

# 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<sub>2</sub> to exit the package and preventing excess O<sub>2</sub> 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<sub>2</sub> from the headspace of cans in a 1938 patent; a 1943 patent from a researcher in England described removing O<sub>2</sub> from a container containing vacuum or gas-packed food in which a metal such as iron absorbed O<sub>2</sub> to form an oxide. In the United States, the removal of O<sub>2</sub> by the catalytic conversion of H<sub>2</sub> to H<sub>2</sub>O was first described in 1955 and applied to spray dried milk powder in initially tinfoil cans and later laminate pouches. The package was flushed with a mixture of H<sub>2</sub> (7%) in N<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>O<sub>2</sub> 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<sub>2</sub> appeared. A 1968 German patent proposed a sodium carbonate powder to absorb O<sub>2</sub> 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<sub>2</sub>. 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<sub>2</sub>H<sub>4</sub> produced by respiring fruits, or O<sub>2</sub> present inside a package), add a desirable compound (e.g., CO<sub>2</sub> 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 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<sub>2</sub> 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<sub>2</sub>) is not intelligent packaging, although some might argue that it does qualify under the aforementioned definition.

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**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

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### 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<sub>2</sub> 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<sub>2</sub> emitters and absorbers.

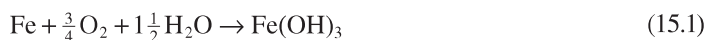
There are several ways in which active packaging systems can be classified; typically, the classification is based on what the system actually does (e.g., absorbs O<sub>2</sub>) rather than its impact on the food (e.g., prevents oxidation). A similar classification will be adopted here. In addition, 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<sub>2</sub> Absorbers

O<sub>2</sub> absorbers (also referred to as O<sub>2</sub> 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:



By using iron powder, it is possible to reduce the O<sub>2</sub> concentration in the headspace to less than 0.01%, which is much lower than the typical 0.3%–3.0% residual O<sub>2</sub> 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<sub>2</sub> (STP), which is equal to approximately 300 mL. Various sizes of O<sub>2</sub> sachets are available commercially, with the ability to consume 20–2000 mL of O<sub>2</sub> (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<sub>2</sub> in the food
- Desired shelf life of the food
- Initial O<sub>2</sub> level in the package headspace
- O<sub>2</sub> 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 24h, 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 7g of iron which is approximately 160 times less than the  $LD_{50}$  for a 70kg 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<sub>2</sub>-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<sub>2</sub> Absorbers/Emitters

Sachets that absorb only CO<sub>2</sub> are rare. CO<sub>2</sub> scavengers can be composed either of a physical absorbent (zeolite or an active carbon powder) or a chemical absorbent such as Ca(OH)<sub>2</sub> or Mg(OH)<sub>2</sub>, typically packaged in small pouches of paper coated with perforated PP:



Sachets that contain Ca(OH)<sub>2</sub>, in addition to iron powder, absorb CO<sub>2</sub> as well as O<sub>2</sub> and find a niche application inside packages of roasted or ground coffee. Fresh roasted coffee releases considerable amounts of CO<sub>2</sub> (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<sub>2</sub> and CO<sub>2</sub> scavengers. They identified significant “parasite” CO<sub>2</sub> absorption for O<sub>2</sub> scavengers (i.e., a carbonation reaction of the iron hydroxide that was formed following O<sub>2</sub> 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<sub>2</sub> or CO<sub>2</sub> scavengers.

Other sachets are available based on either ascorbic acid and ferrous carbonate or ascorbic acid with sodium bicarbonate that absorb O<sub>2</sub> and generate an equivalent volume of CO<sub>2</sub>, thus avoiding package collapse or the development of a partial vacuum, which can be a problem in flexible packages if only O<sub>2</sub> is removed.

CO<sub>2</sub> Fresh Pads (from CO<sub>2</sub> Technologies, Iowa) have been adapted for meat, poultry and seafood processors. The system contains citric acid and sodium bicarbonate as moisture-actuated CO<sub>2</sub> 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<sub>2</sub> is released.

### 15.3.1.3 Ethylene Absorbers

The plant hormone ethylene (C<sub>2</sub>H<sub>4</sub>) 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<sub>2</sub>H<sub>4</sub>-absorbing substances have been described in the patent literature but those that have been commercialized are based on potassium permanganate (KMnO<sub>4</sub>), which oxidizes C<sub>2</sub>H<sub>4</sub> in a series of reaction to acetaldehyde and then acetic acid, which, in turn, can be further oxidized to CO<sub>2</sub> and H<sub>2</sub>O with the overall reaction as follows:



Because KMnO<sub>4</sub> is toxic, it cannot be integrated into food contact packaging. Instead, about 4%–6% of KMnO<sub>4</sub> 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<sub>2</sub> 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<sub>2</sub>-Absorbing Materials

The most common O<sub>2</sub> 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<sub>2</sub> permeation is a prime cause of quality loss, sachets cannot be used. Therefore, a more attractive alternative is the incorporation of O<sub>2</sub>-absorbing materials into the plastics components of packages.

