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Review

Advances in antioxidant active food packaging

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Lipid oxidation is, together with microbial growth, the main cause of spoilage of a great variety of foods, such as nuts, fish, meats, whole milk powders, sauces and oils. It causes a loss of both sensorial and nutritional quality of foods and may even lead to the formation of toxic aldehydes. Some strategies that are commonly used to limit the extent of lipid oxidation of packaged foods are direct addition of antioxidants or packaging under modified atmospheres in which oxygen presence is limited. A novel alternative to these methods is antioxidant active packaging, whose main advantage is that it can provide sustained release of antioxidants during storage. This article reviews the latest advances in antioxidant active food packaging, with special emphasis on antioxidant release systems. The various methods for incorporating antioxidant compounds in the package, the issues to be considered in packaging design, and the various methods employed to date to evaluate the antioxidant effectiveness of active antioxidant materials are reviewed.

Introduction

Lipid oxidation is, after microbial growth, the main cause of food spoilage. In particular, foods with a high lipid content, especially those with a high grade of unsaturation, are susceptible to deterioration following this path. This is the case with nuts, vegetable and fish oils, and meat or fishery products that have been subjected to any preservation treatment or technology that reduces microbial growth. The oxidation of lipids in foodstuffs results in the development of off-flavours, typical of rancidity, rendering the product unacceptable for human consumption (Lindberg Madsen, 1995). Other negative effects are the formation of toxic aldehydes (Guillen & Goicoechea, 2008) and the loss of nutritional quality because of polyunsaturated fatty acid (PUFA) degradation, owing to the fact that the consumption of this type of fatty acid has been positively correlated with the prevention of cardiovascular diseases (Harris, 2007).

Nowadays, consumer demand for healthier and safer food products has prompted research on novel preservation techniques. To reduce lipid oxidation, several strategies have been applied, such as the direct addition of antioxidants to foods or the design of a suitable packaging technology. Vacuum or modified-atmosphere packaging combined with high-barrier packaging materials can limit the presence of oxygen, although it is not always completely and effectively eliminated because of a residual presence at the time of packing or because it permeates in from the exterior through the package wall (Lopez-de-Dicastillo, Alonso, Catala, Gavara, & Hernandez Munoz, 2010). Moreover, some food products such as fresh red meat or some fish products cannot be packaged without oxygen. The direct addition of antioxidant compounds to the food surface may encounter the limitation that once the active compounds are consumed in reaction, the protection ceases and the quality of the food degrades at an increased rate (Mastromatteo, Conte, & Del Nobile, 2010). Currently, antioxidant active packaging systems are being developed. This novel alternative packaging technology is based on the incorporation of antioxidant agents in the package as a way of improving the stability of oxidation-sensitive food products. This review reports on the progress achieved in this technology.

Antioxidant active packaging

Antioxidants are additives commonly used in the polymer industry to prevent thermal degradation of polymers during processing. Traditionally, synthetic antioxidants such as polyphenol, organophosphate and thioester compounds have been used, although the potential toxicity derived from their migration into food products is making their application questionable. To reduce the occurrence

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of this undesired process, food additive antioxidants such as butylated hydroxytoluene (BHT) or butylated hydroxyanisole BHA have been added to polyolefins (Brüggemann, Visnjevski, Burch, & Patel, 2004; Dopico-García, López-Vilariñó, & González-Rodríguez, 2007). In this regard, several groups have reported on the release of antioxidants added to packaging films with the purpose of being delivered to oxygen-sensitive food, improving its chemical stability. Wessling, Nielsen, Leufven, and Jagerstad (1998) reported the release of butylated hydroxytoluene (BHT) and tocopherol from polyethylene films into fatty food simulants, and Torres-Arreola, Soto-Valdez, Peralta, Cardenas-Lopez, and Ezquerra-Brauer (2007) reported the delay of lipid oxidation and protein denaturation by the incorporation of butylated hydroxytoluene (BHT) into low-density polyethylene. However, the presence of synthetic antioxidants in food is questioned, owing to the potential risks, and strict statutory controls are required. The alternative approach that is being studied widely is the use of natural antioxidants, particularly tocopherol, plant extracts, and essential oils from herbs and spices (Almalaika, Ashley, & Issenhuth, 1994; Dopico-Garcia *et al*., 2011; Jipa *et al*., 2005; López-Vilariño, Noguerol, Villaverde, Sabín, & González, 2006; Mallegol, Carlsson, & Deschenes, 2001; Moore *et al*., 2003; Peltzer, Wagner, & Jimenez, 2007; Tovar, Salafranca, Sanchez, & Nerin, 2005; Wessling, Nielsen, Leufvén, & Jägerstad, 1999). Also, it is relevant to mention the potential use of food industrial waste as source of antioxidant agents (Barbosa-Pereira, Angulo, Paseiro-Losada, & Cruz, 2013; Cruz, Conde, Dominguez, & Parajo, 2007; Cruz, Dominguez, & Parajo, 2004). The release of natural antioxidants from the package into food during product commercialization is of high interest for food technologists since this process may reduce lipid oxidation (Barbosa-Pereira, Cruz, *et al*., 2013; Pereira de Abreu, Paseiro Losada, Maroto, & Cruz, 2011a) and can even increase food nutritional value.

