

Trends in the use of natural antioxidants in active food packaging: a review

Ana Sanches-Silva ^{ab}, Denise Costa ^a, Tânia G. Albuquerque ^{ac}, Giovanna Giuliana Buonocore ^d, Fernando Ramos ^{ef}, Maria Conceição Castilho ^{ef}, Ana Vera Machado ^g & Helena S. Costa ^{ac}

^a Department of Food and Nutrition, National Institute of Health Dr. Ricardo Jorge, Lisbon, Portugal

^b Centro de Estudos de Ciência Animal (CECA), Universidade do Porto, Porto, Portugal

^c REQUIMTE/ Faculdade de Farmácia da Universidade do Porto, Porto, Portugal

^d Institute of Composite and Biomedical Materials, National Research Council (CNR), Naples, Italy

^e CEF - Center for Pharmaceutical Studies, Health Sciences Campus, Pharmacy Faculty, University of Coimbra, Coimbra, Portugal

^f CNC - Center for Neuroscience and Cell Biology, University of Coimbra, Coimbra, Portugal

^g IPC - Institute for Polymers and Composites/I3N, Department of Polymer Engineering, University of Minho, Guimarães, Portugal

Abstract

The demand for natural antioxidant active packaging is increasing due to its unquestionable advantages compared with the addition of antioxidants directly to the food. Therefore, the search for antioxidants perceived as natural, namely those that naturally occur in herbs and spices, is a field attracting great interest. In line with this, in the last few years, natural antioxidants such as α -tocopherol, caffeic acid, catechin, quercetin, carvacrol and plant extracts (e.g. rosemary extract) have been incorporated into food packaging. On the other hand, consumers and the food industry are also interested in active biodegradable/compostable packaging and edible films to reduce environmental impact, minimise food loss and minimise contaminants from industrial production and reutilisation by-products. The present review focuses on the natural antioxidants already applied in active food packaging, and it reviews the methods used to determine the oxidation protection effect of antioxidant active films and the methods used to quantify natural antioxidants in food matrices or food simulants. Lastly consumers' demands and industry trends are also addressed.

Keywords: active food packaging; biodegradable packaging; edible films; astaxanthin; chitosan; α -tocopherol; natural antioxidants

Introduction

Food deterioration is responsible for the loss of quality and safety and it can occur during production, transport, processing or storage. Oxidation is the main cause of deterioration of foods and it considerably limits the shelf life of these products (Nerín et al. 2008). The main consequences of oxidation include: (1) a decrease in the nutritional value of food due to the destruction of essential fatty acids, proteins and lipid soluble vitamins; (2) a decrease of the energy content; (3) the production of offflavours and odours; and (4) colour changes (degradation of pigments), which are important in the consumers' decision to purchase the food (Nerín et al. 2008).

Due to the great economic impact of this phenomenon, the food industry is constantly looking for new methods to reduce the effects of oxidation. Although the reduction of oxygen content (by vacuum or modified atmosphere packaging) has an effect on the control of oxidation reactions, this is only partial because the oxygen dissolved in the food at the time of packaging is sometimes very difficult to or cannot be completely eliminated (López-de-Dicastillo et al. 2010). Therefore, the food industry has long recognised the importance of using antioxidants (AOs) for this purpose. According to European Union legislation, Directive 2006/52/EC (European Commission 2006), there are several AOs authorised to be used in foods. Most of the permitted AOs are artificial, such as butylated hydroxyanisole, butylated hydroxytoluene, tertbutylhydroquinone and propyl gallate, and their use is only authorised in processed food.

One of the main roles of food packaging is to retard the natural processes that lead to food deterioration. AOs can be incorporated into food packaging and be released by a controlled mechanism of diffusion. The use of AOs in food packaging may delay both lipid oxidation and protein denaturation (Torres-Arreola et al. 2007). Packaging designed to foster desirable interactions with its content has been called active packaging. According to the European Union legislation for food packaging (European Commission 2004, 2009) (see the section 'Food contact material (FCM) legislation at both European Union and national levels' below), 'active food contact materials and articles are designed to deliberately incorporate "active" components that would release or absorb intended to be released into the food or to absorb substances into or from the packaged food or the environment surrounding the food'.

Due to the increasing importance of active packaging, several reviews can be found in the literature regarding

this subject (Appendini & Hotchkiss et al. 2002; LópezRubio et al. 2004; Ozdemir & Floros 2004; Dainelli et al. 2008; Restuccia et al. 2010; Pereira de Abreu, Cruz, et al. 2012; Gómez-Estaca et al. 2014).

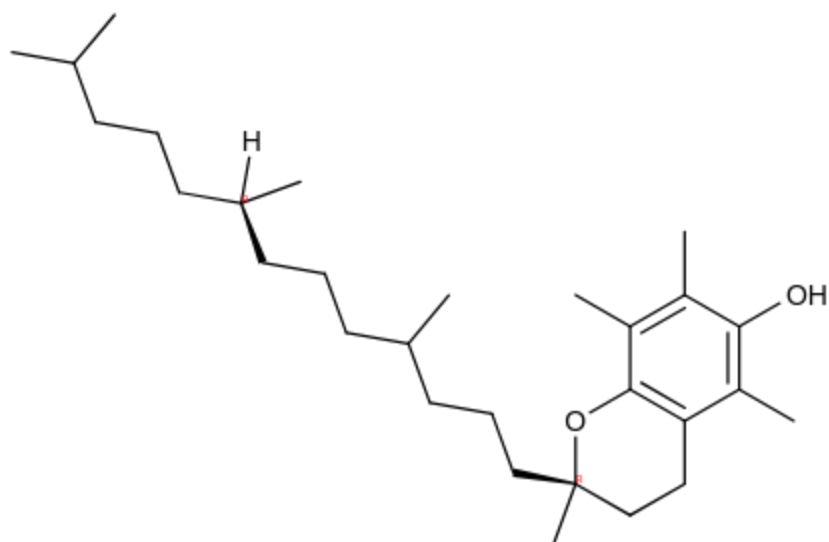
According to Dainelli et al. (2008), active packaging can be classified in non-migratory active packaging that elicits a response without migration of the active compound into the food (oxygen absorbers are an example of these systems), most of them are based on iron oxidation, but they can also be based on ascorbic acid oxidation, catechol oxidation or enzymatic catalysis. They can be found as self-adhesive labels, sachets or be incorporated into the packaging monolayer or multilayer material. Research has also been devoted to