O<sub>2</sub>-absorbing polymers are versatile in that their layer thickness or blend composition can be varied to match the amount of O<sub>2</sub> to be removed. However, one major limitation to the large-scale adoption of the presently available O<sub>2</sub>-absorbing materials is that the speed and capacity of O<sub>2</sub>-absorbing films are considerably lower than the widely used O<sub>2</sub>-absorbing sachets. An additional challenge is that the O<sub>2</sub>-absorbing films must be stable in the O<sub>2</sub>-rich environment of air and not start consuming O<sub>2</sub> 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<sub>2</sub>-absorbing PET preforms in barrier bags with a slight overpressure of N<sub>2</sub> to prevent absorption of O<sub>2</sub> until blown is also used.

The patent literature of the past 80 years contains many ideas for O<sub>2</sub>-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<sub>2</sub>-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<sub>2</sub> permeability of essentially zero for 1 year. More cost-effective ways of providing an O<sub>2</sub> barrier in PET bottles have limited the application of this approach. It should be noted that any O<sub>2</sub> absorber proposed as a middle layer in PET-based structures will not be a rapid headspace scavenger due to the reasonable O<sub>2</sub> 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<sub>2</sub> absorber and a barrier to O<sub>2</sub> permeation into the package. The O<sub>2</sub>-absorbing capability was UV activated, meaning it had to be exposed to UV light before it could begin absorbing O<sub>2</sub>. Another O<sub>2</sub>-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<sub>2</sub> from within the package headspace, as well as any that entered the package by permeation or leakage.

In another approach developed to remove O<sub>2</sub> 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<sub>2</sub>, 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<sub>2</sub> g<sup>-1</sup> 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<sub>2</sub> 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<sub>2</sub>H<sub>4</sub>. These minerals were typically local kinds of clay such as pumice, zeolite, cristobalite (SiO<sub>2</sub>) 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<sub>2</sub>H<sub>4</sub>), increase the shelf life of fresh fruits and vegetables. Although the minerals may have C<sub>2</sub>H<sub>4</sub>-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<sub>2</sub>H<sub>4</sub> 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<sub>2</sub> and ClO<sub>2</sub>, 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  $\text{ClO}_2$ ,  $\text{SO}_2$ ,  $\text{CO}_2$ , 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.

$\text{ClO}_2$  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,  $\text{ClO}_2$  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  $\text{ClO}_2$  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  $\text{ClO}_2$  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  $\text{ClO}_2$  precursors in food packaging films used for uncooked meats such as poultry and seafood. In Europe,  $\text{ClO}_2$  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  $\text{ClO}_2$  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  $\mu\text{m}$ ) 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  $\mu\text{g Ag}^+ \text{kg}^{-1}$  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  $\mu\text{g Ag}^+ \text{kg}^{-1}$  (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<sub>2</sub> particles in particular are promising. However, unlike AgNPs, the AM activity of TiO<sub>2</sub> nanoparticles is photocatalyzed and thus TiO<sub>2</sub>-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 (Yildirim, 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<sub>2</sub>O:



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<sub>2</sub> and emit CO<sub>2</sub>. When the fruits and vegetables are in a sealed package, the atmosphere will reach equilibrium levels of O<sub>2</sub> and CO<sub>2</sub> 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<sub>2</sub> consumption may increase beyond the rate at which O<sub>2</sub> can permeate through the packaging film and high levels of CO<sub>2</sub> 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<sub>2</sub> and CO<sub>2</sub> 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<sub>2</sub> to O<sub>2</sub>, 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<sub>2</sub> permeabilities, specific CO<sub>2</sub>:O<sub>2</sub> permeability ratios ( $\beta$ ) and changes in permeability with temperature.

The membrane is capable of being more than 1000 times more permeable to O<sub>2</sub> and CO<sub>2</sub> than a 50  $\mu$ m LDPE film while still maintaining the same  $\beta$  ratio. Unlike semipermeable films for respiring produce, which typically allow CO<sub>2</sub> out and O<sub>2</sub> in at a 6:1 ratio, by altering the polymer composition used to coat the membrane, it is possible to obtain  $\beta$  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<sub>2</sub>, 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> when the can was opened to produce the traditional creamy head. The widget itself is a small, plastic or aluminum, N<sub>2</sub>-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<sub>2</sub> 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<sub>2</sub> in the can during filling (Briggs et al., 2004).

At filling, a small quantity of liquid N<sub>2</sub> is injected, together with the beer, and the can is rapidly sealed before the N<sub>2</sub> evaporates. After the can is sealed, this liquid N<sub>2</sub> vaporizes and pressurizes the can, forcing a small quantity of beer through the tiny hole of the widget and compressing the N<sub>2</sub> inside. When the can is opened, the pressure inside drops suddenly, the compressed N<sub>2</sub> 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<sub>2</sub>/CO<sub>2</sub> 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<sub>2</sub>S 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).

