC criteria has been presented by Robertson (2009) and will not be repeated here. Suffice it to say that a single packaging choice can have many ecological repercussions and these can sometimes be contradictory. For example, while paper-based packaging uses a renewable resource, it may consume more energy to fabricate and transport than plastic. What may be the most sustainable solution for one product or particular market might not be the same elsewhere.

Rather than trying to define sustainable packaging, U.S.-based Wal-Mart Stores, the world's largest retailer, is promoting itself as a leader in sustainable packaging through initiatives such as its packaging scorecard, a measurement tool that allows suppliers to evaluate themselves relative to other suppliers, based on specific metrics. Wal-Mart is promoting a number of principles including eliminating unnecessary packaging; eliminating materials harmful to human health and the environment; "right-sizing" packaging, for example, by optimizing material strength; use of recyclable or reusable transport packaging; use of renewable, recyclable and recycled content materials and achieving all principles at cost parity or cost savings. The Packaging Scorecard, 1 of 13 measurement tools Wal-Mart has introduced to evaluate the performance of suppliers, is part of its modest commitment to reduce packaging across its global supply chain by 5% by 2013. It aims to encourage suppliers to work toward continuous improvement and assist buyers to select packaging with reduced environmental impacts.

The European Organization for Packaging and the Environment (Europen) believes it makes much more sense to talk about packaging and sustainability rather than sustainable packaging which in its view cannot be an end in itself. It recommends that packaging suppliers tell their customers how their packaging helps them to achieve their corporate sustainability goals. In the context of overall sustainability, packaging should (in their view) be regarded as part of the solution, not part of the problem and as a net contributor to achieving the broad sustainability goal of resource optimization and waste minimization. In its view, packaging makes a valuable contribution to economic, environmental and social sustainability through protecting products, preventing waste, enabling efficient business conduct and providing consumers with the benefits of the products it contains. Europen's vision is presented in Table 23.4.

The Consumer Goods Forum (CGF) was created in 2009 and is a global industry network that brings together the CEOs and senior management of over 650 retailers, manufacturers, service providers and other stakeholders across 70 countries. In 2011 it published the *Global Protocol on Packaging Sustainability* (http://globalpackaging.mycgforum.com/) to provide the consumer goods and packaging industries with a common language with which to discuss and assess the relative sustainability of packaging. That common language consists, not in a definition of sustainable packaging, but a framework and a measurement system. The framework entitled *A Global Language for*

TABLE 23.4
Europen's Vision of Packaging's Contribution to Sustainable Development

Packaging should

- Be designed holistically with the product in order to optimize overall environmental performance
- Be made from responsibly sourced materials
- Be designed to be effective and safe throughout its life cycle
- Meet market criteria for performance and cost
- Meet consumer choice and expectations, and
- Be recovered efficiently after use

"When the aforementioned principles are respected, the sustainability impacts of packaging are minimized and the benefits maximized"

Source: Europen, What is 'sustainable' packaging? Our vision, 2009. www.europen.be/

Packaging Sustainability was first published in June 2010. The metrics deliver the measurement system, which, alongside the framework, offer a standardized way to address a range of business questions about packaging sustainability, either within a company or between business partners.

The indicators and metrics fall into three categories: environmental (35), economic (4) and social (13) and are based on earlier metrics and guidelines developed by Europen and the SPC. As William Bruce Cameron remarked, "Not everything that can be counted counts, and not everything that counts can be counted." For example, consider the social metric "Packaged product shelf life." This is defined as the ratio of a product's shelf life in packaging to a product's shelf life without packaging. The metric is the shelf life of the product in packaging divided by the shelf life without packaging; only the same product types in the same packaging types should be compared. It is not immediately apparent how informative or useful this metric is, as most foods have a shelf life of less than a day if unpackaged, although this depends on the temperature and maybe the RH.

From the earlier discussion, it is clear that trying to reconcile "sustainable packaging" and "packaging and sustainability" is difficult if not impossible and is more than simply an exercise in semantics. How can the FMCG industry expect the public to understand what they are doing to become more sustainable when the language and metrics are so confusing? Reaching a broad consensus on what may constitute sustainable packaging would provide the packaging industry with a platform from which to influence regulation as well as customer and consumer attitudes and expectations.