Active packaging is defined as a package system that deliberately incorporates components that release or absorb substances into or from the packaged food or the environment surrounding the food to extend the shelf-life or to maintain or improve the condition of the packaged food (Regulation (CE) No. 450/2009 (29/05/2009)). Therefore, active packaging does something more than simply providing a barrier to external detrimental factors, as the packaging system plays an active role in food preservation and quality during the marketing process (Lopez Rubio *et al*., 2004; Pereira de Abreu, Cruz, & Paseiro Losada, 2012).

There are two main modes of action for antioxidant packages: the release of antioxidants to the food and the scavenging of undesirable compounds such as oxygen, radical oxidative species or metal ions from the headspace or from the food. Scavengers are substances that react with, modify or trap substances which are involved in any step of the oxidation process. Since these substances are not released into the food, the package should be designed to allow the access of the pro-oxidant substances to the location where scavengers are incorporated.

Regarding the antioxidant releasing packaging materials, one of the main benefits, as compared to the direct addition of antioxidants to food, is that active materials may act as a source of antioxidants that are released to the food at controlled rates, so that a predetermined concentration of the active compound is maintained in the food, compensating the continuous using up of antioxidants during storage (Mastromatteo *et al*., 2010).

A suitable selection of the antioxidant compound to be incorporated in the packaging material is crucial. The antioxidant compound and the packaging material should be compatible in order to achieve a homogeneous distribution, and the partition coefficients of the antioxidant in the different phases should favour its release to the food or headspace. Once released, the solubility characteristics of the antioxidant can determine its effectiveness, and therefore the type of antioxidant should be selected as a function of the type of food. Apolar antioxidants would seem to be more suitable for foods with a high lipid content and vice versa. However, the so called 'antioxidant paradox' should be taken into account. This is a phenomenon where hydrophilic free radical scavengers (FRS) have been shown to be more effective antioxidants than hydrophobic FRS in bulk oils, while hydrophobic FRS are more effective in emulsified oils. This observation was attributed to the ability of polar FRS to concentrate at the oil–air interface of bulk oils where oxidation was most prevalent and the ability of non-polar FRS to concentrate in the lipid phase of emulsions, whereas polar FRS partitioned in both the lipid and the water phases (Decker, 1998).

Edible film and coating technology is close to active packaging technology and may also be a means of reducing oxidative spoilage in foods. The main mechanism of action is the reduction of the oxygen transmission rate, as well as the possibility of incorporating antioxidant compounds in the edible film or coating matrix; this vehicle has the advantage of close contact between coating and food. An edible film or coating does not act as a package itself, but it may reduce the barrier requirements of the package. Edible film and coating technologies are outside the scope of the present article and have been the subject of various reviews (Falguera, Quintero, Jiménez, Muñoz, & Ibarz, 2011; Gennadios, Hanna, & Kurth, 1997; Rojas-Grau, Soliva-Fortuny, & Martin-Belloso, 2009; Tharanathan, 2003).

Antioxidant active packaging manufacture and application

There are basically two methodologies for producing antioxidant packaging systems:

a) Independent devices: An independent device such as a sachet, pad or label containing the agent separately from the food product is added to a conventional 'passive' package.

b) Antioxidant packaging materials: Antioxidant packaging materials are used in the manufacture of the package, that is, the active agent is incorporated in the walls of the package exerting its action by absorbing undesirable compounds from the headspace or by releasing antioxidant compounds to the food or the headspace surrounding it.

