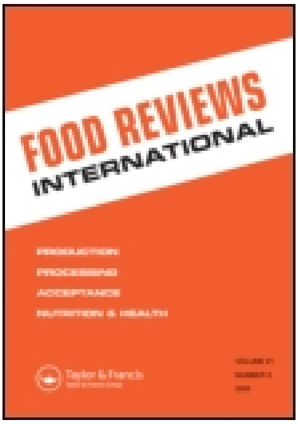

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Active and Intelligent Packaging for the Food Industry

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In the recent past, food packaging was used to enable marketing of products and to provide passive protection against environmental contaminations or influences that affect the shelf life of the products. However, unlike traditional packaging, which must be totally inert, active packaging is designed to interact with the contents and/or the surrounding environment. Active packaging systems are successfully used to increase the shelf life of processed foods and can be categorized into adsorbing and releasing systems (for example, oxygen scavengers, ethylene scavengers, liquid and moisture absorbers, flavor and odor absorbers or releasers, antimicrobials, etc.). Intelligent packaging is characterized by its ability to monitor the condition of packaged food or the environment by providing information about different factors during transportation and storage. Intelligent packaging includes time-temperature indicators, gas detectors, and freshness and/or ripening indicators. At the same time, advances in nanotechnology and the improvement of nanomaterials will enable the development of better and new active and intelligent packaging. Such packaging provides great benefits to the food industry to improve freshness, shelf-life of food, and allows monitoring to control the storage conditions from the place of production to consumption by the final consumer.

Keywords active packaging, bioactive, intelligent packaging, nanotechnology, time-temperature indicators

Introduction

The shelf life of packaged food depends on both the intrinsic nature of food and extrinsic factors. Intrinsic factors include pH, water activity (A_w), nutrient content, presence of antimicrobial compounds, redox potential, respiratory rate, and the biological structure, whereas extrinsic factors include storage temperature, relative humidity, and the surrounding gas composition.(1) The primary purpose of food packaging is to protect the food against attack from oxygen, water vapor, ultraviolet light, and both chemical and microbiological contamination.

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According to the World Health Organization, between 6.5 and 33 million cases of foodborne diseases occur every year in the United States alone, leading to approximately 9000 deaths. It is estimated that in Spain, there are 60 cases of foodborne disease per 100,000 inhabitants per year, which is why biosensors are being developed to detect pathogens in food.[2] Because of this, the use of active and intelligent packaging can extend shelf life and monitor food quality, respectively. Active packaging systems are used successfully to increase the shelf life of processed foods and meet consumer demands in terms of providing high-quality products that are also fresh and safe. Another important aspect of active packaging is to delay the deterioration process of food due to the need of providing sufficient food for a rapidly increasing global population. Furthermore, consumers in the industrialized countries want to be provided with seasonal products throughout the year, which makes lengthy transport necessary, especially for fresh agricultural products, which do not have extended shelf lives. Unlike traditional packaging, which must be totally inert, active packaging is designed to interact with the contents and/or the surrounding environment. Intelligent packaging is another relatively new type of packaging. Such packaging is characterized by its ability to monitor the condition of packaged food or the environment by providing information about different factors during transportation and storage. Recently, a large number of companies sell this type of packaging because of the advantages it has in terms of marketing the product and its acceptance by the consumer. Some companies that sell active and/or intelligent packaging are shown in Table 1. Some commercial active systems, presentations, and functions are listed in Table 2.

Active packaging systems provide different solutions depending on the quality attribute that is to be preserved. For example, if oxidation of a food product has to be slowed down, the packaging must use an active system that contains an oxygen scavenger or antioxidants. If, however, the deterioration of the food is caused by moisture or condensation, the packaging may contain a moisture absorber. Ultimately, the incentive for the deployment of any new technology is cost. Some examples of noncommercial active packaging systems and their effect on various foods are listed in Table 3.

At the present time, active and intelligent packaging systems are mainly used in Asia or the United States, whereas in Europe its use is not widespread. In Europe, active and intelligent systems are governed by regulations (EC) 1935/2004[58] and 450/2009[59], and the deadline for submitting applications to establish the EU positive list is not over yet. In the legal definition, “active food contact materials and articles” (hereinafter referred to as active materials and articles) means materials and articles that are intended to extend the shelf-life or to maintain or improve the condition of packaged food. They are designed to incorporate components that release substances into or absorb substances from the packaged food or the environment surrounding the food. In the legal definition, “intelligent food contact materials and articles” (hereinafter referred to as intelligent materials and articles) means materials and articles that monitor the condition of packaged food or the environment surrounding the food.

To be introduced in the European market the following conditions must be fulfilled[58,59]:

a. The materials must be appropriate and effective for their intended use.
b. Materials and articles, including active and intelligent materials and articles, shall be manufactured in compliance with good manufacturing practice so that, under normal or foreseeable conditions of use, they do not transfer their constituents

Table 1
List of some companies that produce active and/or intelligent packaging

Company	Web page	Country
Artibal	www.artibal.com	Spain
ATCO/Standa Industrie	www.atmosphere-controle.fr	France
BASF Group	www.basf.com	Germany
Bericap GmbH und Co. KG	www.bericap.com	Germany
Bio Fresh PKG	www.biofreshpkg.com	United States
Bioka LTD	www.bioka.fi	Finland
Ciba Inc. (BASF)	www.basf.com	Switzerland
Constar International Inc.	www.constar.net	United States
Cryolog S.A	www.cryolog.com	France
CSIRO	www.csiro.au	Australia
E-I-A Warenhandels GmbH	http://warenhandels.lookchem.com	Austria
Ethylene Control, Inc.	www.ethylenecontrol.com	United States
Evert-Fresh Corporation	www.evertfresh.com	United States
Freund Corporation	www.freund.co.jp	Japan
Grace Darex Packaging Technologies	www.gracedarex.com	United States
Honeywell International Inc.	www51.honeywell.com/honeywell	United States
Hsaio SUNG Non-Oxygen Chemical Co., LTD	www.o-buster.com	Taiwan
Humidipak, Inc.	www.humidipak.com	United States
Infratab, Inc.	www.infratab.com	United States
Inline Packaging LLC.	www.inlinepkg.com	United States
KonteK (S.R.L.) Tecnologie Della Conservazione Ortofrutticola		Italy
M&G Finanziaria s.r.l.	www.gruppomg.com	Italy
Mitsubishi Gas Chemical	www.mgc.co.jp	Japan
Multisorb Technologies	www.multisorb.com	United States
PEAKfresh	http://peakfresh.com	Australia
Powdertech, Co. Ltd.	www.powdertech.com	Japan
Repsol	www.repsol.com	Spain
ScentSational Technologies, LLC	www.scentsationaltechnologies.com	United States
Sealed Air Corporation	www.sealedair.com	United States
Sirane Ltd	www.sirane.co.uk	United Kingdom
Süd-Chemie AG	www.sud-chemie.com	Germany
Techmer PM	www.techmerpm.com	United States
Telatemp Corporation	www.telatemp.com	United States
Tempra Technology and Crown Holdings	www.tempratech.com	United States
Toppan Printing Co.	www.toppan.co.jp	Japan

(*Continued*)

Table 1
(Continued)

Company	Web page	Country
Toxin Alert	www.toxinalert.com	Canada
Toyo Seikan Kaisha, Ltd.	www.toyo-seikan.co.jp	Japan
Tri-Seal (Tekni-Plex)	www.tri-seal.com	United States
UOP LLC.	www.uop.com	United States
Valspar Corporation	www.valsparglobal.com	United States

to food in quantities that could endanger human health, or bring about an unacceptable change in the composition of the food or bring about a deterioration in the organoleptic characteristics.

c. When the action involves release of active substances to food, these will be considered for all purposes ingredients. The materials must not bring about changes that may mislead the consumer, such as masking the spoilage of food. Labeling, presentation, and advertising must not mislead consumers.
d. Even when not in contact with food, the materials must display information about the use or the permitted uses and other relevant information, such as name and quantity of substances released by the active component, so that food business operators using these materials can meet other provisions regarding food labeling.
e. Only substances listed in the Community list of permitted substances may be used in components of the active materials and articles, except the active substances released to comply with Community requirements or being covered by

Table 2
Some commercial active systems, type of presentation and function

Product	Type	Function
Ageless[3]	Sachets and labels	Oxygen scavenger, oxygen scavenger/carbon dioxide emitter
Amosorb[4]	Bottles, film	Oxygen scavenger
Shelfplus[5]	Film, tray, and bottle	Oxygen scavenger
Bioka[6]	Sachets	Oxygen scavenger
Oxyguard[7]	Additive	Oxygen scavenger
valOR Activ100[8]	Bottles	Oxygen scavenger
Wonderkeep[9]	Sachets	Oxygen scavenger
FreshMax[10]	Sachets	Oxygen scavenger/carbon dioxide emitter
Bio-fresh packaging system[11]	Film, sachets	Ethylene scavenger
Profresh[12]	Film	Ethylene scavenger
Evert-Fresh Green Bags®[13]	Sachets	Ethylene scavenger
MiniPax[10]	Sachets	Oxygen scavenger, odor absorber
StripPax[10]	Sachets	Oxygen scavenger, odor absorber
2-in-1 Pak[14]	Sachets	Oxygen scavenger, odor absorber