23.5.3 Sustainability Reporting

A sustainability report (also called a Corporate Social Responsibility (CSR) report) covers the economic, environmental and social performance of a company. It provides evidence of whether a company is a good corporate citizen and not just a financial success. Without a sustainability report, there is no evidence in the public arena to indicate that the company is a good corporate citizen. A wide range of parameters can be found in CSR reports including energy efficiency, community relations, ecodesign, product recyclability, employee relations and materials efficiency.

Today, there are several international guidelines that can assist organizations interested in producing a CSR report. The Global Reporting Initiative (GRI) third generation Sustainability Reporting Guidelines (www.globalreporting.org) released in 2011 provide a very detailed guide, including expanded guidance for reporting on human rights, local community impacts and gender. The latest version of AA1000 Series of Assurance Standards for Social and Sustainability Reporting were released by Account Ability in 2008 (www.article13.com). Preparing a CSR report is no simple task, and the groundwork has to be laid at least 18 months before the report will see the light of day. Many of the major FMCG companies now publish sustainability reports and a selection is available for download from the Europen website.

Recently, the need to expand the ISO LCA framework by integrating social and economic dimensions of sustainable development has been discussed (Heijungs et al., 2010; Jeswani et al., 2010). However, because LCA is already viewed as a complex tool that is too time-consuming for everyday use, more complexity could increase uncertainties and decrease acceptability even further.

23.5.4 Supply Chain Management

Managing the environmental impact of suppliers and subcontractors and taking responsibility for the environmental impact of products and services are clearly important components of any organization's environmental strategy. For many companies, including those in the packaging industry, the number and diversity of their suppliers and products means they have an environmental impact that extends well beyond their own staff and workplaces. This makes effective supply chain management, product stewardship and sustainability a complex and challenging process.

The industrial economy of the twenty-first century is characterized by the development of efficient processes which reduce energy and resource use and decrease the material and energy content of products and packaging. This is being driven largely by economics, but because of increasing consumer (and thus governmental and media) interest in sustainability, companies are highlighting their achievements in this area. Retailers lead by Wal-Mart and the CGF are responding to consumer demands for more sustainable and environmentally friendly products and packaging by requiring their suppliers to provide details of various parameters which relate to these demands. This trend will continue, and the metrics used to assess the sustainability of packaging will be refined and, hopefully, incorporated into an international standard. Meanwhile, much additional research is required so that socially responsible corporations and governments can ensure that the measures they adopt really do lead to a more sustainable society with a minimum of unintended consequences.

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Abbreviations, Acronyms, and Symbols

β	permselectivity
°C	degrees Celsius
δ	dielectric loss angle
ΔH	isosteric net heat of sorption (J mol^{-1})
ΔH_s	heat of solution of permeant in polymer (J mol^{-1})
ε	relative complex dielectric constant or permittivity
ε_0	permittivity in free space
ε'	relative dielectric constant
ε''	relative dielectric loss factor
η	overpotential
γ	surface tension mN m^{-1}
λ	wavelength
μ	coefficient of friction
μg	microgram (1 × 10^{-6} g)
μL	microliter (1 × 10^{-6} L)
μm	micrometer (1 × 10^{-6} m)
μ_{max}	maximum specific growth rate constant
ρ	density
τ	time lag
θ	time
θ_{doub}	generation or doubling time
θ_{lag}	lag time
θ_s	shelf life
A	area (m^2)
Å	Angstrom (1 × 10^{-10} meter)
AA	acrylic acid; also acetaldehyde
ABS	acrylonitrile-butadiene-styrene
ADI	acceptable daily intake
AgNP	silver nanoparticle
AIT	allyl isothiocyanate
ALCVD	atomic layer chemical vapor deposition
ALD	atomic layer deposition
AM	antimicrobial
AmPA	amorphous polyamide
AMS	accelerator mass spectrometry
AN	acrylonitrile
ANMA	acrylonitrile-methyl acrylate
ANS	acrylonitrile-styrene
AOIR	ambient O_2 ingress method
AOX	adsorbable organic halides
APA	amorphous polyamide
AP-DLC	atmospheric pressure-diamond-like coating
APET	amorphous poly(ethylene terephthalate)