Independent antioxidant devices

The first active packaging systems that were commercialized (still widely used today) were based on the incorporation within a conventional package of a sachet containing a compound or a mixture that releases or retains a specific gas or vapour whose presence or absence results in a beneficial effect on food quality and safety. In the case of antioxidant packaging, oxygen scavengers are the only representatives of this group of active packages. Iron and ferrous oxide fine powders are the most common oxygen scavengers, although ascorbic acid, sulphites, catechol, ligands, and enzymes such as glucose oxidase are also utilized (Brody, Bugusu, Han, Sand, & McHugh, 2008). To prevent scavengers from acting prematurely, specialized mechanisms can trigger the scavenging reaction. For example, iron-based scavengers require the presence of humid conditions to activate oxygen removal (Lopez Rubio *et al.*, 2004). Exhaustive reviews regarding the uses and applications of oxygen scavenging packages can be found elsewhere (Brody *et al.*, 2008; Brody, Strupinsky, & Kline, 2001; Rooney, 2005; Suppakul, Miltz, Sonneveld, & Bigger, 2003).

Antioxidant packaging materials

Antioxidant packaging materials are being developed by incorporating the active compounds in the polymer matrix or on the polymeric film surface. The manufacturing procedure should be selected taking into consideration the type of polymer and the characteristics of the antioxidant agents, especially heat resistance and mechanism of action. If the antioxidant activity of the material is based on a migration process into the food, the substances released should be food additives and comply with present regulations in terms of maximum concentration.

From a technological point of view, the agent (or the reactive substances which produce the agent) is intimately mixed with the polymer, either by dissolving both into an appropriate solvent followed by application of the solution to a substrate by coating technologies, or by polymer melting and incorporation and mixing of the agent in the melt using extrusion technologies.

Incorporation of the antioxidant in the bulk of the polymeric matrix by coating technologies

A homogeneous film can be obtained by spreading a polymer solution and evaporating the solvent system (casting). Although the manufacture of active films by casting is a procedure widely used during film development, it cannot be considered a standard production process. Nevertheless, solutions and dispersions are used in the production of polymeric coatings on film surfaces through conventional flexo and gravure printing technologies.

In active packaging technologies, the final coated film should fulfil three main requirements: a) the active coating should present good adherence to the film substrate and should be valid for direct food contact; b) the agent release should be adjusted to produce an efficient antioxidant activity; and c) the final active coated structure should fulfil the functional packaging requirements of the food products, which are basically those of conventional passive packaging. Adherence depends mainly on compatibility between the substrate and coating polymers. To promote adherence, the film substrate surface is treated by physical methods (corona or flame discharge, UV irradiation), by chemical methods (use of primers) or by a combination of both (e.g., corona treatment and primer) immediately before the coating process.

When the active material acts as an antioxidant releasing system, the agent release is controlled by a combination of mass transport processes which involve partition equilibrium of the agents at the interphases and kinetic processes in food, headspace, coating and substrate phases as represented in Fig. 1 (López-Carballo, Gómez-Estaca, Catalá, Hernández-Muñoz, & Gavara, 2012). The active substances are partitioned in all phases constituting the food/package/environment system. In the case of non-volatile agents and at equilibrium, the concentration ratios at the interphases are given by the partition coefficients that describe equilibrium between the film substrate (FS) and film coating (FC), and the FC and the food product (F):

$$K_{\frac{FC}{FS}} = \frac{c_{FC}}{c_{FS}}; \quad K_{\frac{FC}{F}} = \frac{c_{FC}}{c_F}$$

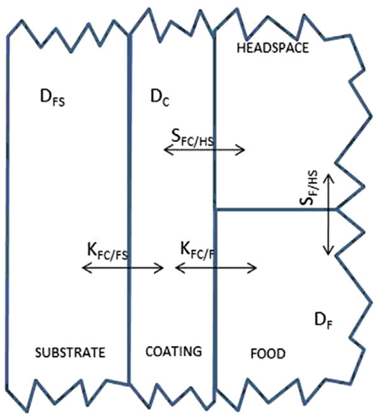

Fig. 1. Diagram of the mass transport parameters (partition *K*, solubility *S* and diffusion *D* coefficients) involved in the various parts of a food packaged in a bag consisting of a coated substrate: substrate (FS), coating (FC), food (F) and headspace (HS).

To obtain a high release of the agent into the food, the coating matrix should be selected to ensure a low value of $K_{FC/F}$. It is also important to design the package with a substrate material with a low affinity for the agent, that is, $K_{FC/FS}$ should have a high value, otherwise the agent would be retained by the substrate.

In the case of volatile agents, the package headspace (HS) is also involved in the mass transport process, and therefore the agent concentration in the headspace is related to those in the food and coating by the corresponding partition coefficients:

$$K_{\frac{FC}{HS}} = \frac{c_{FC}}{c_{HS}}; \quad K_{\frac{F}{HS}} = \frac{c_F}{c_{HS}}$$

Or, alternatively, by the solubility coefficients as described by Henry's law, which expresses the amount of agent in the headspace as partial pressure (p_{HS}):

$$S_{\frac{FC}{HS}} = \frac{c_{FC}}{p_{HS}}; \quad S_{\frac{F}{HS}} = \frac{c_F}{p_{HS}}$$

Low values of the two solubility coefficients would provide a high concentration of the agent in the vapour phase, whereas low $S_{FC/HS}$ and high $S_{F/HS}$ coefficients ensure a high concentration of active compounds on the food surface.