Table 3
Active packaging and its effect on some foods

Author	Type of active package	Food analyzed	Results
Almenar et al. 2009[15]	Antimicrobial	Strawberries	Increase the shelf life
Albanese et al. 2005[16]	Moisture absorber	Squid	Quality improvement
Baiano et al 2004[17]	Oxygen scavenger	Beverages	Inhibition of ascorbic acid degradation
Bailen et al. 2006[18]	Ethylene scavenger	Tomatoes	Reducing the rate of softening in tomatoes
Caillet et al. 2006[19]	Antimicrobial	Carrots	Antimicrobial activity against *Listeria monocytogenes*
Camilloto et al. 2009[20]	Antimicrobial	Cooked ham	Antimicrobial activity against *Escherichia coli* and *Staphylococcus aureus*
Camo et al. 2008[21]	Antioxidant	Lamb steaks	Increase the shelf life
Cha et al. 2003[22]	Antimicrobial	Tofu	Antimicrobial activity against *Listeria monocytogenes*
Charles et al. 2008[23]	Oxygen scavenger	Endives	Increase the shelf life
Chi et al. 2006[24]	Antimicrobial	Bologna	Increase the shelf life
Coma et al. 2002[25]	Antimicrobial	Emmental cheese	Antimicrobial activity against *Listeria monocytogenes* and L. innocua
Conte et al. 2009[26]	Antimicrobial	Fior di Latte cheese	Increase the shelf life
de Oliveira et al. 2008[27]	Antioxidant	Apple slices	Quality improvement
Del Nobile et al. 2004[28]	Antimicrobial	Apple juice	Antimicrobial activity against *Alicyclobacillus acidoterrestris*
Emenhiser et al. 1999[29]	Oxygen scavenger	Sweet potato flakes	Quality improvement
Fava et al. 1999[30]	Liquid absorber	Pizza	Quality improvement
Franzetti et al. 2001[31]	Flavor and liquids absorber	Fillets of sole, steaks of cod, and whole cuttlefish	Increase the shelf life

Gomes et al. 2009[32]	Oxygen scavenger	Cheese-spread	Increase the shelf life
Gomez-Estaca et al. 2009[33]	Antimicrobial	Raw sliced salmon and fish products	Antimicrobial activity against *Lactobacillus acidophilus*, *Pseudomonas fluorescens*, *Listeria innocua*, and *Escherichia coli*
Granda-Restrepo et al. 2009[34]	Antioxidant	Whole milk powder	Quality improvement
Gutierrez et al. 2009[35]	Odor releaser and antimicrobial	Precooked roast beef	Quality improvement and antimicrobial activity
Gutierrez et al. 2009[36]	Antimicrobial	Bakery products	Increase the shelf life
Guynot et al. 2003[37]	Oxygen scavenger	Cakes	Increase the shelf life
Jofre et al. 2008[38]	Antimicrobial	Sliced cooked ham	Increase the shelf life
Marcos et al. 2008[39]	Antimicrobial	Sliced cooked ham	Antimicrobial activity against *Listeria monocytogenes*
Mauriello et al. 2005[40]	Antimicrobial	Milk	Increase the shelf life
Mexis et al. 2009[41]	Oxygen scavenger	Almonds	Increase the shelf life
Mexis et al. 2010[42]	Oxygen scavenger	Dark chocolate	Quality improvement and increase the shelf life
Mohan et al. 2008[43]	Oxygen scavenger	Catfish steaks	Increase the shelf life
Moraes et al. 2007[44]	Antimicrobial	Butter	Antimicrobial activity against filamentous fungi and yeast
Nerin et al. 2006[45]	Antioxidant	Fresh meat	Increase the shelf life
Nguyen et al. 2008[46]	Antimicrobial	Vacuum-packaged frankfurters	Increase the shelf life
Pereira de Abreu et al. 2010[47]	Antioxidant	Blue shark	Increase the shelf life
Pereira de Abreu et al. 2010[48]	Antioxidant	Atlantic salmon	Increase the shelf life
Pereira de Abreu et al. 2010[49]	Antioxidant	Atlantic halibut	Increase the shelf life

(*Continued*)

Table 3
(Continued)

Author	Type of active package	Food analyzed	Results
Pires et al. 2009(50)	Antimicrobial	Sliced mozzarella cheese	Antimicrobial activity against molds and yeasts
Rodríguez et al. 2008(51)	Antimicrobial	Sliced Bread	Antimicrobial activity against *Rhizopusstolonifer*
Shin et al. 2009(52)	Oxygen scavenger	Meatball	Increase the shelf life
Skandamis and Nychas 2002(53)	Antimicrobial	Fresh meat	Increase the shelf life
Soto-Cantu et al. 2008(54)	Antioxidant	Asadero cheese	Increase the shelf life
Winther and Nielsen, 2006(55)	Antimicrobial	Cheese	Increase the shelf life
Yingyuad et al. 2006(56)	Antimicrobial	Grilled pork	Increase the shelf life
Zinoviadou et al. 2010(57)	Antimicrobial	Fresh beef	Increase the shelf life

respective national food regulations (such as for additives, flavorings, and food enzymes), which are separated by a functional barrier. The substances must not be mutagenic, carcinogenic, or toxic to reproduction. However, this positive list does not exist so far but those qualified as food additives or flavoring substances for food can be legally and officially used and do not require to be included in the active and intelligent Community list.

f. Mandatory labeling with the words "DO NOT EAT" must be provided to enable consumers to distinguish nonedible parts, when these may be perceived as edible. This information must be visible, legible, and indelible. The active substances released will be subject to regulations for labeling of foodstuffs. The labeling must also include a statement of compliance to certify compliance with the relevant regulations.

g. Integrated systems have the advantage over separated systems that they will not be accidentally consumed. Integrated systems also have the advantage that they can be used in food in liquid form rather than as separate systems, which are completely counterproductive for liquids.(14)

Active Packaging

Oxygen Scavengers

Packaged foods include a certain amount of headspace gases and entrained oxygen. Permeation of oxygen into plastic containers is also of concern. Although it is desirable to keep the headspace gases to a minimum to provide reliable end closure with hermetic seals, it is also important to minimize the amount of oxygen that can react with the contents of the container.(60) Molecular oxygen (O_2) can be reduced to a variety of intermediate species by the addition of between one and four electrons; these species are superoxide, hydroxy radical, hydrogen peroxide, and water. O_2 and water are relatively unreactive: the three intermediate species are very reactive and carbon-carbon double bonds are particularly susceptible to reaction with the intermediate species. These reactive oxygen species are free radical in nature, and the oxidative reactions in which they participate are therefore autocatalytic. Virtually any product that contains complex organic constituents will possess such carbon-carbon double bonds or other oxygen-reactive components, and hence can undergo oxidative reactions.(61)

The presence of oxygen, if not desired, may result from inadequate or insufficient evacuation during the packaging process, presence in the food itself or the packaging material and release into the headspace, permeation through the package, introduction of air due to a poor sealing, or microperforations in the packaging material. A high level of oxygen reduces the nutritional value of food and reduces its shelf life. The oxygen in headspace gases will react with sensitive foods. Oxygen present inside the package accelerates the deterioration of many food products(43) (meats, sausages, milk powder, or spices), degradation of vitamins, and rancidity of oils, nuts, and fatty foods, and also encourages microbial growth.

Oxygen in the headspace of food packaging can be removed by vacuum sealing or by inert gas atmosphere in the packaging (N_2, CO_2), or both. Such systems are used in packaging orange juice and in the brewing industries, and in modified-atmosphere packaging of food products. This technology can remove about 90–95% of the oxygen present in air from the packed food prior to or during packaging. This makes removal of the last traces of oxygen an expensive process.(61,62) Control of the residual oxygen level in the package by use of oxygen absorbent materials limits the rate of deterioration and food spoilage.[17,23,29,32,43,61–66] Zerdin et al.[67] found that the rapid removal of oxygen was an important factor in sustaining a higher concentration of ascorbic acid over long storage times in orange juice. Browning of orange juice or vegetables is also associated with oxygen content.[17,67] In cakes, the use of oxygen scavenger led to a significant increase of cakes with mold-free shelf life.[37]

In fresh meat, the presence of oxygen allows oxygenation of myoglobin, which provides the characteristic red color; this is important because consumers judge meat by its appearance, texture, and flavor.[68–70] However, high levels of oxygen promote the oxidation of muscle lipids, which eventually has detrimental effects on the color of fresh meat.[63,64] The shelf-life of meat is increased by decreasing oxygen levels,[52,68,71] as this prevents growth of fungi and aerobic bacteria.[64] In fresh endives, browning was delayed by oxygen scavengers.[23] Oxygen scavengers reduce and actively control the residual levels of oxygen inside the package, in some cases to $<0.01\%$ oxygen, which is impossible with other packaging systems. Examples of commercial oxygen scavengers are listed in Table 4.

Oxygen scavengers have the following advantages:

- They prevent oxidation phenomena: rancidification of fats and oils and consequent emergence of off-odors and off-flavors, loss or change of colors characteristic of food, loss of oxygen-sensitive nutrients (vitamins A, C, E, unsaturated fatty acids, etc.).
- They prevent the growth of aerobic microorganisms.
- They reduce or eliminate the need for preservatives and antioxidants in food by incorporating the added value of “fresh” or “natural.”
- They are an economical and efficient alternative to the use of modified atmosphere and vacuum packaging.
- They slow down metabolism of food.

The use of these systems, either alone or in combination with other traditional packaging systems, and the use of modified atmospheres can therefore extend the commercial life of a food product.