Ar	argon
ASLT	accelerated shelf life testing; also accelerated shelf life time
ASTM	American Society for Testing and Materials
ATBC	acetyltributyl citrate
atm	atmosphere
ATP	adenosine triphosphate
a_w	water activity
B	barrer
BA	batch annealed
B&B	blow and blow
BADGE	bisphenol A diglycidyl ether
BC	bacterial cellulose
BCE	before common era
BDO	butanediol
BFDGE	bisphenol F diglycidyl ether
BHA	butylated hydroxyanisole
BHET	bis(hydroxyethyl) terephthalate
BHT	butylated hydroxytoluene
BIB	bag-in-box
BIF	barrier improvement factor
bioPE	biopolyethylene
bioPET	biopoly(ethylene terephthalate)
BO	biaxially oriented
BON	biaxially oriented nylon
BOPLA	biaxially oriented poly(lactic acid)
BOPP	biaxially oriented polypropylene
BP	benzophenone
BPA	bisphenol A
BPP	biopolypropylene
BSO	butyl stearate oil
BTU	British thermal unit (≈1055 J)
BUR	blow-up ratio
BVS	Bague Vin Suisse
c	concentration of permeant in polymer; also speed of light
C_0	cooking index
c_p	specific heat
C2C	coil-to-can
CA	cellulose acetate; also continuously annealed
CAGR	compound annual growth rate
CAP	controlled atmosphere packaging; also cellulose acetate propionate
CAS	controlled atmosphere storage
CBA	cost–benefit analysis
CCVD	combustion chemical vapor deposition
CD	cross direction
CDHM	cyclohexanedimethanol
CDL	container deposit legislation
CDTR	carbon dioxide transmission rate
CE	common era
CEDI	cumulative estimated daily intake
CF	consumption factor
CFC	chlorofluorocarbon

CFD	computational fluid dynamics
CFP	carbon footprint
CFR	Code of Federal Regulations
CFSAN	Center for Food Safety and Applied Nutrition
cfu	colony forming unit
CGF	Consumer Goods Forum
C_2H_4	ethylene
CHDM	cyclohexane dimethanol
CIJ	continuous inkjet
CLC	calcium lactate crystals
ClO_2	chlorine dioxide
cm Hg	centimeters of mercury
CMC	carboxymethylcellulose
CNW	cellulose nanowhiskers
CO_2	carbon dioxide
CO_2e	carbon dioxide equivalent
COC	cyclic olefin copolymer
COF	coefficient of friction μ
COMb	carboxymyoglobin
COP	cutoff point
CPET	crystalline poly(ethylene terephthalate)
CPP	cast polypropylene; also crystalline polypropylene
cps	cycles per second
CSA	camphorsulfonic acid
CSR	corporate social responsibility
CTMP	chemithermomechanical pulp
CUK	coated unbleached kraft
CVD	chemical vapor deposition
d	diameter of pore in polymer
D	diffusion coefficient ($cm^2\ s^{-1}$); also decimal reduction time
D&I	drawn and ironed
DAA	diacetone alcohol
DBP	dibutyl phthalate
DCP	dichloropropanol
DDR	draw-down ratio
DEHA	diethylhexyl adipate
DEHP	diethylhexyl phthalate
DEP	diethyl phthalate
DFD	dark, firm and dry (meat)
DI	dispersity index
DiDP	di-isodecyl phthalate
DiNA	di-isononyl adipate
DiNP	di-isononyl phthalate
DiOP	di-isooctyl phthalate
DIPN	di-isopropylnaphthalene
DLC	diamond-like carbon
DMA	dimethyl anthracene
DMDS	dimethyl disulfide
DMN	dimethyl naphthalene
DMT	dimethyl terephthalate
DO	dissolved oxygen