Various studies have been conducted on release tests and different analytical methods of compound quantification have been tested (Granda-Restrepo *et al.*, 2009; Peltzer, Wagner, & Jimenez, 2009; Tovar *et al.*, 2005; Wessling *et al.*, 1998). Release is completely dependent on the compatibility of the antioxidant and the food product (often substituted in experimental studies by a food simulant). Every food (or simulant) shows characteristic profile and extent of the antioxidant release, owing to differences in polarities, pH, viscosity and swelling effect of solvent on the polymer. These analyses give us information about the affinity of the food product and the active materials, making it possible to choose the most appropriate active material for each type of food. Some authors have observed that increasing the amount of antioxidant incorporated produces an increase in antioxidant activity, but not always in a linear way (Bentayeb, Rubio, Batlle, & Nerin, 2007; Lopez-de-Dicastillo *et al.*, 2010). Considerable decreases have even been observed in some cases (Lopez-de-Dicastillo, Balasubramanian, Yam, & Schaich, 2009). This can be attributed to an interaction between the antioxidant compounds and the polymer matrix, or a reduction in activity due to a too high antioxidant concentration. Several studies on food protection have shown that antioxidants, such as tocopherols, exhibit their greatest antioxidant potency at optimum concentrations and at high concentrations this activity decreases, or they can even exhibit prooxidant behaviour (Huang, Frankel, & German, 1994; Jung & Min, 1990; Niki, 1991; Zuta, Simpson, Zhao, & Leclerc, 2007).

The above-mentioned partition and solubility coefficients characterize the extent of the mass transport process and denote the final concentration of the agent throughout the various phases that constitute the food packaging system, assuming that equilibrium is achieved. However, the pace at which the system advances towards equilibrium is dependent on the kinetics of agent diffusion in the various system phases. According to Fick's laws the flow of a substance (J) in a phase is proportional to the concentration gradient established ($\partial c/\partial x$):

$$J = -D_\alpha \frac{\partial c}{\partial x}; \quad \alpha = \mathrm{FC, FS, F, HS}$$

Commonly, the diffusion of the agent in the coating is the slowest process and therefore the agent mass transport process is controlled by the D_{FC} value.

Faster releases can be obtained by increasing polymer chain mobility in the coating matrix by the addition of plasticizing compounds. The deliberate addition of polymer plasticizers has been reported to accelerate diffusion processes in biopolymers (Hernandez-Munoz, Kanavouras, Ng, & Gavara, 2003). Farris, Piergiovanni, Ronchi, Rocca, and Introzzi (2010) patented the development of a biopolymeric coating which is plasticized by sorption of water from the environment, modifying its barrier characteristics. Cerisuelo, Hernandez-Munoz, Gomez-Estaca, Gavara, and Catala (2010) reported the use of an EVOH coating containing essential oil, release of which was triggered by exposure to humid environments. Gemili, Yemenicioglu, and Altinkaya (2010) studied the release of ascorbic acid and L-tyrosine from a cellulose acetate-based film into water and found that ascorbic acid was released faster than L-tyrosine. Garces, Nerin, Beltran, and Roncales (2004) patented antioxidant varnishes based on the addition of plant extracts to polyester, nitrocellulose, acrylic and vinyl polymer solutions for food protection and Nerín *et al.* (2006) reported the efficiency of these varnishes in the stabilization of beef meat, although they also reported a drawback derived from a collateral effect on sensory properties of food owing to the release of highly aromatic substances.

Valid solutions for slowing down the releasing process are the inclusion in the matrix of particles that increase the tortuosity of the diffusion path such as clay nanoparticles (Cerisuelo, Lopez-de-Castillo, Hernandez Munoz, Gavara, & Catala, 2010), the reduction of chain mobility by polymer cross-linking (Hernandez-Munoz, Kanavouras, Lagaron, & Gavara, 2005; Pau Balaguer, Gomez-Estaca, Gavara, & Hernandez-Munoz, 2011) or encapsulation (Jung *et al.*, 2009).

Although agent release is the most common mechanism of action, active materials can also provide an antioxidant effect as scavengers of substances involved in the oxidation process (Nerin, Tovar, & Salafranca, 2008; Pezo, Salafranca, & Nerin, 2008).