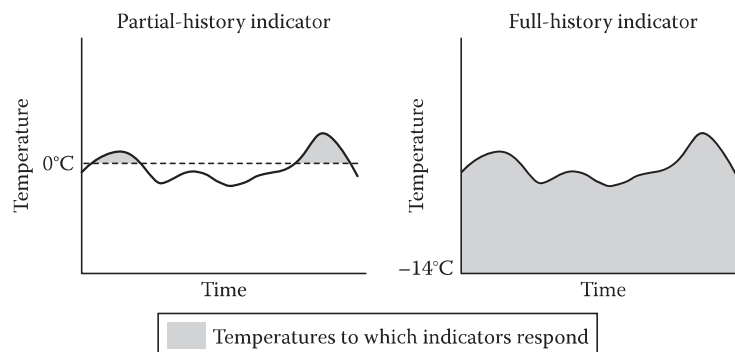


FIGURE 15.1 Two major categories of TTIs.

#### 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  $-24^{\circ}\text{C}$ .

#### 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)<sup>®</sup> 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  $\pm 25$  kJ mol<sup>-1</sup> 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<sup>-1</sup>, Fresh-Check<sup>®</sup> 80–90 kJ mol<sup>-1</sup>, TT Sensor<sup>™</sup> 112–126 kJ mol<sup>-1</sup>, (eO)<sup>®</sup> 100–110 kJ mol<sup>-1</sup>, OnVu<sup>™</sup> 90–150 kJ mol<sup>-1</sup> and CheckPoint<sup>®</sup> from 50 kJ mol<sup>-1</sup> for Type C to 195 kJ mol<sup>-1</sup> for Type L. Apparent  $E_{AS}$  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<sup>-1</sup> for vegetables, 48–61 kJ mol<sup>-1</sup> for fruit, 54–74 kJ mol<sup>-1</sup> for meat and 44–49 kJ mol<sup>-1</sup> for fish, although the  $E_A$  of spoilage indices for fish has also been reported as 82 kJ mol<sup>-1</sup>, 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<sup>-1</sup>. The response of the L5–8 CheckPoint<sup>®</sup> 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<sup>™</sup> 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<sub>2</sub>. 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)<sup>®</sup> 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).

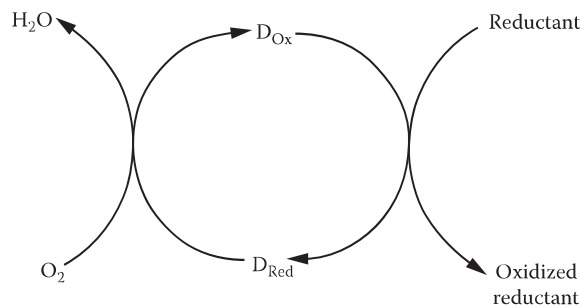
#### 15.4.1.3 Gas Concentration Indicators

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<sub>2</sub> and, to a lesser extent, CO<sub>2</sub>.

An *ideal* O<sub>2</sub> 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<sub>2</sub> indicator when the package has been sealed and is largely or wholly O<sub>2</sub> free. An ideal O<sub>2</sub> indicator should also exhibit an irreversible response toward O<sub>2</sub> to avoid false negatives. Finally, an ideal O<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> indicator inserted inside the package that changes from pink when the ambient O<sub>2</sub> concentration is ≤0.1% to blue when the O<sub>2</sub> concentration is ≥0.5%. Such indicators can be included in anoxic packages to indicate the effective absorption of all O<sub>2</sub>, and to warn of a breakdown in the O<sub>2</sub> barrier. The presence of O<sub>2</sub> 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<sub>2</sub> concentration is ≤0.1% to blue when the O<sub>2</sub> concentration is ≥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<sub>2</sub> 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<sub>2</sub> (i.e., ≤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 ≥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<sub>2</sub> 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:



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<sup>®</sup> 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<sub>2</sub>Dot<sup>®</sup>) 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<sub>2</sub>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<sub>2</sub>Sense™ 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<sup>®</sup> 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<sup>™</sup> 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<sup>™</sup> 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<sup>™</sup> 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  $-25^{\circ}\text{C}$  to  $70^{\circ}\text{C}$ .

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 ( $\text{RRO}_2$ ) continuously in fresh-cut broccoli florets at  $5^{\circ}\text{C}$ ,  $10^{\circ}\text{C}$  and  $20^{\circ}\text{C}$  and at modified gas compositions (decreasing  $\text{O}_2$  and increasing  $\text{CO}_2$  levels). WSNs offer the potential to monitor the postharvest  $\text{RRO}_2$  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  $\text{NH}_3$  and  $\text{H}_2\text{O}$  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<sub>2</sub> 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<sup>-1</sup>).

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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