DOA	dioctyl adipate
DoD	drop on demand
DoF	degree of filling
DOP	dioctyl phthalate
DOS	dioctyl sebacate
DOVID	diffractive optically variable device
d_p	penetration depth
DP	degree of polymerization
DR	double reduced
DRD	drawn and redrawn
DS	degree of substitution
DSD	Duales System Deutschland
DWI	drawn and wall ironed
E	Young's modulus; also electric field strength
E_A	activation energy (kJ mol^{-1})
EA	ethyl acetate
EAA	ethylene acrylic acid
EAN	European Article Number (now International Article Number)
EAS	electronic article surveillance
EB	electron beam
EBM	extrusion blow molding
EC	European Community
ECCS	electrolytically chromium-coated steel
ECF	elemental chlorine free
ECH	epichlorohydrin
ECR	electron cyclotron resonance
$\mathrm{E_d}$	activation energy for diffusion (kJ mol^{-1})
EDC	endocrine disrupting chemical
EDI	estimated daily intake
EDTA	ethylenediaminetetraacetic acid
EE	ethanol emitter
EFSA	European Food Safety Authority
EG	ethylene glycol
$\mathrm{E_h}$	redox potential
EHDAB	ethylhexyldimethylaminobenzoate
E_j	extrinsic factors
EMAP	equilibrium modified atmosphere packaging
EMS	environmental management system
EOE	easy open end
EOL	end of life
EOO	essential onion oil
E_p	activation energy for permeation (kJ mol^{-1})
EP	electrophotography
EPA	Environmental Protection Agency
EPC	electronic product code
EPR	extended producer responsibility
EPS	expanded polystyrene
$\mathrm{E_r}$	nonsterility rate
ESBO	epoxidized soy bean oil
ESC	environmental stress cracking
ESCR	environmental stress crack resistance

ESE	easy serving espresso
ESEFA	epoxidized sucrose esters of fatty acids
ESL	extended shelf life
ETD	energy transfer device
ETP	electrolytic tinplate
EU	European Union
EVA	ethylene-vinyl acetate copolymer
EVOH	ethylene-vinyl alcohol copolymer
EVOO	extra virgin olive oil
F	force (N)
FA	formaldehyde
FAE	fatty acid ester
FAO	Food and Agriculture Organization
FAP	food additive petition
FBB	folding box board
FCM	food contact material
FCN	Food Contact Notification
FCOJ	frozen concentrated orange juice
FCS	food contact substance
FDA	Food and Drug Administration; also furandicarboxylic acid
FDCA	Food, Drug and Cosmetic Act
FEA	finite element analysis
FFS	form-fill-seal
FMCG	fast-moving consumer goods
FND	first noticeable difference
F_o	lethality of thermal process in minutes at 121.1°C
FRF	fat reduction factor
FRH	flameless ration heater
FSC	Forest Stewardship Council
FSMA	Food Safety Modernization Act
fT	food-type distribution factors
FTC	film transistor circuit
FTIR	Fourier transform infrared
GAB	Guggenheim-Anderson-de Boer
GDP	gross domestic product
GHG	greenhouse gas
GHz	gigahertz
GIP	glazed imitation parchment
GLC	glass-like coating
GPPS	general purpose polystyrene
GRAS	Generally Recognized As Safe
GRI	Global Reporting Initiative
gsm	grams per square meter
GSMP	Global Standards Management Process
GTIN	Global Trade Item Number
GTR	gas transmission rate
GWP	global warming potential
H	magnetic field strength
HACCP	hazard analysis critical control point
HB	hydroxybutyrate
HC	hydrocarbon