grafting of AOs onto the polymer (Al-Malaika & Suharty 1995; Curcio et al. 2009; Spizzirri et al. 2009) or active packaging allowing a controlled migration of non-volatile agents or an emission of volatile compounds into the atmosphere surrounding the food. This innovative food packaging concept can extend the shelf life of food through the release of AOs by a controlled mechanism of diffusion from the packaging to the food surface and dissolution in it or in the inner atmosphere of the product or by the scavenging of free radicals (Nerín et al. 2006). The release mechanism provides a continuous replenishment of AOs to foods and therefore, can reduce the direct addition of chemicals to the food (Jongjareonrak et al. 2008; López-de-DiCastillo, Gómez-Estaca, et al. 2012).

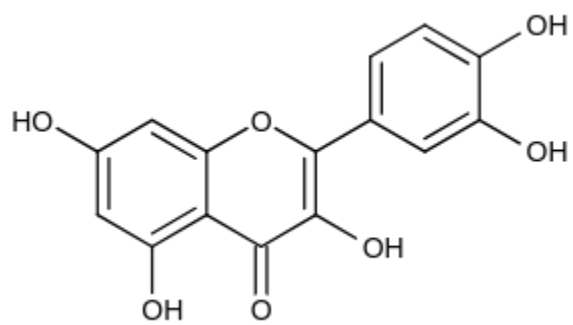
Several studies have reported that the addition of AOs to packaging increases food stabilisation (GrandaRestrepo, Peralta, et al. 2009; Peltzer et al. 2009; Pereira de Abreu et al. 2011c). Regarding the techniques for manufacturing active packaging, most of the times the polymers are mixed with the AOs and then converted (e.g. by extrusion or co-extrusion) into plastic films and sheets (Camo et al. 2011).

Nowadays, especially due to consumers' demands, there is a tendency to search for natural AO molecules that are not related to possible toxicological side-effects, e.g. suspected carcinogenic potential (Imaida et al. 1983; Chen et al. 1992), but have the same AO properties as artificial molecules. The demand for AO-active packaging is increasing due to their unquestionable advantages compared with the addition of AOs directly to the food, which include the lower amount of active compounds required, an activity focused at the surface of the food, extended AO effect due to controlled migration from the film to the food matrix, simplification of industrial processing of the food (no need of additional steps such as mixing, immersion or spraying to include the active substances) (Bolumar et al. 2011).

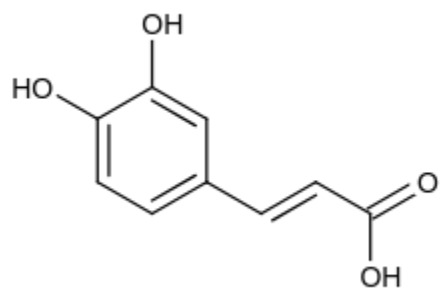
Therefore, the search for AOs perceived as natural, namely those that naturally occur in herbs and spices, is a field that is attracting great interest by the scientific community due to their lower toxicity and higher safety (Nerín et al. 2006, 2008). In line with this, in the last years different pure standards of natural AOs were incorporated into food packaging such as α -tocopherol, caffeic acid, catechin (López-de-Dicastillo et al. 2010; López-de-Dicastillo, Pezo, et al. 2012), quercetin (López-de-Dicastillo et al. 2010; López-de-Dicastillo, GómezEstaca, et al. 2012; López-de-Dicastillo, Pezo, et al. 2012) or carvacrol (Figure 1). Sources of natural AOs were also incorporated in packaging for food applications: essential oils such as cinnamon (*Cinnamomum zeylanicum* L.), oregano (*Origanum vulgare* L.), clove (*Syzygium aromaticum* L.), rosemary (*Rosmarinus* (a)



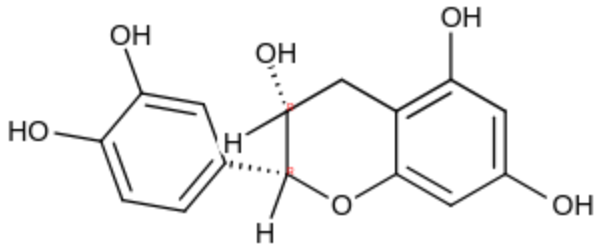
(d)



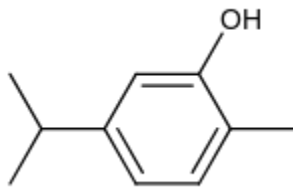
(b)



(e)



(c)



(f)