The different mechanisms of action of oxygen scavengers are

- Oxidation of iron and iron salts. This is the most widely used mechanism today and one of the most effective. Oxygen scavenger systems that are based on iron oxidation reactions are explained by the following equation[72]:
  $4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$
- Oxidation of photosensitive coloring matter.
- Oxidation of ascorbic acid and unsaturated fatty acids (oleic, linoleic).
- Enzymatic oxidation (glucose oxidase/catalase, alcohol oxidase). Glucose oxidase is an oxidoreductase, which transfers two hydrogens of the CHOH group of glucose to oxygen with the formation of glucono-δ-lactone and hydrogen peroxide.[73]

The systems based on the oxidation of iron and ferrous salts react with water provided by food to produce a reaction that moisturizes the iron metal in the product packaging and irreversibly converts it to a stable oxide. The iron powder is contained within small oxygen-permeable bags that prevent contact with food. The main advantage of using this type of oxygen absorber is that they can reduce oxygen levels to $< 0.01\%$, which is much lower than the typical level of 0.3–3.0% obtained with residual oxygen-modified atmosphere packaging. This lower level of oxygen can be maintained for long periods depending upon the oxygen permeability of the packaging material. However, the disadvantages of sachets include the need for additional packaging operations to add the sachet to each package,

Table 4
List of some commercial oxygen scavengers

Commercial product	Company
ActiTUF™	M&G Finanziaria s.r.l.
Aegis HFX Resin	Honeywell International Inc.
Aegis OXCE Resin	
Ageless®	Mitsubishi Gas Chemical
Amosorb®	ColorMatrix Group Inc.
Amosorb SolO2	
Celox™	Grace Darex Packaging Technologies
Desi Pak®	Süd-Chemie AG
Sorb-It®	
Tri-Sorb®	
Getter Pak®	
2-in-1 Pak®	
Cryovac® OS Film	Sealed Air Corporation
O2S®	Bericap GmbH und Co. KG
O-Buster®	Hsaio Sung Non-Oxygen Chemical Co., Ltd.
Oxbar®	Constar International Inc.
MonOxbar®	
DiamondClear®	
Bioka Oxygen Absorber Sachets	Bioka Ltd.
Bioka Oxygen Scavenging Film Laminate	
ATCO®	ATCO/Standa Industrie
Ciba® Shelfplus™ O2	Ciba Inc. (BASF)
Oxyguard™	Toyo Seikan Kaisha, Ltd.
ZERO2	CSIRO
valOR Activ100	Valspar Corporation
valOR ActivBloc100	
Wonderkeep	Powdertech, Co. Ltd.
Powdertech's	
FreshMax®	Multisorb Technologies
FreshPax®	
FreshPax® CR	
FreshCard®	
StripPax®	
MiniPax®	
Freshilizer®	Toppan Printing Co.
Tri Sorb EVA	Tri-Seal (Tekni-Plex)
Tri Shield Tri Sorb EVA	
Tri Shield EVA blue	

certain atmospheric conditions (e.g., high humidity, low CO_2 level) in the package are sometimes required, very low oxygen absorption rates at low temperatures, and the fact that they cannot be used in beverages or foods containing high levels of water because they become inactive when wet.[1,74,75] When moisture enters the package containing the absorbent, an aqueous slurry of oxygen absorbent is formed. The aqueous slurry oozes out of the package on to the foodstuff, spoiling its appearance.[76] In contrast, ascorbic acid can be used in liquid food or beverage as an efficient oxygen scavenger.

Another oxygen scavenger uses immobilized yeast within wax or paraffin to reduce oxygen in the package; this system can also be used in solid foods and beverages. The wax or paraffin only permits the yeast to come in contact with water that penetrates through. The immobilized yeast is coated on the inner surface of a container or on a surface of a closure such as a stopper. After adding a food or beverage and closing the container, the immobilized yeast removes oxygen from the container. The closed container and its contents can be pasteurized and the yeast retains sufficient viability to remove oxygen.[77]

Commercial presentations of oxygen scavengers (Table 5) include

- Independent systems such as bags, strips, or labels, which are incorporated into or attached to the inside of the package, but are separate elements. They are the most widely used systems and must be appropriately labeled and identified as inedible. These systems are also used in the closures of alcoholic and nonalcoholic drinks to eliminate both the residual oxygen in the headspace and that permeating through the packaging. Examples of independent systems of oxygen scavengers include Ageless®, ATCO® oxygen scavengers, FreshPax®, FreshMax®, FreshCard®, Freshilizer®, and O-BUSTER. These are based on finely divided iron powder with excipients (salts and minerals to provide the moisture content and suitable specific surface for the oxidation of iron to be effective as possible) and can reduce the residual oxygen levels to approximately 0.01%.[29,61,78–81]
- Systems integrated into the packaging material itself, not visually perceptible as distinct elements. Iron, ascorbic acid, and low-molecular-weight ingredients are extruded or coated in the polymer.[41,42,73,75,82] Such integration minimizes rejection by the consumer and also minimizes the risk of accidental breakage of the sachet and involuntary consumption of the contents.[83,84] Examples of systems integrated into the packaging material are SHELFPLUS® O2, Oxyguard™, Oxbar™, Cryovac OS, valOR Activ100, valOR ActivBloc100, Amosorb series, ZERO2, Bioka Oxygen Scavenging Film Laminate, and ActiTUF®.

All these systems require that the active material be not affected by oxygen before use. Some are covered in an airtight package, whereas others require activation prior to use (activated by water, swelling of the polymer, the action of light, etc.). They can be used alone or in combination with other active systems that enhance their action, such as moisture absorbers. For example, a blend of ethylene methylacrylate cyclohexenylmethyl acrylate (EMCM) is an oxygen-scavenging system that requires activation with ultraviolet light prior to use. Once the filled package is sealed, the EMCM polymer will scavenge any residual headspace oxygen in the package as well as any oxygen that may permeate through the passive barrier in the package.[84]

Selection of oxygen scavenger (shape, size, ability to absorb oxygen, time to reach equilibrium) must be very strict and tailored to the needs and characteristics of each food (liquid, solid, dry, fat, water content, activity water, etc.) and storage temperature.[100] The speed and ability to scavenge oxygen in integrated systems are lower than in iron-oxidation-independent systems.[73] In integrated systems, oxygen-scavenging multilayer systems are more effective than single-layer oxygen scavengers.[66]

The scope of these systems covers all oxygen-sensitive food products. These include fresh fish, fish products, seafood, meats, vegetables, cured fish, cold appetizers (scallops, fish cake, salad), chips, nuts, bakery products and pastry, fresh and precooked pasta, pizza,

Table 5
Properties and characteristics of commercial oxygen scavengers[3–10,66,73,85–99]

Product name	Type	Intended type of foods	Water activity of food	Characteristics of the system
Ageless®[3]	Z-PT	Dry foods, fatty foods	>0.95	Deoxygenation between the first and fourth day Increased resistance of the wrapping Sachet
	Z-PU	Dry foods	<0.90	Deoxygenation between the first and fourth day Sachet
	Z-PK	Dry foods	<0.65	Deoxygenation between the first and fourth day Sachet
	FX	Moist foods	≥0.85	Rapid deoxygenation. Deoxygenation between 12 hours and 1 day Sachet Excellent water resistance
	S	Nonfatty Foods	>0.65 and <0.95	Rapid deoxygenation. Deoxygenation between 12 hours and second day Sachet
	SS	Fatty foods	>0.65 and <0.95	Rapid deoxygenation. Deoxygenation between 12 hours and second day Sachet It can be used at lower temperatures
	FS	Rice, processed meats, and microwavable food	Between 0.85 and 1	Deoxygenation between 12 hours and 1 day Autoadhesive sachet
		Rice, processed meats, and microwavable food	Between 0.75 and 0.85	Deoxygenation between the first and second day Autoadhesive sachet

(*Continued*)

Table 5
(Continued)

Product name	Type	Intended type of foods	Water activity of food	Characteristics of the system
	FL		Between 0.80 and 1	Deoxygenation between 12 hours and 1 day Autoadhesive sheet (label type)
			Between 0.75 and 0.80	Deoxygenation between the first and second day Autoadhesive sheet (label type)
	FC		Between 0.80 and 1	Deoxygenation between 12 hours and 1 day Autoadhesive sheet (circular card type)
			Between 0.75 and 0.80	Deoxygenation between the first and second day Autoadhesive sheet (circular card type)
	E	Roasted Coffee	0.3 or lower	Sachet Dual scavenger (oxygen and carbon dioxide)
O-Buster®[94]	FT	Dried and oily Foods	<0.85	
	TY	Fatty food		
	DR		High	
Wonderkeep[9]	RP	Dry foods, nuts and cakes	Between 0.3 and 0.85	
	LP	Cake, vegetables and dried meats	Between 0.6 and 0.9	Resistant to water and oil
	EP	Dairy products, fresh bread and cakes		Developed for those foods that deteriorate rapidly or are subject to mould growth and need rapid deoxygenation
	X	Fresh pasta or food with creams	High	
Powdertech[9]	K			It is marketed for those food industries that use metal detectors on their production lines
Freshilizer[91]	FD	Nuts Or Chocolate, Among Others	<0.8	