Finally, the coated material should fulfil the packaging requirements of the food product in terms of functional requirements (mechanical, optical, barrier, hermeticity, thermosealability …), these properties ideally being independent of the agent concentration in the structure.

The difficulties of this technology are related to chemical compatibility with polymer and solvents, the loss of agent during drying, especially with volatile substances, and changes induced in surface properties of the structure (antifogging, sealability, machinability …). However, the coating technology presents several advantages in the development of active materials, including distribution of the agent in the innermost layer of the package, in direct contact with the food, and, overall, a non-aggressive thermal treatment. Thermo-labile agents can be incorporated in the package with a minimum loss of activity.

Incorporation of the antioxidant in the bulk of the polymeric matrix by extrusion technologies

The incorporation and mixing of the agent with the melted polymer during the extrusion process has also been explored and it is currently used in the manufacture of active packages. This technique is preferred by many converters since most conventional packaging structures are manufactured completely or partially by extrusion processes. The critical issue to be considered is whether the active substance is degraded by severe thermo-mechanical treatment.

Finely divided inorganic compounds (fillers, clays, colourants …) are substances that in general resist extrusion processes. Indeed, they are commonly added to polymers to modify mechanical, optical or barrier properties and were the first active agents to be incorporated in packaging walls. Among active antioxidant packaging materials, oxygen scavengers are the ones that are being most widely produced by the extrusion technique. Iron and ferrous oxide fine powders, ascorbic acid, some nylons, photosensitive dyes and unsaturated hydrocarbons are being used in the manufacture of extruded films with oxygen scavenging properties, as has been reported in previous reviews (Brody *et al*., 2008; Lopez Rubio *et al*., 2004).

Many different active packaging structures can be built with active materials prepared by extrusion processes, including coextruded and laminated multilayers. The design is dependent on the type of agent and the type of polymer matrix, but primarily on the packaging requirements of the food product. Fig. 2 presents diagrams of a simple and a complex structure design.

When the active extruded film presents adequate antioxidant activity and provides the rest of the packaging requirements of the packaged product, the active packaging system may consist of a monolayer film of the active material. The activity of this system is controlled by the agent release extent and kinetics, as already commented in the previous section (López-Carballo *et al*., 2012). However, the use of monolayer active films might involve activity of the material towards the environment, which could reduce package efficiency.

Unfortunately, such a simple solution is not always valid. Some substances and the active materials containing them cannot be in direct contact with food, as in the case of some oxygen scavenger layers (Lopez Rubio *et al*., 2004). The package design must include a functional or protective layer (P) to limit the migration of potentially hazardous compounds. This solution can also be used to modify the kinetics and extent of release of the antioxidant agent. In other cases, the active film does not provide the mechanical, barrier or printing properties required for adequate packaging of the product. Lamination or coextrusion of the active layer to a structural mono or multilayer film (S) can solve the packaging design. Fig. 2 shows a diagram of the most complex solution, which includes a structural and a protective layer. The use of mathematical models based on numerical approximations such as finite difference methods can provide predictions of the release behaviour of this kind of complex structure, since no analytical solutions to Fick's laws are available.

There are not many studies dealing with the development of antioxidant active packaging materials by extrusion. Tovar *et al.* (2005) demonstrated the release of rosemary extract, incorporated in coextruded polypropylene films, on four different food simulants, although migration was low. Wessling *et al.* (1999) found negligible migration of α-tocopherol from PP and a very reduced release from LDPE, which depended on the fat content of the food tested. This emphasizes the importance of compatibility between active ingredient, polymer and type of food. Byun, Kim, and Whiteside (2010) developed polylactic acid (PLA) films incorporating α-tocopherol by the extrusion technique. Although they did not evaluate the possible loss of α-tocopherol during processing (at temperatures up to 193 °C), they found a considerable antioxidant activity of the film by the DPPH method, indicating that at least some of the antioxidant incorporated was present in the final material. Additionally, the resulting material showed an improved water barrier capacity as a result of the hydrophobic nature of α-tocopherol and a loss of clarity, as compared to the film produced without α-tocopherol addition. Granda-Restrepo *et al.* (2009) also developed an antioxidant active material based on α-tocopherol and LDPE, agent release from which accelerated with an increase in temperature. The final structure consisting of several layers (high-density polyethylene, ethylene–vinyl alcohol and a layer of low-density polyethylene containing the antioxidant) was effective as an inhibitor of lipid oxidation of whole milk powder. Lopez de Dicastillo *et al.* (Lopez-de-Dicastillo *et al*., 2010; Lopez de Dicastillo *et al*., 2011) produced extruded ethylene–vinyl alcohol copolymer (EVOH) films containing catechin, quercetin and tea extract as antioxidant agents. In these studies, the addition of these bioactive compounds did not greatly modify their water and oxygen permeability, glass transition temperature (T_g) or crystallinity, but improved their thermal resistance. Release studies showed that both antioxidants were released in