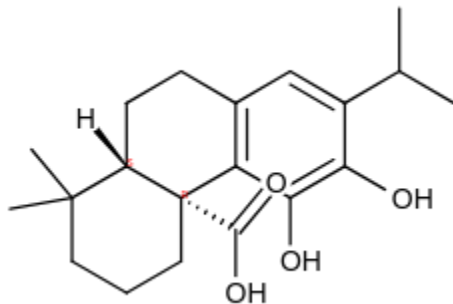


Figure 1. Chemical structures of some natural antioxidants incorporated in active food packaging: (a) α -tocopherol, CAS no. 59-02-9; (b) caffeic acid, CAS no. 331-39-5; (c) carvacrol, CAS no. 499-75-2; (d) quercetin, CAS no. 117-39-5; (e) catechin, CAS no. 154-23-4; and (f) carnosic acid, CAS no. 3650-09-7. officinalis L.), ginger (*Zingiber officinale* Rosc.) and lemongrass (*Cymbopogon citratus* (DC.) Stapf.); extracts such as barley husks (*Hordeum vulgare* L.), green tea (*Camellia sinensis* L.), mint (*Mentha spicata* L.) and pomegranate peel (*Punica granatum* L.). Plant extracts can indeed impart a slight flavour that can be highly appreciated, for instance in the case of smoked fish (Gómez-Estaca et al. 2007).

Food contact material (FCM) legislation at both European Union and national levels

Any plastic material intended to come in contact with food must comply with the FCM legislation at both European Union and national levels. Regarding the European Union legislation for FCMs, it includes framework Regulation (EC) 1935/2004 (European Commission 2004), Regulation (EC) 2023/2006 on good manufacturing practices (European Commission 2006), Regulation (EU) 10/2011 on plastics (European Commission 2011), and in the case they are active or intelligent materials, also Regulation (EC) 450/2009 (European Commission 2009). Regulation (EC) 1935/2004, regarding all materials and articles intended to come into contact with food, establishes the general requirements for the safe use of active and intelligent packaging (European Commission 2004). Regulation (EC) 450/2009 (European Commission 2009) lays down specific rules for active and intelligent materials and articles in addition to those of Regulation (EC) 1935/2004. According to Regulations (EC) 1935/2004 and (EC) 450/2009, the release or absorption of substances should not mislead the consumer (e.g. by masking spoiled food) and they should be adequately labelled to indicate that the materials or articles are active and to identify the non-edible parts with the words 'Do not eat' or with a symbol. Moreover, these regulations also address the requirements for the authorisation of substances. First, the application requires a technical dossier containing specific information on the active substances. Secondly, EFSA carries out an evaluation and, based on this, the European Commission can grant a petitioner authorisation for the submitted active substances that will subsequently enter into legislation (European Commission 2004; Restuccia et al. 2010).

Regulation (EU) 10/2011 replaces the Plastics Directive (2002/72/EC) and its amendments, as various Directives on migration testing. Regulation (EU) 10/2011 (European Commission 2011) is directly applicable in all European Union member states as of 1 May 2011, while the Plastics Directive (2002/72/EC) (European Commission 2002) requires the transposition into national laws of the individual member states. Once the industry requires time to establish compliance according to the new requirements (particularly the migration tests requirements), its implementation has a transitional period.

There are two types of migration tests, overall migration (OM) tests and specific migration tests including both limits of migration, the overall limit of migration and the specific limit of migration (SML) (European Commission 2011). The results of these tests must comply with the corresponding limits, the overall migration limits (OML) and the SML. OML is the maximum permitted amount of non-volatile substances total mass transferred from the packaging to the food simulant, and the identity of the substances that migrate is not known. It is 10mgdm^{-2} of food contact surface area. This value corresponds to a cubic packaging containing 1 kg of food to a migration of 60mgkg^{-1} food. When the surface-to-volume ratio is higher (in the case of small packaging), the resulting migration into food is higher. For instance, infants and small children have a higher consumption of food per kilogram bodyweight than adults and do not yet have a diversified nutrition. Therefore, OML should be linked to the limit in food and not to the surface area in the case of FCMs that are intended for packaging foods for infants and small children.

SML is the maximum permitted amount transfer of one identified compound from the material or article to the food or food simulant and it is expressed in mg of substance per kg of food (mgkg^{-1}). Not all the substances included in the list of authorised substances to be used in the manufacture of plastic materials have a SML. In the case of substances that are unstable in food simulant or food or for which no adequate analytical method is available, it is indicated that verification of compliance should be undertaken by verification of residual content of a monomer or additive in the material per 6dm^2 of contact surface (European Commission 2011). According to Regulation (EU) 10/2011 on plastics (European Commission 2011), the OM test is not mandatory for dry foods but SM tests are. In this case simulant E (Tenax^(R), poly (2,6-diphenyl-p-phenylene oxide) polymer) should be used.

Generally, very low levels of AOs are found in the food or food simulants tested, therefore accurate and very sensitive analytical methods are essential to determine the migration of monomers or additives from FCMs to food or food simulants (Tovar et al. 2005). Also, it is important to know the amount of AO required to stabilise the food in order to simulate the amount of AO that should migrate from the packaging into the food.

Regulation (EU) 10/2011 introduces several new definitions related to plastic food contact materials. For example, although the term 'non-intentionally added substance' (NIAS) has been used to generically describe impurities present in the FCMs that can migrate to foods, it was not previously defined by regulation. Regulation (EU) 10/ 2011 provides a broader definition for NIAS (e.g. including substances that can be formed during the manufacture of FCMs), and specifies the obligation of the manufacturer to ensure safety of FCMs even in the case that they may contain and release NIAS (European Commission 2011).