	FH	Meat and sausages	Between 0.6 and 0.99	It was developed to maintain the characteristic red color of meat
	FT	Pizza	High	Higher oxygen scavenging capacity
FreshMax®[10]	M	Moist or semimoist foods	>0.65	Moisture and grease resistant Autoadhesive patch Oxygen scavenging capacity of between 5 and 10 cm^3 per patch Deoxygenation between 1 and 3 days
	B	Moist or semimoist foods where a carbon dioxide flush has been used	>0.65	Moisture and grease resistant Autoadhesive patch Oxygen scavenging capacity of between 5 and 10 cm^3 per patch Deoxygenation between 4 and 7 days
FreshPax®[10]	B	Moist or semimoist foods	>0.7	Moisture and grease resistant Sachet Deoxygenation between 1 and 3 days
	D	Dehydrated or dry foods	<0.7	Moisture and grease resistant Sachet Deoxygenation between 12 hours and 4 days
	R	Refrigerated or where rapid deoxygenation is required	All	Moisture and grease resistant Sachet Deoxygenation between 8 hours and 2 days
	CR	Meat chilled (beef, pork, lamb, etc.)	High	Conservation of meat chilled in optimal condition for a period ranging between 15 and 30 days Used in combination with modified atmosphere packaging
	M	Moist or semimoist foods where a carbon dioxide flush has been used	>0.65	Moisture and grease resistant Sachet Deoxygenation of 30% to 60% between the second and fifth day and complete deoxygenation between the fifth and seventh day

(*Continued*)

Table 5
(Continued)

Product name	Type	Intended type of foods	Water activity of food	Characteristics of the system
ATCO[92]	LH	Wet and dry food		Sachet Rate of absorption increases with increasing temperature. Deoxygenation at 20 °C in 15 hours and at 10 °C in 1 day. At 5 °C needed between 30 and 36 hours. Direct contact with food should be avoided.
	HV	Wet and dry food		Sachet Rapid deoxygenation even at low temperatures. Deoxygenation at 20 °C in less than 12 hours. Direct contact with food
	FT			Sachet In foods that do not require very rapid absorption of oxygen and may come in direct contact with food Direct contact with food
	10S	Wet foods	>0.85	Label with AST technology (Active sticker technology) It is placed in the package like a label, and has the advantage that the consumer cannot confuse it with a sauce or spice as with sachets. Slower absorption of oxygen because it absorbs water vapor emitted by the food before absorbing oxygen.
	OS100	Moist foods	>0.85	Label with AST technology (Active sticker technology) Direct contact with moist food Avoid contact with fatty foods and high temperatures

	OS200	Moist foods	>0.85	Label with AST technology (Active sticker technology) Direct contact with moist food Avoid contact with fatty foods and high temperatures
Bioka[6]				Sachets Oxygen scavenger based on an enzymatic oxidation process. The enzyme reacts with a substrate to consume oxygen. It is very sensitive to temperature, pH, water activity, and solvent or substrate present in the sachet[66] More expensive than iron-based systems
Oxbar®[95]		Beer and flavored alcoholic beverages	High	Oxbar® is incorporated into the center layer of multilayer containers Oxygen scavenger based on an enzymatic oxidation process. Is an active, oxygen-scavenging material that rebalances its rate of reaction to follow changes in temperature.
Celox[96]		Beer, juice, tea, sports drinks	High	Celox is an oxygen scavenger that uses a reducing agent as an active ingredient. Lids or bottle caps Ascorbic acid is oxidized to ascorbate by reacting with oxygen.[86] Reduces the oxygen content in the headspace and dissolved in the beverage itself.
SHELFPLUS® O2[5]		Food and beverages	All	Based on iron and incorporated in multilayer packaging structure during co-extrusion or lamination. Compatible with polyethylene and polypropylene. Absorbs residual oxygen (2%) in headspace in 3 and 5 days when residual oxygen in headspace is 5%. It can be incorporated into a wide range of plastic packaging structures (rapid multilayer containers, flexible films, cap liners) tor chilled or microwavable foods, retort or nonretort, with or without a modified atmosphere.

(*Continued*)

Table 5
(Continued)

Product name	Type	Intended type of foods	Water activity of food	Characteristics of the system
OSP®				Oxidizable resin It is activated by ultraviolet light.
Oxyguard™[7]		Soup and beverage		Based on iron and incorporated in multilayer films. Contents can be heated in the microwave, retortable, and nonreactive to metal detector
ZERO2[85]				Film that contains dissolved photosensitive dye and an oxygen scavenger agent that is activated by ultraviolet light prior to use.[73,87,88]
Cryovac® OS[93]				Oxygen scavenging organic compound To use as a layer in a laminated packaging film Deoxygenation in 3 days Film that contains dissolved photosensitive dye and an oxygen scavenger agent that is activated by ultraviolet light prior to use.[73,87,88]
Actituf[97]		Wine, foods, beer, malts, juices	All	Resin Bottles The oxygen scavenging is triggered on filling. Increases the life of the alcoholic beverage without affecting taste Actituf has been successfully used in Russia, Eastern Europe, Korea and Belgium in the development of plastic beer bottles.
valOR[8]	Activ100	Beverage, dressings and sauces, and fresh foods	All	Resin Bottles and containers made of polyethylene terephthalate (PET) Approved by the FDA for use in direct contact with food Used in monolayer or multilayer packaging Improved processability, delamination resistance, and compatibility with PET High clarity; low haze

	ActivBloc100	Beer, carbonated juice and flavored alcoholic beverages, dressings and sauces, and fresh foods	All	Resin approved by the FDA for use in direct contact with food Bottles and containers Used in monolayer or multilayer packaging Improved processability, delamination resistance, and compatibility with PET Use in any multilayer PET bottle for high CO_2 retention and low O_2 content Has maintained O_2 levels below 0.8 ppm after 8 months of storage
Amosorb[4]		Beverages, fruit juices, UHT milk, tomato-based products, and teas	High	Transparent polymer Compatibility with PET Bottles and containers Effective elimination of oxygen from the walls, neck, and contents of the containers The oxygen scavenger is based on a cobalt salt that catalyzes the oxidation of unsaturated double bounds in hydrocarbon chains.[89,90] Amosorb granules are added to polyethylene terephthalate in amounts ranging between 1% and 5%, depending on the sensitivity of the packaged product to oxygen, the presence of vitamins and/or minerals, extension of the desired shelf-life, storage form, cover, and packaging design.
	SolO2	Beer, wine, and other alcoholic beverages	High	Improves in the oxygen scavenger capacity Transparent polymer Compatibility with PET Bottles Effective elimination of oxygen from the walls The oxygen scavenger is based on a cobalt salt that catalyzes the oxidation of unsaturated double bounds in hydrocarbon chains.[89,90]

(*Continued*)

Table 5
(Continued)

Product name	Type	Intended type of foods	Water activity of food	Characteristics of the system
Tri-Sorb®[99]	EVA	Beverages, foods	All	Single-extruded solid material. Approved by the FDA for food contact
	Tri Shield	Beverages	High	Multilayer oxygen absorbing system recommended for drinks that require extra protection to prevent loss of CO_2 and O_2 ingress in the headspace Approved by the FDA for food contact
Aegis®[98]	HFX	Noncarbonated beverage	High	Bottles Made with polyamide that provides a high barrier to oxygen even at high humidity Used as additive at concentrations of between 5% and 8%
	OXCE	Carbonated beverages	High	Multilayer bottles Made with polyamide that has been specially designed for carbonated beverages since offering an excellent barrier to oxygen and carbon dioxide even in environments with high humidity Used as additive at concentrations of between 5% and 8%

chocolates and confectioneries, marron glacé, raw or cured meat products, beer, wine, fruit juices and soft drinks, dairy products, coffee, tea, milk powder, and spices.

Oxygen scavengers that contain ethanol or release antimicrobials inhibit microbial growth more effectively than an oxygen absorber alone. Fruits and vegetables, seafood, cheeses, baked goods, pastries, cookies, pizza crusts, and pasta can benefit from packaging systems with both oxygen absorption and antimicrobial release systems. Moreover, dual-function systems with the capacity to absorb as much oxygen as ethylene (such as fresh food packaging for high economic value) slow down decomposition due to the decreased growth of microorganisms and respiration.[(66)]

Attempts have been made to incorporate oxygen-scavenging systems in a container lid or closure. Ascorbates or isoascorbates, alone or in combination with sulfite, are preferred oxygen scavengers. These compositions may be in fluid or meltable form for application to a closure or as a deposit on the closure in the form of gaskets of bottles. Again, the scavenging properties of these compounds are activated by pasteurizing or sterilizing the deposit when sealing a container with the gasket on a closure or metal cap.[(61,101)]

Ethylene Scavengers

The control of ethylene in stored environments plays a key role in prolonging the postharvest life of many types of fresh produce.[(102)] Most fruits and vegetables release ethylene after they are harvested. Ethylene is a phytohormone that initiates and accelerates ripening, produces softening and degradation of chlorophylls, and inevitably leads to deterioration of fresh or minimally processed fruits and vegetables. Ethylene scavengers are useful for preserving ethylene-sensitive fruits and vegetables such as apples, kiwis, bananas, mangos, tomatoes, onions, carrots, and asparagus.