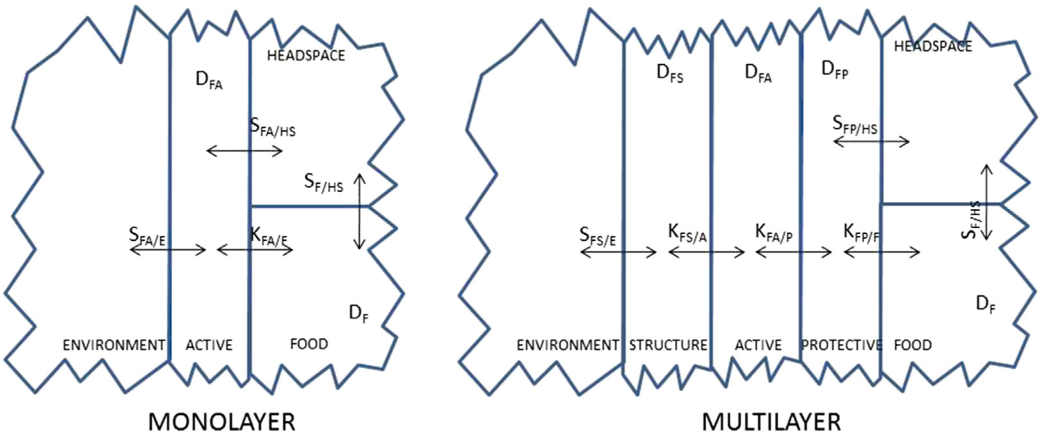

Fig. 2. Diagram of the mass transport parameters (partition *K*, solubility *S* and diffusion *D* coefficients) involved in the various parts of a food packaged in a bag consisting of a monolayer or a multilayer structure containing the active agent: structural layer (FS), active layer (FA), protective layer (FP), food (F), environment (E) and headspace (HS).

aqueous and alcoholic food simulants, the release being higher in the case of catechin-containing samples.

Immobilization of the antioxidant on the film surface

Antioxidants can also be immobilized on the polymeric surface, exerting their activity by direct contact with the food product without mass transfer. Since the agent does not migrate, its activity is limited to the contact surface only. Therefore, this kind of development may be especially useful for the packaging of liquid foods, such as oils. In solid or semi-solid foods, the activity is limited to the area of contact between the packaging system and the food, and therefore these systems have found applications in vacuum packaging and/or the manufacture of slide separators.

Arrua, Strumia, and Nazareno (2010) immobilized caffeic acid on a polypropylene film by covalent binding of caffeoyl chloride on a modified polymeric surface of PP films grafted with hydroxyethyl methacrylate as monomer. The films thus obtained were shown to have available phenolic groups by the Folin–Ciocalteu method as well as antioxidant activity by the DPPH and ABTS assays. Furthermore, the polymer obtained showed a good protective activity against ascorbic acid oxidation in orange juice.

In another development, Goddard *et al.* (Barish & Goddard, 2011; Tian, Decker, & Goddard, 2012) modified the surface of LDPE by grafting a biocompatible polymer (polyethylene glycol, PEG) to its ozone-treated surface. The resulting surface was then functionalized with a range of amine-terminated bioactive molecules. Ethylenediamine or polyethyleneimine was covalently attached to the PEG-grafted film and the metal chelator poly(acrylic acid) (PAA) was attached to the amines to increase the number of available carboxylic acids. The final material showed to have a higher affinity to Fe^{3+} than Fe^{2+} with the optimum binding pH at 5.0.

Antioxidant activity assays

Packaging in direct contact with food

There are several ways to measure the effectiveness of antioxidant active materials. Several studies (listed in Table 1) have demonstrated antioxidant activity by measuring the degree of lipid oxidation of oxygen-sensitive foods packaged with active materials, using established methods that have been proved suitable for studying

Table 1. Methods for the estimation of antioxidant activity in active packaging systems.