Natural antioxidants already applied in active food packaging

The most recent contributions on active packaging with natural AOs have been reviewed in order to understand the near future tendencies in the field of AO active food packaging. Natural AOs can be used in the packaging with the aim of (1) having an action in the packaging or (2) with the intention of being released into the food to avoid its oxidation. Therefore in the first case, natural AOs should respect the packaging legislation and, in the second case, they should respect the food legislation (Community or national provisions) (European Commission 2009; Regulation (EC) 450/2009).

Tocopherols are classified as substances generally recognised as safe for food products according to the Code of Federal Regulations (FDA 2013). α -tocopherol is one of the most used AOs to protect the polymer during processing and as an additive for active packaging (Siró et al. 2006). Table 1 summarises some of the applications of α -tocopherol in food packaging. Granda-Restrepo, SotoValdez, et al. (2009) have developed a multilayer active packaging with high-density polyethylene (HDPE), ethylene vinyl alcohol copolymer (EVOH) and an internal layer of low-density polyethylene (LDPE) in which the LDPE layer incorporates α -tocopherol. This new packaging has delayed the lipid oxidation of milk powder.

During storage, the concentration of α -tocopherol in the polymer decreases due to its diffusion to the film surface and consequent migration at the surface to the inner

atmosphere of the packaging or directly to the food. The rate of migration can be slowed by using a film layer that has low diffusion into the AO (Wessling et al. 1998) or through the use of cyclodextrin (Wood 2001; Astray et al. 2009). Incorporation of α -tocopherol in polymers has been widely investigated, but not much in biopolymers (Jongjareonrak et al. 2008).

Carvacrol has also been used to prepare active packaging but it has the drawback of the potential sensory effects in foods. Quercetin and catechin are two non-volatile flavonoids; this is a great advantage compared with other AOs because it reduces the loss of agent during packaging manufacturing (López-de-DiCastillo, Pezo, et al. 2012).

Regarding the addition of plant or fruit extracts to polymer matrices, this can greatly improve their properties, like antimicrobial or AO capacities (Almenar et al. 2007; López et al. 2007; Nerín et al. 2008) and some physicochemical properties such as mechanical properties, colour or water vapour barriers.

The composition of the essential oils can vary considerably according to the plant variety, the processing and drying procedures, and the climate. This originates great differences among batches, therefore the AO properties of the final packaging should be measured and controlled (Bentayeb et al. 2009).

Rosemary extract is one of the plant extracts that has already been incorporated into food packaging. Rosemary (*Rosmarinus officinalis*) is a member of the Lamiaceae family. Traditionally it has been used in both food and medicine due to its organoleptic and medical properties. It is composed by flavones (apigenin, genkwanin, hesperetin and cirsimaritin), phenolic diterpenes (carnosic acid, carnosol, rosmadial, epirosmanol, rosmanol, carnosic acid o-quinone), and phenolic acids (caffeic acid and rosmarinic acid). Carnosic acid is one of the most important compounds responsible for AO capacity. Some of the other phenolic diterpenes are degradation products of carnosic acid and are part of the so-called 'cascade of carnosic acid'. Several authors have reported the effectiveness of rosemary in delaying the lipid oxidation, for instance of meat (Sánchez-Escalante et al. 2001; O'Grady et al. 2006) or in maintaining the quality of fresh-cut pears (Xiao et al. 2010).

Oregano extract has also been incorporated into food packaging. Oregano is obtained by drying leaves and flowers of *Origanum vulgare*, a plant used to yield a characteristic aroma and taste. The oregano essential oil has both antimicrobial and AO properties. The main constituents of oregano essential oil are carvacrol, thymol, *p*-cymene and *c*-terpinene. One of the most potent AOs present in the oregano is rosmarinic acid (Camo et al. 2011). Bentayeb et al. (2009) have confirmed the effectiveness of the films with oregano extract when comparing the AO capacity of various natural extracts incorporated in active packaging. Therefore, oregano essential oil has been used to prepare active packaging that was efficient in increasing beef shelf life (Camo et al. 2011).

Green tea has potent AO capacity since it is a good source of polyphenolic compounds like catechin, theaflavins and thearubigins, which have the ability to scavenge reactive oxygen and nitrogen species (Siripatrawan & Harte 2010). Therefore, green tea extract has already been used successfully to prepare active packaging (López-de-DiCastillo et al. 2011; Colon & Nerín 2012) and active edible films (Siripatrawan & Harte 2010; Siripatrawan & Noipha 2012).

Grapefruit seed extract is made from seeds and pulp of grapefruit and it contains tocopherol, citric and ascorbic acids (Song et al. 2012). The AO and antimicrobial effects of this extract in different products such as ground beef have been reported (Song et al. 2012).

Barley husks were also used to prepare an active food packaging due to their composition in phenolic compounds. Barley is one of the most important cereals cultivated worldwide. The grain is used in the brewing process and about 15 – 20% of the dry weight of the grain is the husk of the spent grains and it has no useful purpose. After Table 1. Films with α -tocopherol.