Several mechanisms of action are available commercially:

- One of the main mechanisms of action of ethylene scavengers is based on the use of potassium permanganate, which oxidizes ethylene to carbon dioxide and water. The typical permanganate content is between 4%and 6%.[(103)] It is prepared on suitable substrates that favor the redox process (for example, a high specific surface area is very important, as in alumina, clays, silica gel, activated carbon, etc.). Various substances can also be incorporated as catalysts in the process. Potassium permanganate oxidizes ethylene acetate and ethanol and changes color from purple to brown, and thus, a color change indicates its residual ethylene absorbing capacity.[(1)] However, potassium permanganate cannot be used in direct contact with food because of its toxicity.
- Other systems are based on the ability of certain materials to absorb ethylene, alone or with any oxidizing agent (for example, finely divided and dispersed minerals such as zeolites, silicates, activated carbon, etc.). For example, palladium has been shown to have a higher ethylene adsorption capacity than permanganate-based scavengers in situations of high relative humidity.[(102,104)] Use of palladium with charcoal is good for preventing accumulation of ethylene and is effective in reducing the rate of softening in kiwifruits, bananas, and tomatoes and of chlorophyll loss in spinach leaves.[(18,103)]

Commercial products with the ability to absorb ethylene include Bio-fresh packaging system, Ethylene Control Power Pellet sachets, Ethysorb, Evert-Fresh Green Bags®, Retarder®, PEAKfresh,® and Profresh.

As with oxygen scavengers, products are commercialized as separate elements or integrated into packaging. Permanganate-based products, such as Ethylene Control Power Pellet sachets and Retarder®, may be contained in sachets or integrated directly into the polymeric material as finely dispersed minerals. In the case of PEAKfresh® and EvertFresh, absorption is based on zeolites dispersed in polymeric material. However, the use of permanganate as active agent in contact with food is not permitted in Europe.

PEAKfresh® is a polyethylene bag impregnated with minerals, developed to absorb ethylene and moisture generated by respiration.[105] EvertFresh has the ability to absorb ethylene, ammonia and carbon dioxide.[13] PEAKfresh® and EvertFresh also provide a controlled humidity atmosphere to absorb moisture generated by the respiration of fruits or vegetables.

Profresh is an additive made with low-density polyethylene (LDPE) that is able to absorb ethylene, ethanol, ethyl acetate, ammonia, and hydrogen sulfide and to keep food fresh for longer and eliminate odors. It is used in the manufacture of monolayer or multilayer LDPE and HDPE films at concentrations of between 5% and 20% for use as packaging material in the food industry. Bio-fresh is a film used in combination with the technology of modified atmosphere packaging and like Profresh has the ability to absorb various substances responsible for both ripening and bad odors.[12]

Liquid and Moisture Absorbers

Many food products require control of water, either in liquid or vapor. The presence of oozing liquids (water, blood, or other fluids) in meat products and fish detracts from presentation of the products. High levels of water inside packaging favor growth of microorganisms, causes the softening of dry and crunchy products, such as pasta, cookies, and biscuits, and causes caking and hardening in milk powder or freeze-dried coffee. Excessive water loss may also promote oxidation of fat.

To prevent microbial growth in these nutrient-rich exudates organic acids and surfactants have been incorporated into absorbent pads.[106]

Products packaged with a high relative humidity in the headspace are susceptible to temperature fluctuations during transport or storage, which favors the formation of condensation and mist. In such foods, an antifog additive is used to reduce the interfacial tension between the condensed water and the film. This contributes to the transparency of the film and allows consumers to see packaged foods clearly, but does not affect the amount of water present inside the container.[64,86]

The mechanism of action is based on an absorption process, which in some cases removes excess liquid water and other cases controls the relative humidity in the headspace. Highly hygroscopic and dehydrating agents are used for these purposes. Cellulose fibers, polyacrylate salts, polypropylene glycol, carbohydrates, minerals, silica gel, montmorillonite, molecular sieves, and calcium oxide can be used.

Commercial presentations can be classified into two categories:

- Liquid absorbers (pads, sheets) generally consisting of two or more layers of microporous polymeric materials containing hygroscopic agents. These are used to absorb fluid oozing from cut meat and fish, to improve the appearance to the consumer, and to prevent microbial growth.
- Relative humidity regulators (sachets or tags) containing dehydrating agents. They are used to regulate humidity in a wide range of products such as cheeses, meats, nuts, and spices.

Selection of the type of moisture absorber will depend on the size and weight of the food and its initial water activity, water vapor transmission from the package, temperature and humidity of storage, food sensitivity to moisture, and length of commercial life. Selection of type, size, and capacity of moisture absorber is very important to avoid adverse effects in meat; for example, the lack of oxygen on the side of meat that is in contact with the moisture absorber can produce a color change in the product from red to brown. To avoid this, the company Sirane(107) commercializes moisture absorbers with a surface permeable to oxygen that keeps the meat red while absorbing the exuded liquid.

Some examples of these liquids and moisture absorbers (Table 6) include MOLSIV, Toppan™, ADP™ Advanced Desiccant Polymer, Crisp-it™, Dri-Fresh™, Dri-Fresh™ Inflex™, Dri-Fresh™ Resolve, Eat-Fresh™, Supa-Loc®, Dri-Loc®, Lite-Loc® Plus, Humidipak, Luquasorb® FP 800, Luquasorb® P 1480, NatraSorb®, ATCO Pad, and Pichit.

Liquid and moisture absorbers can be used for fresh fish, seafood, meats, cheeses, nuts, spices, bakery products, candies, pizza, dried food, freeze dried, cut fruits and vegetables, amongst others.(16,30)

Flavor and Odor Absorber/Releaser

In Europe, article 4 (3) of Directive 1935/2004(58) indicated: “Active materials and articles shall not bring about changes in the composition or organoleptic characteristics of food, for instance by masking the spoilage of food, which could mislead consumers.” The release of odor or absorption of degradation indicators such as amines must not suggest a “better than real” quality of a product. Additionally, the regulations concerning addition of ingredients and flavors have to be maintained (Directive 89/107/EEC(109), Directive 95/2/EC(110) and amendments).

Some commercial products (ABSCENTS, Aroma-Can®, ATCO® oxygen scavengers, CompelAroma®, ODORLESS D, and Sincera®) have been developed to eliminate, in some cases selectively, undesirable compounds or compounds that release odors. Retarder®, which is marketed as an ethylene absorber, is also used to absorb undesirable odors. Minipax in the version that combines clay with activated carbon or silica in a 50/50 or 60/40 ratio has both drying and odor-absorption capacities. Natrasorb is a multipurpose absorbent capable of acting on moisture, odors and oxygen.(10) The 2-in-1 Pak® product is a combination of silica gel and activated carbon that can be used to absorb moisture, gases and odors.(14,73)

EKA Noble commercializes BHM powder for incorporation into packaging materials, especially paper and cardboard. It has the ability to absorb undesirable odors produced from aldehydes.(70) ABSCENTS produces UOP’s ABSCENTS Deodorizing powders that are incorporated as an additive to the package material to eliminate unwanted odors and flavors.(111)

Addition of essences and odors can increase the desirability of the food to the consumer, to improve the aroma of fresh product itself, or to enhance the flavor of food when the package is opened. CompelAroma(112) encapsulate flavors and/or odors within the structure of plastic packaging at the time of manufacture.

These flavors and aromas are released slowly and evenly in the packaged product during its shelf life or release can be controlled to occur during opening the package or food preparation. Gradual release of odors can offset the natural loss of taste or smell of products with long shelf lives. Aroma-Can® offers the possibility of incorporating smells such as lemon or orange into the products.(14)

Table 6
Properties and characteristics of liquid and moisture absorbers[9,10,14,93,107,108]

Product name	Characteristics of the system
Supa-Loc® Dri-Loc®[93]	Absorbent pads based on cellulose and composed of different layers. Meat, fish, and poultry pads. Bottom film perforated with hundreds of one-way valves to ensure moisture is locked in.
Lite-Loc® Plus[93]	Absorbent pads based on cellulose and composed of different layers. For all food applications.
Pichit®[9]	Remove moisture and odor. Semipermeable membrane. It is a material that contains moisturizers such as propylene glycol or carbohydrate embedded between two sheets of polyvinyl alcohol that is used to wrap meat or fish. For use in chicken, crisp potato chips, tofu, tomatoes, sardines, mackerel, etc.
Humidipak[14]	Responds continuously to adapt to changes in humidity and temperature, either by addition or absorption of moisture to maintain a certain level of relative humidity (RH) inside the food package during the shelf life of food. Available in virtually any RH level, from 10% to 95% RH. Marketed on the basis of water activity of food, weight and volume of food, tolerance to loss and gain of moisture, shelf-life desired of the product marketing, amongst other features.
Luquasorb® FP 800[108]	White granulated preparation of sodium polyacrylate that is a super absorbent polymer capable of absorbing large amounts of liquids. Used to manufacture super absorbent polymers that absorb water and maintain the product cold for longer after being removed from the refrigerator. Approved for indirect food contact by the US Food and Drug Administration (FDA) and The German Federal Institute of Risk Assessment (BfR).
Luquasorb® P 1480[108]	White granulated preparation of sodium polyacrylate that is a super absorbent polymer capable of absorbing large amounts of liquids. Used to manufacture super absorbent polymers that absorb water and maintain the product cold for longer after being removed from the refrigerator. It has the advantage of being able to maintain its absorptive capacity through multiple cycles of freezing and thawing.
Minipax®	It is available in a variety of mixtures of absorbent (silica, molecular sieve, montmorillonite, activated carbon) and sizes.
StripPax®[10]	Sachets or strips. Protect food from moisture, odors, and other harmful elements. Minipax® has been approved by the FDA for use in preparations that come in contact with food. Minipax® has a high absorbent capacity with a small size, and was designed for those packages with limited space available.