HCCB	High Capacity Color Barcode
HCF	heat-cool-fill
HDPE	high density polyethylene
HDT	heat distortion temperature
HF	high frequency
HIPS	high impact polystyrene
HMDSN	hexamethyldisilazane
HMDSO	hexamethyldisiloxane
HPC	hydroxypropyl cellulose
HPMC	hydroxypropyl methylcellulose
HPP	high pressure processing
HPT	high pressure thermal
HQL	high quality life
HRS	heat resistant sporeformer
HSC	heat sealable coating
HSFE	high shape factor engineered
HTST	high temperature short time
HTW	hole through the wall
HV	hydroxyvalerate
HVLD	high voltage leak detection
I_a	intensity of absorbed light
IBM	injection blow molding
ICI	Imperial Chemical Industries
IE	impact extrusion
IGC	inverse gas chromatography
I_i	intrinsic factors; also intensity of incident light
IML	in-mold label
IPA	isophthalic acid
IR	infra-red
IS	individual section
ISO	International Organization for Standardization
ISWM	integrated solid waste management
ITX	isopropylthioxanthone
J	flux of permeant in polymer; also joule
JECFA	Joint Expert Committee on Food Additives
JND	just noticeable difference
k	rate constant
K	Kelvin; also partition coefficient
kGy	kiloGray
kJ	kilojoule
kPa	kilopascal
LbL	layer-by-layer
LCA	life cycle assessment or analysis
LCB	long chain branching
LCI	life cycle inventory
LCIA	life cycle impact assessment
LCT	life cycle thinking
L/D	length to diameter ratio
LDPE	low density polyethylene
LED	light-emitting diode
LF	low frequency

LISIM	linear motor simultaneous stretching system
LLDPE	linear low density polyethylene
lm	lumen
LMB	leucomethylene blue
LMWO	low molecular weight oligomer
LOQ	limit of quantification
LPB	liquid packaging board
LS	longitudinal seal
LTLT	low temperature long time
LUC	land-use change
lx	lux = lm m^{-2}
M_n	number-average molecular weight
M_w	weight-average molecular weight
MA	methyl acrylate; also modified atmosphere
MAP	modified atmosphere packaging
MAS	modified atmosphere storage
Mb	deoxymyoglobin
MBP	methyl benzophenone
MC	methyl cellulose
MCP	*m*-cresol purple; also methyl cyclopropene
MCPD	monochloropropanediol
MD	machine direction
MDI	microwave doneness indicator
MDPE	medium density polyethylene
MetMb	metmyoglobin
MF	machine finished
MFC	microfibrillated cellulose
mg	milligram (1×10^{-3} g)
MG	machine glazed
MHz	megahertz
MIC	minimum inhibitory concentration
MJ	megajoule
mL	milliliter (1×10^{-3} L) = cc = cm^3
mLDPE	metallocene low density polyethylene
mM	millimolar
mmol	millimole
MMT	montmorillonite
mN	millinewton
MOAH	mineral oil aromatic hydrocarbons
MOH	mineral oil hydrocarbons
MOSH	mineral oil saturated hydrocarbons
MPa	megapascal
mPET	metallized poly(ethylene terephthalate)
MPFVs	minimally processed fruits and vegetables
MRA	metmyoglobin reducing activity
MRE	Meals, Ready-To-Eat
MRF	materials recovery facility
MSW	municipal solid waste
Mt	million metric tons
MTCE	million tonnes of carbon equivalent
MW	molecular weight or microwave

MWD	molecular weight distribution
MXD6	poly(meta-xylylene adipamide)
MXD	*m*-xylylene diamine
MZCR	multizone circulating reactor
MZU	modified Zobel unit
n	refractive index
N	thickness normalized flux
N_c	critical limit of microbial cell density (cfu g^{-1})
NDC	dimethylnaphthalene dicarboxylate
NEB	nonenzymic browning
NIAS	nonintentionally added substance
NIMBY	not in my backyard
nm	nanometer (1×10^{-9} m)
N_{max}	maximum microbial cell density (cfu g^{-1})
NMOR	*N*-nitrosomorpholine
NNPB	narrow neck press and blow
N_o	initial microbial cell density (cfu g^{-1})
NO	nitric oxide
NOGE	novolac diglycidyl ether
NO_x	oxides of nitrogen
N_2O	nitrous oxide
NOAEL	no observable adverse effect level
NOEL	no observable effect level
NOMb	nitrosylmyoglobin
NOMetMb	nitrosylmetmyoglobin
NPN	nonprotein nitrogen
NSSC	neutral-sulfite semichemical
NTP	nonthermal plasma
OBD	oxo-biodegradable polymer
OD	optical density
OECD	Organisation for Economic Co-ordination and Development
OFAS	Office of Food Additive Safety
OLED	organic light-emitting diodes
OM	overall migration
OML	overall migration limit
OMMT	organophilic montmorillonite
O_2Mb	oxymyoglobin
OPA	oriented polyamide
OPET	oriented polyester
OPLA	oriented poly(lactic acid)
OPP	oriented polypropylene
OPS	oriented polystyrene
ORP	oxidation reduction potential
OS	oxygen scavenger
OTR	oxygen transmission rate
p	partial pressure (cm Hg)
P	permeability coefficient (mL cm cm^{-2} s^{-1} (cm Hg^{-1}))
Pa	pascal
P&B	press and blow
P/X	permeance
PA	polyamide