Type of packaging	Polymeric matrix	Complexation of α -tocopherol with other molecules	Other antioxidants used	Food matrix or food simulants used	Results	Reference

Plastic	LDPE		BHT	Sunflower oil 95% ethanol (v/v)	<p>α-tocopherol migration from LDPE films was slower than BHT, being a more stable antioxidant Active packaging with α-tocopherol could increase oxidation stability of the products and prolong shelf life</p> <p>α-tocopherol-impregnated LDPE film apparently could not prolong shelf life of oatmeal</p>	Wessling et al. (1998)
Plastic	LDPE		BHT	Oatmeal		Wessling et al. (2000)

Coating polymer	EVA		Nisin	Milk cream Model emulsion (66% water, 32% paraffin oil with 2% emulsifier)	α -tocopherol incorporation retarded lipid oxidation and showed a potential for preserving food quality in terms of chemical quality and microbial growth, prolonging shelf life of foods	Lee et al. (2004)
Plastic	LDPE	Free or complexed with β -cyclodextrin		95% ethanol (v/v)	Complexation by β -cyclodextrin allowed a controlled release of α -tocopherol and the migration was slower compared with free α -tocopherol	Siró et al. (2006)

Edible film	Fish skin-based gelatin		BHT		Films incorporated with α -tocopherol showed increased antioxidative activity with increasing storage time and were able to retard lard oxidation increasing storage time and were able to retard lard oxidation	Jongjareonrak et al. (2008)
Plastic	HDPE (BHA or α -tocopherol) EVOH/LDPE (BHT) Composite of HDPE/EVOH/LDPE with BHT and α -tocopherol		BHA BHT	Whole milk powder		Granda-Restrepo, Peralta, et al. (2009)

Plastic	LDPE			Corn oil	LDPE films containing α -tocopherol in concentrations between 19 and 30mgg ⁻¹ maintained the oxidative stability of the oil during storage at 30°C	Graciano-Verdugo et al. (2010)
Plastic	LLDPE	Free or complexed with β -cyclodextrin	Quercetin (free or complexed with β -cyclodextrin)	Coconut oil 95% ethanol (v/v)	The diffusion coefficient of α -tocopherol can be reduced in its inclusion complexed form. Controlled-release packaging allows an optimal antioxidant concentration delivery and achievement of prolonged activity	Koontz et al. (2010)

Table 1. Continued.

Type of packaging	Polymeric matrix	Complexation of α -tocopherol with other molecules	Other antioxidants used	Food matrix or food simulants used	Results	Reference
Plastic	PET		Citrus extract	Turkey meat	The results of TBARS analysis of samples stored on α -tocopherol trays showed that this packaging was not effective on delaying lipid oxidation	Contini et al. (2012)
Blend polymer	LDPE/PP			Linoleic acid 95% ethanol	LDPE/PP blending may allow a modulation of the release of tocopherol optimizing antioxidant effectiveness	Zhu et al. (2012)

Note: BHA, butylated hydroxyanisole; BHT, butylated hydroxytoluene; EVA, ethylene-vinyl acetate copolymer; EVOH, ethylene-vinyl alcohol copolymer; HDPE, high-density polyethylene; LDPE, low-density polyethylene; LLDPE, linear low-density polyethylene; PET, polyethylene terephthalate; PP, polypropylene; and TBARS, thiobarbituric acid reactive substances assay. pre-hydrolysis and delignification of barley husks, it is possible to obtain a rich AO extract. The main phenolic compounds of this extract are *p*-coumaric and ferulic acid (Pereira de Abreu et al. 2011b). In a new development, LDPE films were coated with two different

concentrations of barley husks extracts with AOs properties. The coated LDPE films were used to package fish samples like salmon (Pereira de Abreu et al. 2010), halibut (Pereira de Abreu et al. 2011a), blue shark (Pereira de Abreu et al. 2011c), hake (Pereira de Abreu et al. 2011b) and cod (Pereira de Abreu, Maroto, et al. 2012), and its ability to protect against oxidative processes was demonstrated.

Another work carried out by Sanches-Silva et al. (2013) reported the incorporation of a potent AO, astaxanthin, obtained from shrimp by-products in an LDPE matrix. These by-products were fermented and the silage was centrifuged, originating three phases: a solid phase (from which chitin is obtained), a liquid phase with proteins, minerals and free amino acids, and a lipid phase that contains astaxanthin.

Astaxanthin is a carotenoid with an AO activity 10 and 100-500 times higher than β -carotene and vitamin E, respectively. Moreover, this compound is responsible for the pink-red colour of salmonids and shellfish. LDPE films were prepared with different amounts (2%, 3% and 4% w/w) of the lipid fraction of fermented shrimp waste by extrusion in order to evaluate further their astaxanthin migration from the plastic samples into fatty food simulants. Strips of plastic films (10 cm²) containing the lipid fraction of fermented shrimp waste were used to carry out the migration tests. Migration tests were carried out at 40°C for 10 days and at 70°C for 2 days with isooctane and ethanol 95%(v/v) in aqueous solution as fatty food simulants. Strips were fully immersed in 10 ml of simulant. Isooctane extracts were evaporated to dryness in a rotary evaporator, redissolved in 10 ml of methanol, while ethanol 95%(v/v) extracts were directly injected into the ultra-performance liquid chromatography (UPLC®). For each film, three independent tests were carried out in order to measure astaxanthin as a result of its migration into food simulants. Astaxanthin migration into the tested fatty food simulants from LDPE films (produced by extrusion with the lipid fraction of the fermented shrimp waste) was not detected ($< 0.054 \mu\text{g ml}^{-1}$).

Methods used to determine the oxidation protection effect of the natural antioxidant-active film

The AO capacity of food is influenced by its composition/ nature, the packaging film type and the atmosphere in the inner inside of the packaging (Bentayeb et al. 2009). The AO properties of the film depend on the AOs incorporated, the thickness of the film and the nominal concentration of the AOs in the film. Although the AO capacity increases with the concentration of the incorporated AOs, this is not linear. Bentayeb et al. (2009) reported that for higher concentrations the slope is smoother, probably due to an interaction between the AOs and the film or a loss of AOs during the manufacturing of the active films.