(*Continued*)

Table 6
(Continued)

Product name	Characteristics of the system
Natrasorb®[10]	Absorbs moisture, odors, and oxygen in the package. Bags. Natrasorb M (montmorillonite) is made from magnesium and aluminum silicate with a high capacity to absorb moisture without swelling or apparent substantial deterioration. Natrasorb S (silica gel) contains a large number of sub microscopic pores that attract water vapor and physically maintain it by surface adsorption and capillary condensation. Natrasorb S can absorb water weight in equivalent to 40% of his weight. Natrasorb Hi-Dry® (molecular sieve, sodium aluminum silicate) contains a uniform network of pores and cavities that have a high capacity for water absorption. Natrasorb C (calcium oxide) is capable of adsorbing water at low relative humidities, which is useful for the preservation of dehydrated food. The sachet can withstand the pressure of calcium oxide when it adsorbs water.
Tri-Sorb®	Contain dehydrating agents (Desi Pak® contains bentonite clay, Sorb-It® silica gel, and Tri-Sorb® molecular sieve).
Sorb-it®	Sachets or strips.
Desi Pak®[14]	Protect food from moisture, odors, and other harmful elements.
Advanced Desiccant	Additive.
Polymer (ADP™)	It can be molded into any shape or size and is included in the formulation of the package. It has the advantage that the volume of package is used entirely for storage of the product, as it is part of the package. ADP™ has the disadvantage of that it has lower moisture absorption capacity than absorbent pads.
Dri-Fresh™[107]	Absorbent pads with absorption capacities of 1700 and 3000 cc/m^2.
Dri-Fresh™ Inflex™[107]	A rigid and flat absorbent pad. It can be used with foods that are subjected to high temperatures and microwave energy.
Dri-Fresh™ Resolver[107]	Absorbent pad. Eliminates completely the problem of discoloration on the surface of red meat. Available with an absorption capacity from 800 to 5000 cc/m^2.
Eat-Fresh™ sandwich pads[107]	A contoured absorbent material. Is used on both sides of the food to prevent fogging of the container and to improve the appearance of the product. Bakery products. Absorption level of 600 cc/m^2.

Antimicrobials

When inadequate processing or underprocessing occurs during manufacture, or package integrity is compromised due to a ruptured seal, puncture dents, or incomplete glass finishes, microbiological contamination due to pathogenic or spoilage bacteria may occur.(113) Traditional methods of preserving food from the damaging effects of microbial growth include heat treatment, drying, freezing, refrigeration, irradiation, modified-atmosphere packaging, and addition of salts or antimicrobial agents. However, in Europe some of these techniques are not applicable to foodstuffs such as fresh meat,(114) and fresh fish and seafood. According to article 4 (2) Directive 1935/2004,(58) active substances are ingredients in the sense of article 6 (4 a) Directive 2000/13/EC.(115) Thus, the active substances have to be allowed as additives for the respective foods (Directive 89/107/EEC,(109) Directive 95/2/EC,(116) and amendments).

Antimicrobial packaging include systems such as adding a sachet into the package, dispersing bioactive agents in the packaging, coating bioactive agents on the surface of the packaging material, or utilizing antimicrobial macromolecules with film-forming properties or edible matrices.(88) A large number of agents with antimicrobial properties (ethanol, carbon dioxide, silver ions, chlorine dioxide, antibiotics, organic acids, essential oils and spices, etc.) have been tested for the purpose of inhibiting the growth of microorganisms that can lead to deterioration of foodstuffs (bacteria can also attack the packages affecting their functions and properties). However, few such systems are commercially available.(117)

In Japan, ethanol-releasing products are used with great success, as the use of ethanol at low concentrations in the headspace (4–12%) acts effectively to prevent growth of microorganisms, bacteria, and molds.

The size and capacity of the sachet containing the ethanol-releasing agent will depend on the weight of food, water activity, type of food, and shelf-life required. When food is packaged with an ethanol-releasing agent, the moisture is absorbed and ethanol is released to the headspace of the package.(1)

In commercial preparations, a sachet containing ethanol on a base of finely divided silica with an adequate degree of humidity is placed on the inside of the package. Antimold mild® is highly effective as a food preservative that protects against microbial growth. Antimold mild® consists of a mixture of ethanol and water adsorbed on silicon dioxide, which releases ethanol by absorbing moisture. In contrast, Negamold® releases ethanol when it absorbs oxygen.(73,118) Antimold mild® and Negamold® are used successfully in bakery products, confectionery and dry or semidry food.(118)

Packaging systems that release volatile antimicrobials also include chlorine dioxide, plant extracts, sulfur dioxide, essential oils(53,117,119,120), carbon dioxide, and allylisothiocyanate(50,55,121) release systems. The theoretical advantage of volatile antimicrobials is that they can penetrate most of the food matrix and the polymer is not necessarily in direct contact with food. This type of active packaging is suitable for applications where contact between the portions of food and packaging does not occur, as in the case of ground beef.(65,122,123)

Chlorine dioxide can exist in gaseous, liquid, or solid form. It has proven effective not only against bacteria and fungi but also against viruses. Potential applications of chlorine dioxide include meat, poultry, fish, dairy products, and confectionery and baked goods.(88) However, in Europe chlorine dioxide is not regulated as food additive and, therefore, cannot be used either in active food packaging.

Sulfur dioxide is the most effective material for controlling decomposition of grapes and is much more effective than the combination of γ-radiation and heat. However, it has drawbacks that include bleaching of grape skin and the fact that some sulfur dioxide may remain on grapes.[124] The residues may cause rejection of the product by consumers because sulfur dioxide has a strong characteristic odor.

The role of carbon dioxide in the packaging atmosphere is to suppress microbial growth[70] and to slow down the rate of respiration of fruits and vegetables. Because the permeability of carbon dioxide is between 3 and 5 times that of oxygen in most packaging films, carbon dioxide must be continuously released to maintain the desired concentration in the package.[66] High levels of carbon dioxide (10–80%) are suitable for foods such as meat and poultry in order to inhibit microbial growth on the surface of the products and to extend the shelf life.[45,64]

The advantages of carbon dioxide are that it acts on all the food inside the packaging and does not require contact between the food and package, whereas the disadvantages are that it changes the color of meat and blanches vegetables. CO_2 may be used in conjunction with oxygen scavengers to maintain an atmosphere that is favorable for the preservation of certain products. In the case of fishery products, fresh and processed meats, cheeses, and baked goods, a high concentration of carbon dioxide in the atmosphere of the package is advantageous because it maintains the organoleptic properties of the products and exerts a bacteriostatic effect.

Collapse of the package or development of a partial vacuum may also be a problem for food packed with oxygen absorbers. To overcome this problem, the dual action of oxygen absorber/emitter of carbon dioxide absorbs oxygen and generates an equivalent volume of carbon dioxide.[1] Ageless® G and FreshPax exert dual effects as they have the ability to absorb oxygen and emit carbon dioxide.[3,10] Freshilizer® is another CO_2-releasing product manufactured as Freshilizer® C and Freshilizer® CW.[91]

Verifrais™ packaging, manufactured by Codimer SARL (Paris, France), is used to extend the shelf-life of fresh meat. This innovative package consists of a tray with a perforated false bottom in which a porous sachet containing sodium bicarbonate/ascorbate is deposited.[88] When exudates from meat come in contact with the sachet, it releases carbon dioxide, so that the carbon dioxide absorbed by the meat is replaced continuously.[70]

ATCO CO2 is a sachet capable of absorbing carbon dioxide produced from a mixture of sodium hydroxide, calcium, and potassium.[92] It is based on the reaction of carbon dioxide with a base of sodium, potassium, and calcium:

$$CO_2 + MOH \rightarrow HCO_3$$

$$M = Na, K, Ca$$

ATCO CO_2 is used in foods with water activity greater than 0.8 and marketed with an absorption capacity of 450 mL CO_2 per sachet of 5.2 g. This product removes accumulated carbon dioxide in an airtight container as a result of desorption phenomena or a chemical reaction that could cause the collapse of the airtight container. Its use is strongly discouraged if the carbon dioxide is generated by microorganism growth.[92] Ageless E is another carbon dioxide absorbent recommended for the conservation of roasted coffee. It is available in four capacities of absorption of carbon dioxide.[3]

Other antimicrobials can be incorporated directly into the polymer either by coating technology or by extrusion of the material. For instance, active packaging systems based on the release of 2-nonanone[15,125] or plant extract[117] have been shown to be capable of increasing the postharvest shelf life of strawberries and inhibiting fungal growth. In the latter, the active agents can decompose or be lost by volatilization, which is one of the main drawbacks of the active packaging production. To avoid these problems, the encapsulation of the active agents has been proposed, but there are also additional problems in this case. For example, allyl-isothiocyanate has been encapsulated in cyclodextrins, which are used in coatings of the package. These cyclodextrins can function as antimicrobial delivery systems, as they can release antimicrobial and/or antioxidant compounds as the humidity levels increase in the headspace.(126)

Another way of tackling the problem of microbial growth is by the use of nonvolatile antimicrobial additives. Many preservatives (sorbic acid, benzoic acid, propionic acid and its salts, or bacteriocins such as nisin, natural spices, silver ions, chelators, etc.) are added to plastic films and materials used as antimicrobials. The potential of these packages is based on the reduction in the amount of additive that is incorporated into the device to exert the antimicrobial effect. But these nonvolatile antibacterial require direct contact with the food to be active.