PAA	peracetic acid
PAAE	polyamidoamine-epichlorohydrin
PAN	polyacrylonitrile
PANI	polyaniline
PAS	publicly available specification
PBAT	poly(butylene adipate-*co*-terephthalate)
PBS	poly(butylene succinate)
PBSA	poly(butylene succinate-*co*-adipate)
PBSPS	poly(butylene succinate-*co*-propylene succinate)
PBST	poly(butylene succinate-*co*-terephthalate)
PBT	poly(butylene terephthalate)
PC	polycarbonate
PCDDs	polychlorinated dibenzodioxins
PCDFs	polychlorinated dibenzofurans
PCL	poly(caprolactone)
PCN	polymer-clay nanocomposite
PCR	postconsumer recycled
PCT	poly(cyclohexylenedimethylene terephthalate)
PCTA	acid-modified PCT
PE	polyethylene
PCTFE	poly(chlorotrifluoroethylene)
PCTG	PCT glycol copolyester
PDA	polydiacetylene
PDF	portable document format
PDO	propanediol
PDLA	poly(*D*-lactide)
PDLLA	poly(*D*,*L*-lactide)
PECVD	plasma-enhanced chemical vapor deposition
PEFC	Program for Endorsement of Forest Certification
PEG	poly(ethylene glycol)
PEN	poly(ethylene naphthalate)
PEPU	polyester-polyurethane
PET	poly(ethylene terephthalate) = polyester
PETG	poly(ethylene terephthalate) glycol copolyester
PETRA	PET Resin Association
PFOA	perfluorooctanoic acid
PGA	poly(glycolic acid)
PHA	polyhydroxyalkanoate
PHB	polyhydroxybutyrate
PHBV	poly(hydroxy butyrate-*co*-valerate)
PHTC	post-heat treatment contamination
PHV	polyhydroxyvalerate
PHVB	poly(hydroxyvalerate-*co*-butyrate)
PLA	poly(lactic acid)
PLLA	poly(*L*-lactide)
PLS	polymer-layered silicate
PME	polymethylesterase
PO	propylene oxide
POSH	polyolefin oligomeric saturated hydrocarbons
PP	polypropylene
ppb	parts per billion (1×10^{-9})

PPC	poly(propylene carbonate)
ppm	parts per million (1×10^{-6})
PPP	polluter pays principle
ppt	parts per trillion
PRO	Packaging Recovery Organisation
PS	polystyrene
PSA	pressure-sensitive adhesive
PSE	pale, soft and exudative (meat)
PSL	practical storage life
PTFE	poly(tetrafluoroethylene)
PU	Pasteurization Unit
PV	peroxide value
PVA	poly(vinyl acetate)
PVB	poly(vinyl butyral)
PVC	poly(vinyl chloride)
PVD	physical vapor deposition
PVdC	poly(vinylidene chloride)
PVOH	poly(vinyl alcohol)
Q	total amount of permeant passing through polymer
Q_{10}	temperature quotient = ratio of reaction rates for 10°C temperature difference
QLF	quartz-like film
QR	quick response
R	ideal gas constant (= 8.314 J K^{-1} mol^{-1} = 1.987 cal K^{-1} mol^{-1}); also permeance
R&G	roast and ground
RAT	reflect, absorb, transmit
RCF	regenerated cellulose film
RCRA	Resource Conservation and Recovery Act
RDF	refuse-derived fuel
REPFEDs	refrigerated, processed foods with extended durability
RFID	radio frequency identification
RH	relative humidity
RMP	refiner mechanical pulp
ROP	ring-opening polymerization
ROPP	roll-on pilfer proof
ROTE	roll-on tamper evident
RP	retortable pouch
rPET	recycled poly(ethylene terephthalate)
RQ	respiratory quotient
RR	respiration rate
RTD	ready-to-drink
RWB	roast whole beans
S	solubility coefficient of permeant in polymer (mL cm^{-3} (cm $Hg)^{-1}$); also circumferential stress
SAN	styrene-acrylonitrile
SAT	standard area of tinplate
SATP	standard ambient temperature and pressure
SB	styrene-butadiene copolymer
SBB	solid bleached board
SBM	stretch blow molding
SBS	solid bleached sulfate
SCC	side chain crystallizable; also stress crack corrosion