Radical scavenging capacity 2,2-diphenyl-1-picrylhydrazyl (DPPH•) is the most common test used to evaluate the AO activity of the extracts, essential oils or compounds incorporated into the films (Tables 2 and 3). Thiobarbituric acid reactive substances assay (TBARS) is the most used for the determination of the degree of protection given to the foodstuffs, although other methods are also used (peroxide value, free fatty acids, conjugated dienes and conjugated triene hydroperoxides, *p*-anisidine value and hexanal

analysis). Most of the methods mentioned are global and non-specific, therefore there is no consensus on the best test and it is essential to use several methods in parallel in any study of the AO activity or the lipid oxidation state.

Methods used to quantify natural antioxidants in food matrices or food simulants

Due to its health implications, migration of substances from packaging into foods has been the target of reviews (Lau & Wong 2000; Arvanitoyannis & Bosnea 2004; Sanches-Silva et al. 2006; Arvanitoyannis & Kotsanopoulos 2014) and books (Cooper 2007; Rijk 2007; Veraart & Coulier 2007; Franz & Störmer 2008; Veraart 2010). Some of the papers dedicated to the development of active packaging with natural AOs have carried out migration tests to allow the verification of active compound release from the films in the worst conditions that can be foreseen in its real application. Specific migration tests are done either in food matrices or in food simulants. Depending on the polarity of the migrant, greater migration levels can be achieved in aqueous or fatty foods/food simulants (Table 3). For AO determination and quantification in foods or food simulants, HPLC is the most used technique. Increased shelf life was obtained in most cases by means of controlled AO release.

Consumers' demands and industry trends: biodegradable and edible films

In the design of natural AO active materials systems for food packaging, four types of plastics materials could be used as matrices. The commercially available plastics can be (Mecking 2004; Reddy et al. 2012; Peelman et al. 2013; Reddy et al. 2013): (1) non-bio-based non-biodegradable conventional plastic materials - e.g. polyethylene (PE), polypropylene (PP), poly (ethyleneterephthalate) (PET), and polystyrene (PS); (2) biobased biodegradable plastic materials - e.g. poly(lactic acid) (PLA), poly(hydroxybutyrate) and (PHB), chitosan); (3) bio-based non-biodegradable plastic materials - e.g. the commonly advertised as 'green' PE, PP and PET; and (4) non-bio-based biodegradable plastic materials - e.g. aliphatic-aromatic polyesters and polycaprolactone (PCL).

The last three categories are usually called 'bioplastics' (Reddy et al. 2012, 2013; Peelman et al. 2013), following the European Bioplastics Organisation's definition. Bio-based plastics materials are obtained from renewable resources (e.g. sugarcane bagasse, corn, other natural feedstock). Non-bio-based plastics materials are manufactured from non-renewable resources (oil and natural gas).

Due to environmental motivation there is increasing interest in the use of biodegradable/compostable packaging and/or edible materials. This tendency increases when materials come from industrial waste or renewable resources (Gómez-Guillén et al. 2007). Edible films can be protein-based (casein, collagen, corn zein, gelatin, wheat gluten, whey protein and soy protein), carbohydrate-based (alginate, cellulose, chitosan,

starch), or made from lipids or fruit biomass (Gómez-Estaca et al. 2007; Pruneda et al. 2008).

Gelatin was one of the first materials used in edible films. It is obtained by physical, chemical or biochemical denaturation and hydrolysis of collagen present in bones or skins (Gómez-Guillén et al. 2007; Andevvari & Rezaei 2011). Gelatin is used to improve the elasticity, consistency and stability of food products, but it can also be used as a film to protect foods from drying, light and oxygen. It has good qualities as a material for food contact purposes like transparency, absence of colour and flavour, reversibility at a melting point close to body temperature and easy dissolution (Gómez-Guillén et al. 2007; Song et al. 2012). It is also economic (although the cost is higher than that of plastic films), abundant and it has good functional properties. All these advantages made gelatin one of the first matrices used to release AOs. Gelatin may be used pure or in combination with other biopolymers. Although mammal gelatins (bovine and porcine) are generally used due to their better rheological properties, fish gelatin has the advantage of not transmitting diseases such as spongiform encephalopathy (Gómez-Guillén et al. 2007). Fish gelatine (from tuna) has also been used to prepare transparent edible films with acceptable mechanical and barrier properties to water vapour and ultraviolet (UV) light and with AO capacity due to the addition of natural extracts with a high polyphenol content (Gómez-Guillén et al. 2007).

Soy protein films have poor water barrier properties, although they are good oxygen and lipid barriers. However, to enhance their properties, food additives can be added to edible films. Pruneda et al. (2008) have developed a soy-based edible film with Mexican oregano Table 2. Films with natural antioxidants.