The antimicrobial chemicals most commonly used by researchers are different organic acids such as sorbic acid, acetic acid, and lactic acid, because of their efficiency and profitability.(44,57,88,127–131) Chitosan, nisin, lacticin, and pediocin also have been used to inhibit or slow down microbial growth.(24,25,33,38,56,124132–141) Chitosan is a polymeric sugar-derivative that can perform a dual role as a film matrix and an antimicrobial. However, the antibacterial effect of chitosan decreased with time due to a decreasing availability of amino-groups of chitosan.(25) In turn, chitosan has been chemically modified to produce quaternary ammonium salts in order to improve its antimicrobial activity and physicochemical properties.(142) In some cases, the role of chitosan is that of a matrix for the delivery of other antimicrobials such as acids and salts, plant extracts (essential oils of clove, cinnamon, pepper, rosemary, oregano, winter savory, etc), lysozyme, and nisin.(19,137,143–149)

Nisin is a bacteriocin of small molecular size that enables production of films that release the peptide after contact with food or liquid but is not permitted its use in all kind of foods. Other bacteriocins used in development of active packaging include lactocin 705 and lactocin AL705 produced by *Lactobacillus curvatus* CRL705,(150) bacteriocin 32Y from *Lactobacillus curvatus*,(151,152) enterocin 416K1 produced by *Enterococcus casseliflavus* IM 416K1,(153) enterocins A and B and sakacin K,(154) pediocins produced by *Pediococcus* sp.,(155) bacteriocins lacticin 3147 and Nisaplin®.(138) Nisin is often incorporated into coatings together with acids and only occasionally with other compounds(156). The advantages of bacteriocins are that they are thermo-stable, apparently hypoallergenic, and easily degraded by proteolytic enzymes in the human gastrointestinal tract.(39,88)

Spices, basil, mustard flour, and natural extracts have proven useful in food preservation.(53,157,158) Other antimicrobial agents, such as the enzymes lactoperoxidase, lysozyme, glucose oxidase, and lactoferrin, antimicrobial peptides such as magainins, cecropins, natural phenols such as hydroquinones and catechins, fatty acid esters, phenolic antioxidants, antibiotics, chelating agents and metals such as copper and others, are useful for incorporation into packaging.(26,159–170) Because these compounds are not volatile, there must be contact between the packaging and food so that they exert their antimicrobial effect.(88)

With regard to the application of enzyme immobilization systems, nanostructures offer new and great perspectives. The high surface/volume ratio, Brownian motion of nanoparticles, the possibility of producing porous structures, and the ability to optimize the production of materials compatible with typical polymers used in food packages offer huge opportunities for development in food packaging.[167,171,172]

Edible coatings and films made from polysaccharides, proteins, and lipids have several advantages, including biodegradability, biocompatibility, and aesthetics. Edible coatings may be produced by the addition of antioxidants or antimicrobials and placed directly on the surfaces of meat,[46] cheese, bread, vegetables, fish, and fruits.

Agion® Antimicrobial, Microbeguard® antimicrobial paper, Food Touch™ and Ciba®IRGAGUARD® B antimicrobials are based on incorporation of silver zeolite into the food contact material, which then exerts its action on the surface of the food to inhibit the growth of gram-positive and gram-negative bacteria, molds, and yeasts.[5,173] Zeolites are open-structured aluminosilicates with a negative charge that is compensated by cations such as sodium and silver. The cations are mobile and interchangeable (for example, H^+/H_2O). They are designed specifically to release silver ions and prevent microbial growth because the silver ions disrupt replication of the microorganisms' RNA, thus slowing down the development of odors and loss of food texture.

Food Touch™ is inert, colorless, odorless, and tasteless and is approved for use by the U.S. Food and Drug Administration (FDA). Similarly, Agion® Antimicrobial consists of a zeolite carrier of silver ion containing the active ingredient, which is active against any moisture on the package surface without affecting the taste of food. Microbeguard® antimicrobial paper is produced to suit customer needs and can be marketed in a wide range of colors, paper type or size.[173] IRGAGUARD B 5000 is another antimicrobial silver-based zeolite that has been optimized for polyolefins such as polypropylene (PP), high-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE). IRGAGUARD B5120 is commercially available in pellet form and can be used at concentrations between 0.5% and 7.5% in PP, HDPE, LDPE, and LLDPE, whereas IRGAGUARD 5000 is marketed as a fine powder and is recommended for use at concentrations of between 0.1% and 1.5% for addition to PP, HDPE, LDPE, and LLDPE.[5]

Antimicrobial packaging can play an important role in reducing the risk of contamination of food by pathogens,[20] as well as in extending the shelf life of foods, but should never replace the use of quality raw materials and the proper use of good manufacturing practices.[65] On the other hand, some foods can have their shelf-life extended with incorporated volatile antimicrobial compounds in the headspace of the package.

Antioxidants

Oxidation of fats is one of the most important mechanisms leading to food spoilage, second only to growth of microorganisms. The oxidation of lipids in food leads to a reduction in shelf-life due to changes in taste and/or odor, deterioration of the texture and functionality of muscle foods, and a reduction in nutritional quality.[48]

Oxidation of food can be avoided by use of oxygen scavengers and antioxidant agents in the packaging. Such packaging is intended to prevent or slow down the oxidation reactions that affect the quality of food[48,49]. However, radicals, mainly oxo, hydroxyl, and superoxide, are originated from oxygen and they are the main initiators of oxidation. Thus, oxidation can be avoided by eliminating radicals as soon as they are formed. Some natural compounds act this way and react very efficiently with the radicals by trapping them, thus avoiding further oxidation. In such a case, neither high-barrier nor vacuum packaging materials would be required to avoid oxidation, but only the presence of a radical scavenger to protect the food against the oxidation process.[174] In turn, the materials containing radical scavengers do not need to be protected or activated before using.

A varnish with natural antioxidant of rosemary extract, which acts as a radical scavenger either in the vapor phase or by direct contact, can eliminate or delay the oxidation of foods inside the food package. This eliminates the need to add antioxidants to the package or the food.[174,175]

The additives that are gaining increased attention are natural antioxidants such as vitamin E and natural extracts rich in phenolic compounds and/or terpenes (barley, rosemary, clove, oregano, cinnamon, ginger, etc.).[21,48,49,174,176,177] Spices contain large amounts of phenolic compounds such as flavonoids and phenolic acids, which exhibit antimicrobial and antioxidant properties.[83,178]

The use of antioxidant active film in the conservation of fresh meat can enhance the stability of myoglobin and fresh meat against oxidation processes.[45] In fact, the use of a rosemary active film or an oregano active film has shown an increase of fresh odor and enhanced oxidative stability in lamb steaks.[21] Migration of α-tocopherol from a multilayer active packaging (made of high-density polyethylene, ethylene vinyl alcohol, and a layer of low-density polyethylene containing the antioxidant α-tocopherol) shows a delay in lipid oxidation in whole milk powder.[34] However, in Europe, antioxidants base on tocopherols (e.g., E 306, E 307, E 308, E 309) are not allowed to be used in milk powder according to Directive 95/2/EC.[110] Cellulose films have been incorporated with cysteine and sulpfite and used to cover apples slices. Brighter apples and less browning was obtained with these cellulosic films.[27] The antioxidant content decreases during storage due to diffusion of the antioxidant through the film and its subsequent evaporation at the surface. This decrease in the concentration of the antioxidant can be prevented by adding an extra layer of film that has a low permeability to antioxidant[45,179] or through the use of cyclodextrins.[126]

Antioxidants can be used for oil, nuts, butter, fresh meat, meat derivatives, bakery products, fruits and vegetables, among others.

Intelligent Packaging

The headspace of food packages undergoes changes in their composition over time. Devices capable for identifying, quantifying, and/or reporting changes in the atmosphere within the package, the temperatures during transfer and storage, and the microbiological quality of food provide valuable information both to the final consumer and producer and/or marketer about the effectiveness of the conservation strategies used in the marketing chain.

For packaging intended to be used in the food industry, some very strict requirements must be fulfilled: the indicators should be easily activated and exhibit a change (or show an indication) that is easily measurable and irreversible, time- and temperature-dependent changes must be reproducible and ideally matched or readily correlated with the food quality, and also provide information regarding the status of the package.

Time-Temperature Indicators

The best-before date printed on food packaging is only an indicative value and does not take into account possible fluctuations in temperature that food may suffer during storage. The best-before date must therefore be within the shelf-life of the food to ensure that food is safe to consume. They fall into two types: visual indicators or radio frequency identification (RFID) tags.

The basic idea underlying visual indicators is that the quality of food deteriorates more rapidly at higher temperatures because chemical reactions, biochemical reactions, and microbial growth are speeded up. The indicators change color in response to cumulative exposure to temperature. The main mechanisms of action include enzymatic reactions, polymerization, or chemical diffusion. These products are used to monitor exposure to unsuitable temperatures during transport and storage and are an indication of quality for the producer because they ensure that the product reaches the consumer in optimal conditions. It is important that the indication is irreversible. The following indicators are currently being marketed; OnVu™ and OnVu Ice,[180] Monitor Mark™, WarmMark Time-Temp Tags, CheckPoint, ColdSNAP Temperature Recorders, Fresh-Check®, VarioSens®, Log-ic®, ThermRF tag, 3M™ Freeze Watch, ShockWatch, Coldmark, HeatWatch, ThermRF Logger, and ThermRF Tag.