SCF	Scientific Committee for Food
scl	short chain length
SD	sustainable development
SED	sacrificial electron donor
SGS	soluble gas stabilization
SHMP	sodium hexametaphosphate
SI	Système International d'Unites
SiO_2	silicon dioxide
SiO_x	oxides of silicon
SITA	Système International Tinplate Area
SLO	sulfur-like odor
SM	specific migration
SMA	styrene-maleic anhydride
SML	specific migration limit
SMP	skim milk powder
SO	sunflower oil
SODIS	solar water disinfection
SO_x	oxides of sulfur
SPC	Sustainable Packaging Coalition
SPPF	solid phase pressure forming
SR	single reduced
SSCC	serial shipping container code
SSCCM	shelf stable canned cured meat
SSL	sensory shelf life
SSP	solid state polymerization
SSO	specific spoilage organism
STP	standard temperature and pressure
SUP	standup pouch
SUS	solid unbleached sulfate
TAPPI	Technical Association of the Pulp and Paper Industries
TBA	tribromoanisole
TBHQ	tertiarybutylhydroquinine
TBP	tribromophenol
TBT	tributyl tin
TCA	trichloroanisole
TCDD	tetrachlorodibenzodioxin
TCF	total chlorine free
TCP	trichlorophenol
TD_{50}	median toxic dose
TD	transverse direction
TDI	tolerable daily intake
TeCA	tetrachloroanisole
TEF	toxic equivalency factor
TEOS	tetraethoxysilane
TEQ	toxic equivalent
TFE	tetrafluoroethylene
TFS	tin-free steel
T_g	glass transition temperature
TiO_2	titanium dioxide
T_m	crystalline melting temperature
TMA	trimethylamine; also trimellitic acid

TMAO	trimethylamine oxide
TMDPM	trimethyldiphenylmethane
TMP	thermomechanical pulp
TOR	threshold of regulation
TPA	terephthalic acid
TPO	Total Package Oxygen
TPS	thermoplastic starch
TR	transmission rate
TTI	time-temperature indicator
TTM	time-temperature monitor
TTT	time-temperature-tolerance
TULC	Toyo Ultimate Can
UD	Universal Design
UF	uncertainty factor
UHF	ultrahigh frequency
UHT	ultraheat treated or ultrahigh temperature
ULDPE	ultra low density polyethylene
UPC	universal product code
USC	United States Congress
USP	United States Pharmacopoeia
UV	ultraviolet
VA	vinyl acetate
VC	vinyl chloride
VCM	vinyl chloride monomer
VdC	vinylidene chloride
VFPE	very flexible polyethylene
VLDPE	very low density polyethylene
VOC	volatile organic compound
VOH	vinyl alcohol
vpd	vapor pressure deficit
VSP	vacuum skin packaging
WHC	water-holding capacity
WHO	World Health Organization
WLC	white lined chipboard
WMP	whole milk powder
WMP&B	wide mouth press and blow
WP	whey protein
WSN	wireless sensor network
WVP	water vapor permeability
WVPD	water vapor pressure deficit
WVTR	water vapor transmission rate
X	thickness of polymeric material
z	temperature change required for 10-fold change in D value
Z-N	Zeigler–Natta