PolymERIC matrix	Source	Antioxidant compounds	Antioxidant activity tests used	Food matrix or food simulants used	Method to determine antioxidant compounds in the packaging	Method to determine the oxidation protection effect of the active film	Migration tests	Determination and quantification of the antioxidants in foods or food simulants	Results	Reference
------------------	--------	-----------------------	---------------------------------	------------------------------------	--	--	-----------------	---	---------	-----------

LD PE		α - toco pher ol or BHT		Sun flow er oil 95% etha nol		Free fatty acid s. Pero xide valu es. P - anisi dine valu e. Ran cim at valu e at 110°C toco pher ol cont ent	Pla stic wa s im me rse d in the foo d sim ula nts an d sto red at 4 an d 20°C for 7 we eks	HPL C quan tifica tion of the antio xida nts for sunfl ower oil and GC/ MS for etha nol simu lant	α - toco pherol is a more stabl e antio xida nt than BHT when incor porat ed in LDP E film	We ssli ng et al. (19 98)
----------	--	--	--	--	--	---	---	--	---	---

LD PE		α - toco pher ol or BHT		Oat meal		Hex anal cont ent by GC/ MS. Vola tile prof ile by elect roni c nose syst em	Fil ms wer e pac ked wit h oat meal and stor ed at 20°C for 10 we eks , 30°C and 40°C for 8 day s	BHT was rapid ly lost from the film at all temp eratu res, wher eas α - toco pherol was retai ned for a longe r perio d of time. The oatmeal store d in the BHT- impr egnate d LDP E film has unde rgone the least chan ge durin g the 8 – 10- week	We ssli ng et al. (20 00)
----------	--	--	--	-------------	--	---	---	---	---

									storage period	
PP	Rosemary extract			Water 10% aqueous ethanol (v/v) 3% aqueous acetic acid (w/v) isoocetane	Aqueous simulants : by SPM E-GC/MS Fatty simulant (isoocetane): by GC/MS after concentration		Plastic wares immersed in the food simulants at 40°C for 10 days		Migration results gave values 20 times lower than the established limits in the worst case. Analytical procedure provides detection limits in the sub μgkg^{-1} range	To var et al. (2005)

PP	Rosemary extract			Pure myoglobin and fresh beef steaks		Redness index (Colour) TBA RS Sensory evaluation of discoloration			The active film containing natural AO efficiently enhanced the stability of both myoglobin and fresh meat against oxidation processes, being a promising way to extend the shelf life of fresh meat	Nerín et al. (2006)
----	------------------	--	--	--------------------------------------	--	---	--	--	---	---------------------

LD PE	α - toco pher ol com plexe d and nonc ompl exed with β cyclo dextr in		Eth anol 95% (v/v)			Pla stic bag s wer e sto red at 7°C for 65 an d 145 day s	HPL C- UV	Migr ation of comp lexed antio xida nt was slow er than migr ation of free antio xida nt. A contr olled relea se of α toco pherol is possi ble	Sir ó et al. (20 06)
----------	---	--	---------------------------------	--	--	---	-----------------	---	----------------------------------

PE	Rosemary extract			Extraction with methanol followed by SPE and UPLC/MS analysis			A new method was developed for the direct determination of carnolic acid into a rosemary based active packaging	Benta et al. (2007)
----	------------------	--	--	---	--	--	---	---------------------

PP	Rosemary extract			Model compounds: L-ascorbic acid; iron (II); fatty acids from flax seed oil		TBA RS ascorbic acid and iron (II) oxidation studies		The new active food packaging has greatly inhibited oxidation reactions and behaved as a scavenger of oxygen radicals	Nerín et al. (2008)
----	------------------	--	--	---	--	--	--	---	---------------------

Table 2. Continued.

Polymeric matrix	Source	Antioxidant compounds	Antioxidant activity tests used	Food matrix or food simulants used	Method to determine antioxidant compounds in the packaging	Method to determine the oxidation protection effect of the active film	Migration tests	Determination and quantification of the antioxidants in foods or food simulants	Results	Reference
------------------	--------	-----------------------	---------------------------------	------------------------------------	--	--	-----------------	---	---------	-----------

<p>Plastic (both protected by European Patent 1477 519-A1)</p>	<p>Oregano rosemary</p>			<p>Fresh lamb</p>		<p>Met myoglobin percentage TBA RS. Instrumental colour (redness). Sensory analysis</p>				<p>The rosemary extract, rosemary film and oregano film resulted in enhanced oxidative stability of lamb steaks. Films with oregano were significantly more efficient, exerting a similar effect to</p>	<p>Camonet al. (2008)</p>
--	-------------------------	--	--	-------------------	--	---	--	--	--	---	---------------------------

									the direct addition of rosemary	
EV OH with natural antioxidants EV OH and <i>m</i> PE with antioxidant compounds	Rosemary, ginger propolis, cinnamonoregano, clove or citronella	Quercetin, catechin, thymol or ferulic acid			Antioxidant capacity (with respect to hydroxyl radicals) is indirectly assessed by HPLC-FL determination of the 2,5-dihydroxybenzoic acid formed				Polymers with clove and oreganowerethe most efficient ones	Pezo et al. (2008)

PP	Clove, organo, cinnamon, rosemary or ginger essential oils		ORAC adapted to a liquid chromatographic device						The most powerful antioxidant films are those made with 8% of cinnamon. This study indicates that it is possible to manufacture films with a lesser quantity of essential oils by raising film	Bentayeb et al. (2009)
----	--	--	---	--	--	--	--	--	--	------------------------

									thickness	
LDP E		α -tocopherol		Corn oil		Hexanal analysis (SPME and GC)	Bags containing the oil were replaced in racks and stored for 12 weeks at 5,	HPLC	LDP E films containing α tocopherol increased the shelf life of the oil in 4 weeks by maintaining oxidative stability for longer periods	Graciano-Verdugo et al. (2010)