OnVu™ is an indicator label that can also be printed directly on the packaging. The indicator window is a heart shape within an apple. The window contains organic pigments that are activated by ultraviolet (UV) light and that change color with increasing time and temperature of exposure. Exposure of food to fluctuations in temperature accelerates the discoloration process of the indicator label. OnVu™ is calibrated to the shelf life and storage temperature of the food being monitored.[180] Freshtime also commercializes a thaw indicator (Onvu ice) with a snowflake design that changes color irreversibly when the product has been subjected to a temperature above that required for storage.

Checkpoint® I is recommended for frozen foods and fresh foods such as salads, whereas Checkpoint® III is useful for high-volume, low-cost foods such as poultry, pork, and seafood packaged in modified atmospheres.[181] Another example of an intelligent system is MonitorMark™, which indicates the number hours or days that the product temperature has exceeded the maximum storage temperature.[182]

The RFID tag is an advanced form of data carrier for automatic product identification and traceability. In an RFID system, a reader emits radio waves to capture data from an RFID tag, and the data are then passed to a host computer for analysis and decision making. The RFID tag contains a minuscule microchip connected to a tiny antenna. RFID tags may be classified into two types: passive tags, which have no battery and are powered by the energy supplied by the reader, and active tags, which have their own battery for powering the circuitry of the microchip and broadcast signals to the reader.[183] Intelligent packaging, which is characterized by being able to accumulate and transmit data includes Log-ic® RFID and VarioSens® products.[184,185]

Seal and Leak Indicators

The gas composition in the package headspace often changes as a result of the activity of the food product, leaks, nature of the package, or environmental conditions. O_2 and CO_2 can be used to monitor food quality, as seal indicators (leaks), or to verify the effectiveness of an oxygen absorber. Most O_2 or CO_2 indicators change color as a result of chemical or enzymatic reactions. A color change indicates when the oxygen concentration exceeds the limit established in a sealed food package.[180] Redox dyes such as methylene blue can be used. Other redox dyes that are used in O_2 indicators are 2,6-dichoroindophenol[186] and *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine.[187] For CO_2 indicators, color change occurs when CO_2 concentration decreases to a certain level in the package.

Ageless Eye® is an oxygen indicator[187] inserted inside the container that changes in color from pink to blue in the presence of oxygen (>0.5%). Similarly, Wondersensor indicates oxygen concentrations >0.5% by the development of a blue color. Furthermore, in an environment with an oxygen concentration of less than 0.1%, Wondersensor is pink. Wondersensor is useful, either alone or in combination with Wonderkeep oxygen absorber, in products with A_w between 0.2 and 0.9, such as dry food, pasta, peanuts, and biscuits. Hong and Park[188] reported that visual indicators of carbon dioxide formed by calcium hydroxide and a redox indicator incorporated into polypropylene and carbon nanotubes have shown great sensitivity in the detection of gases such as ethanol[189] or oxygen.[190] O2Sense is an indicator of oxygen for products packed in Modified Atmosphere Packaging (MAP) under development by Freshpoint.[180] A major problem with such indicators is that they require storage under anaerobic conditions, since they quickly deteriorate in air, ceasing to work in a few hours as the strong reducing agent is used up in a direct, or indirect, reaction with oxygen.[191] A new approach is the use of intelligent ink/indicator that changes its color in the presence of oxygen. This ink must be activated with UV light and is stored in aerobic conditions.[192]

Foods that are easily damaged by the presence of moisture can be monitored by the use of devices such as moisture indicators. Maximum Humidity Indicator Cards and Maximum and current Humidity Indicator Cards are examples of currently available systems. These indicators are able to monitor the storage humidity between 50% and 90% in increments of 10%.

Freshness and/or Ripening Indicators

Freshness and/or ripening indicators provide an indication of the deterioration or loss of freshness of packaged goods. They are described as indicating different mechanisms of volatile metabolites, such as diacetyl, amines, carbon dioxide,[193] ammonia and hydrogen sulfide, produced during the aging of foods.[194]

Changes in the concentration of hydrogen sulfide or organic acids such as *n*-butyrate, L-lactic, D-lactate, and acetic acid during storage are offered as viable indicators of the formation of metabolites in meat products,[195] fruits, and vegetables[196]. Indicators based on color changes due to changes in pH are of great potential use as indicators of microbial metabolites and ripeness.[188,193]

Products formed during microbial growth (carbon dioxide and hydrogen sulfide) and biogenic amines are of great potential use in indicating the freshness of meat and fish.[70,194] Biogenic amines (putrescine, cadaverine, histamine, and others) are formed by degradation of protein-containing food to amino acids and by enzymatic decarboxylation of the latter. Thus, biogenic amines are an indicator of food deterioration and only an indirect indicator of food freshness in meat[197] and fish.[198,199]

Freshness and/or ripening indicators are available as FreshTags®,[200] (Eo)®,[201] Timestrip®,[202] ripeSense®,[203] and SensorQ™.[204] A change in color indicates decomposition of the food.

FreshTag® is useful for monitoring the freshness of shrimp, shellfish, and white meat fish, because they react with volatile amines produced during storage. (EO)® is another indicator for meat products that indicates the level of freshness by use of a microorganism that simulates the deterioration of the food being monitored.[201,205] The label is calibrated according to the type of food, storage condition, freshness requirements, and the type and number of microorganisms in the food.[201] SensorQ™ is designed especially for beef and poultry and is based on an increase in gases inside the package, especially sulfide gas, by microbial growth.[204] RipeSense® indicates the ripening of fruits. This sensor changes color when it reacts with aromatic compounds responsible for the odor that fruit gives off while ripening.[203]

Others

Biosensors are compact devices that enable detection, recording, and transmission of information about biological reactions. 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.

The taste and quality of fruit is closely linked to the content of sugars.(206) For this, the quality of fruit and fruit and vegetable beverages can be determined by use of a biosensor for glucose based on glucose oxidase or lactate.(206,207)

Commercially available visual systems are Food Sentinel System™ and Toxin Guard™, which indicate by a color change in the food package that food must not be consumed. The Food Sentinel System™ is capable of detecting the presence of harmful microorganisms to health through immune reactions that make the barcode unreadable.(208) An antibody specific for the pathogen to be monitored (*Salmonella* sp., *Escherichia coli* 0157:H7, *Listeria monocytogenes*, etc.) is fixed to a membrane that forms part of the product barcode. Toxin Guard™ is an indicator of freshness degradation, genetic modification, and food safety consisting of biochemical sensors that incorporate monoclonal antibodies in a polyethylene base. It is able to detect, among other pathogens such as *Salmonella* sp., *Campylobacte*r sp., *Escherichia coli*, and *Listeria* sp., bacterial degradation, chemicals such as pesticides, and genetic modification markers.(209) The presence of these substances is alerted by an irreversible color change in the indicator.

Toxin Guard™ prints a pattern containing several antibodies or aptamers onto a packaging material. The agents are protected by a special abrasion-resistant gel coat, where the porosity is tailored to control the ability of certain antibodies or toxic substances to migrate through. Each antibody or aptamer is specific to a particular biological material and is printed having a distinctive icon shape. The detection system may contain any number of antibodies capable of detecting a variety of common toxic food microbes. With Toxin Guard™, a packager or processor can independently determine the multiplicity and identity of those biological materials against which the packaged product is to be protected. One means of providing enhanced sensitization is by including a scavenger antibody, which is a biologically active ligand characterized as having a higher affinity for the particular toxic substance than the capture antibody. The scavenger antibody is provided in a sufficient amount to bind with the particular toxic substance up to and including a specific threshold concentration. In this manner, the capture antibody will be prevented from binding with a detector antibody until the concentration of the particular biological material surpasses the specific threshold concentration. The biological material detecting system visually reports only those instances where concentration levels are deemed harmful by health regulatory bodies. An important feature of the biological material detection system is its all-encompassing presence around and upon the product being packaged. Because the biological material detecting system is designed as an integral part of 100% of the packaging material and covers all surfaces as utilized, there is no part of the packaged product that can be exposed to undetected microbes.(210–213)

Nanotechnology offers new routes for the development of innovative solutions for improved food packaging. Nanospheres, nanofibers, and encapsulated microfibers can retain or encapsulate bioactive molecules, such as α-chymotrypsin or glucose oxidase, releasing them slowly and steadily to show good prospects in the future development of biosensors for the food packaging industry.(214) Damage to a food can be detected, for example, with a change of color from these nanosensors to detect the presence of pathogens or their metabolic products and decomposition products of the food.(215,216) Nanocantilevers are another kind of nanosensor in which the principle of detection is based on the ability of the substances to detect biological interactions binding between antigens and antibodies, enzymes and substrate or cofactor, and receptor and ligand through a physical and/or electromechanical signal. Nanocantilevers have been used successfully in the study of molecular interactions and the detection of chemical contaminants, toxins and antibiotic residues in food.(217,218) However, the use of nanoparticles in contact with food is not permitted in Europe.

Conclusion

The package as a simple instrument for the marketing of food is changing to match the needs of consumers and the food industry. New types of active and intelligent packaging have been and will be developed to meet these needs. The effectiveness of active and intelligent packaging has been demonstrated by the large number of scientific studies that confirm their application. Currently, oxygen scavenger and moisture absorbers are found on the market in increasing numbers. However, antioxidants and antimicrobial active packaging and freshness and/or ripening indicators will be increasingly important and in future demand by the food industry. The correct use of one or more types of active or intelligent packaging will increase the shelf-life and food safety. However, the development and implementation of this type of packaging will depend on the acceptance and cost-effectiveness for industry and consumers.

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