Application	Method used	References
Packaging of frozen fish	PV, CD, TH, FFA, TBARS, AV	Pereira de Abreu *et al.*, 2010
Packaging of fresh meat	MetMb, colour, PV, aldehydes	Nerín *et al.*, 2006
Rosemary containing plastic films	Adapted ORAC	Bentayeb *et al.*, 2007
Antioxidant PLA film	ABTS and DPPH	Byun *et al.*, 2010
Antioxidant cellulose a cetate film	ABTS and DPPH	Gemili *et al.*, 2010
Antioxidant EVOH film	ABTS and DPPH	Lopez-de-Dicastillo *et al.* 2010; Lopez de Dicastillo *et al.*, 2011
Antioxidant gelatin film	Metal chelating activity	Gomez-Estaca *et al.*, 2009
Rosemary containing plastic films	Radical scavenging activity	Pezo *et al.*, 2006, 2008
Antioxidant EVOH film	Radical scavenging activity	Lopez-de-Dicastillo *et al.* 2012

Peroxide values (PV), conjugated dienes (CD), conjugated triene hydroperoxides (TH), free fatty acids (FFA), thiobarbituric acid index (TBARS) and *p*-anisidine value (AV), metmyoglobin (MetMb), Oxygen Radical Absorbance Capacity (ORAC).

lipid hydrolysis and primary and secondary lipid oxidation (Andre, Castanheira, Cruz, Paseiro, & Sanches-Silva, 2010; Camo, Beltran, & Roncales, 2008; Montero-Prado, Rodriguez-Lafuente, & Nerín, 2011; Nerín *et al*., 2006; Pereira de Abreu, Losada, Maroto, & Cruz, 2010; Pereira de Abreu, Paseiro Losada, Maroto, & Cruz, 2011b; Wu, Wang, & Chen, 2010). For instance, Pereira de Abreu *et al*. evaluated the effectiveness of a new active packaging film, based on low-density polyethylene film containing natural antioxidants from barley husks, by determining the retardation of lipid damage in frozen Atlantic salmon, measuring various parameters, such as peroxide values (PV), conjugated dienes (CD), conjugated triene hydroperoxides (TH), free fatty acids (FFA), thiobarbituric acid index (TBARS) and *p*-anisidine value (AV) (Pereira de Abreu *et al*., 2010). In the case of meat, it is common to monitor metmyoglobin (MetMb) percentage (spectrophotometrically) and colour (reflectance spectrophotometer) values as well (Nerín *et al*., 2006). As more magnitudes are measured, a better understanding of oxidation protection will be obtained, since oxidation is a complex process that occurs in stages: initial, auto-oxidation and final phase. During each stage, products are formed at fluctuating rates. Primary oxidation products, such as hydroperoxides, are formed when molecular oxygen and unsaturated fatty acids are combined in the presence of a catalyst, such as iron, light or heat, during the initial stage. Peroxide compounds are reactive and can combine with fats to form additional reactive products during the auto-oxidation stage. Secondary oxidation products, alkanes, alkenes, aldehydes and ketones are formed during the final stage.

Moreover, antioxidant activity provided by films can also be evaluated by measuring the radical scavenging ability of food simulants, since scavenging of radicals is one of the main antioxidant mechanisms. Various procedures have been proposed, based on producing and measuring radicals to evaluate the antioxidant properties of antioxidants released from packaging materials.

There are several antioxidant capacity assays, based on multifaceted aspects of antioxidants and the basic kinetic models of inhibited autoxidation. These methods are generally used to measure the antioxidant activity of foods, natural extracts or species, but they can be very useful to give us an idea of the antioxidants released from films in release studies, or from solvent extractions.

Antioxidants can deactivate radicals by two major mechanisms, Hydrogen Atom Transfer (HAT) and Single Electron Transfer (SET), depending on the kinetics and potential for side reactions (Huang, Ou, & Prior, 2005; Prior, Wu, & Schaich, 2005). HAT-based methods measure the ability of an antioxidant to quench free radicals by hydrogen donation. Reactivity in HAT methods is determined by the BDE (bond dissociation energy) of the H-donating group in the potential antioxidant. Oxygen Radical Absorbance Capacity (ORAC), and Total Radical-trapping Antioxidant Parameter (TRAP) are the two most important antioxidant methods utilizing HAT reaction mechanisms. ORAC measures antioxidant inhibition of peroxyl radical-induced oxidations and thus reflects classical radical chain breaking antioxidant activity by H atom transfer (Cao, Alessio, & Cutler, 1993; Glazer, 1990; Ou, Hampsch-Woodill, & Prior, 2001). Bentayeb *et al*. (2007) have recently proposed adaptation of the ORAC assay to measure the activity of antioxidant plastic films. After extraction of the active compounds, the ORAC assay with some modifications is carried out in order to maximize the signal and find the best efficiency.

SET-based methods detect the ability of a potential antioxidant to transfer one electron to reduce any compound, including metals, carbonyl and radicals. Relative reactivity in SET methods is based primarily on deprotonation and ionization potential (IP) of the reactive functional group. One of the most useful methods is the Ferric Reducing Antioxidant Power (FRAP) assay, which measures reduction of ferric 2,4,6-tripyridyl-s-triazine (TPTZ) to a coloured product (Benzie & Szeto, 1999; Pulido, Bravo, & Saura-Calixto, 2000).

Furthermore, some antioxidant capacity methods utilize both HAT and SET mechanisms. This is more convenient, as in most food samples SET and HAT mechanisms may occur together, with the balance determined by antioxidant structure and pH (Ou, Huang, Hampsch-Woodill, Flanagan, & Deemer, 2002). Although the ABTS and DPPH assays are usually classified as SET reactions, these two indicator radicals may in fact be neutralized either by direct reduction via electron transfers or by radical quenching via H atom transfer. The ABTS assay, also known as the TEAC method, is based on the ability of antioxidants to scavenge the long-lived radical anion 2,2′-azinobis(3-ethylbenzothiazoline-6-sulphonic acid), ABTS•+, while the DPPH method is based on measurement of the ability of antioxidants to reduce the radical 2,2-diphenyl-1-picrylhydrazyl, DPPH•. Both methods are widely used because of their simplicity, needing only a UV–vis spectrophotometer. Some authors have applied these methods to determine the antioxidant activity of films (Byun *et al*., 2010; Gemili *et al*., 2010; Lopez-de-Dicastillo *et al*., 2010; Lopez de Dicastillo *et al*., 2011).

Another antioxidant mechanism involves the metal chelating activity of some molecules. The involvement of transition metals such as Fe^{2+} or Cu^{2+}, which act as electron donors/receptors, in the catalysis of oxidation reactions is well known. This effect is especially important when evaluating the antioxidant effectiveness of antioxidants on muscle foods, as they are rich in proteins such as myoglobin and haemoglobin in which iron ions are present. Some antioxidants may act as metal chelators that retard the progression of oxidation reactions, so that some methods have been developed in order to evaluate the chelating activity of antioxidant compounds separately or incorporated into films (Gomez-Estaca, Gimenez, Montero, & Gomez-Guillen, 2009).

When the antioxidant capacity of the films obtained is taken into account, as well as the antioxidant capacity of the antioxidants, the antioxidant concentration in the films can be inferred. When comparing the calculated antioxidant concentration in the film (as concentration initially added to the film), significant differences have been observed. One of the main reasons is the reduction due to the manufacturing process. High temperature conditions during the extrusion process are one of the reasons for antioxidant degradation or evaporation. Some studies have demonstrated casting processes that produce materials with less loss of antioxidant in the film with respect to the nominal content owing to less aggressive processing and manufacture conditions (Lopez-de-Dicastillo *et al.*, 2010). Consequently, the final antioxidant activity of the films should be calculated once the film is obtained.

Packaging in indirect contact with food

Several studies have demonstrated that active materials can present antioxidant activity without the need to be in contact with the food, through a radical scavenging activity of free radicals in the package headspace. This second proposed mechanism was proved by an innovative method based on hydroxyl radical scavenging activity developed by Pezo, Salafranca, and Nerin (2006) (Pezo *et al.*, 2008). The method is based on the hydroxylation of salicylic acid by OH radicals and the reduction of hydroxylated products in the presence of antioxidant plastic. This method has the limitation that it only presents the antioxidant activity as a hydroxyl radical scavenger. Some studies have also revealed that the maximum antioxidant activity of active materials, as hydroxyl radical scavengers, was reached at certain concentrations, but when the concentrations of antioxidants added to the polymer were higher this activity decreased. Lopez de Dicastillo *et al.* (2011) have shown that antioxidant activity results obtained with this method were in accordance with those obtained by monitoring peanut oxidation. Active samples had comparable results from scavenging hydroxyl radical tests and evaluation of peanut oxidation.

Concluding remarks

Active packaging is receiving considerable attention as an emerging technology that can be used to improve the quality and stability of food, reducing the direct addition of chemicals and the need for changes in formulation. Among these technologies, antioxidant active packaging systems based on the incorporation of antioxidant agents in the package are being developed as a way of improving the stability of oxidation-sensitive food products. Active materials have proved to work by releasing antioxidant agents to the food product and/or by reducing the presence of reactive oxygen species which act as initiators of oxidation processes. These developments are to be designed and optimized for each specific product and in brief, they will be ready to be implemented by the food industry.

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