<p>HD PE with BH A or α tocopherol EV OH /LD PE with BH T HD PE/ EV OH /LD PE with BH A and α tocopherol</p>		<p>BH A, BH T, α-tocopherol</p>		<p>Whole milk powder</p>	<p>For plastics: extraction with acetonitrile and HPLC-FL analysis. For milk: extraction with methanol and HPLC analysis</p>	<p>Monitoring of vitamin A. Hexanal, pentanal and heptanal content</p>	<p>20 and 30°C Migration test during 30 days at 30°C</p>	<p>The active films have transferred the antioxidants to the whole milk powder. α-tocopherol showed a more gradual release compared with BH T and BH A</p>	<p>Granda-Resepo, Peralta, et al. (2009)</p>
--	--	---	--	--------------------------	--	--	--	--	--

<p>Multilayer active packaging of EV OH and LDP E</p>		<p>α-tocopherol</p>		<p>Whole milk powder</p>			<p>Pouches filled with whole milk powder were stored for 90 days at 20°C and for 60 days at 30 and 40°C</p>	<p>RP-HPLC (quantification in the film and food simulant)</p>	<p>The migration of α-tocopherol was not greatly affected by storage temperature from 20 to 40°C. This demonstrates that the antioxidant can protect whole milk powder in warm/hot climate</p>	<p>Granda-Respero, Soto-Valdez, et al. (2009)</p>
---	--	---------------------------------------	--	--------------------------	--	--	---	---	--	---

Table 2. Continued.

Polym eric ma trix	So urc e	Anti oxid ant com pou nds	Anti oxid ant acti vity test s use d	Fo od ma trix or foo d sim ula nts use d	Met hod to deter mine anti oxid ant com pou nds in the pac kagi ng	Meth od to deter mine the oxida tion prote ction effect of the active film	Mig rati on test s	Deter mina tion and quan tifica tion of the antio xidants in foods or food simul ants	Resu lts	Ref ere nce
-----------------------------	----------------	--	--	---	---	--	--------------------------------	--	-------------	-------------------

HD PE		Carv acro l		Oli ve oil. Dis till ed wat er			She ets wer e im mer sed in the sim ula nts and inc uba ted at 25 or 40°C for 30 day s. Ext ract s of sim ula nts wer e tak en at 2,5,10 , 20 and 30 day s	GC/ MS (qua ntific ation in olive oil). HPL C-UV (qua ntific ation in water)	Carv acrol migr ated in both simu lants but the amo unt that migr ated to olive oil was high er. This com poun d coul d be used as an addit ive for activ e pack aging	Pel tze r et al. (20 09)
----------	--	-------------------	--	--	--	--	---	---	--	---

PP		Caffeic acid	DP PH• ABT S•+. Inhibition of linoleic acid oxidation and β -carotene	Orange juice	Folin-Ciocalteu			The film showed a good protective activity against oxidation of orange juice, demonstrating a possible application as food packaging	Arrua et al. (2010)
----	--	--------------	---	--------------	-----------------	--	--	--	---------------------

LL DP E		α - toco pher ol (free or com plex ed with β cycl odex trin) or quer cetin (free or com plex ed with γ cycl odex trin)		Co con ut oil. Eth an ol 95 % (v/ v)	HP LC- DA D	Perox ide value	LL DP E film s wer e sub mer ged in coc onu t oil or in eth ano l 95 % in test cell s, plac ed in an inc uba tor sha ker at 30°C and 100 rpm for 0, 1, 3, 7, 14, 21 and 28 day s	HPL C- DAD (dete rmin ation in coco nut oil)	Incre asing the mole cular weig ht of α - toco pher ol and quer cetin by cycl odex trin in com plexa tion can great ly redu ce its diffu sion coeffi cient in LLD PE, allow ing a contr olled relea se of the antio xida nts	Ko ont z et al. (20 10)
---------------	--	--	--	--	----------------------	-----------------------	---	---	--	--

LD PE	Barley husks			Atlantic salmon (Salmon oil L.)		Peroxide value. Free fatty acids. TBARS. Conjugated diene s and triene hydro perox ides, Totox and <i>p</i> - anisidine value s				The antioxidants from barley husks have been shown to be effective in slowing lipid hydrolysis and increasing oxidative stability of salmon	Per eira de A br eu et al. (20 10)
----------	-----------------	--	--	---	--	---	--	--	--	---	---

PP	Oregano extract			Fresh beef steaks		Metmyoglobin percentage . TBARS. Instrumental colour (redness). Sensory analysis			Active packaging significantly enhanced the oxidative stability of beef steaks, depending on the oregano concentration of the active film. The most suitable oregano extract concentration is in the range of 1 – 2%	Camonet al. (2011)
----	-----------------	--	--	-------------------	--	--	--	--	--	--------------------

LD PE	Rose mary extract	Carn osic acid		Chi cke n me at (mi nce d chi cke n bre ast)		TBAR S. ESR (anal ysis of radic al forma tion)		Lipid oxida tion was restr aine d at the surfa ce of the activ e pack aging and the oxida tion indu ced by high- press ure proc essin g was delay ed. Shelf life was exten ded	Bol um ar et al. (20 11)
----------	-------------------------	----------------------	--	--	--	---	--	--	--

Table 2. Continued.

Polymeric matrix	Source	Antioxidant compounds	Antioxidant activity tests used	Food matrix or food simulants used	Method to determine antioxidant compounds in the packaging	Method to determine the oxidation protection effect of the active film	Migration tests	Determination and quantification of the antioxidants in foods or food simulants	Results	Reference
------------------	--------	-----------------------	---------------------------------	------------------------------------	--	--	-----------------	---	---------	-----------

LD PE	B a r l e y h u s k s			Atla n t i c h a l i b u t (H i p p o g l o s s u s h i p p o g l o s s u s)		P e r o x i d e v a l u e. F r e e f a t t y a c i d s. T B A R S . C o n j u g a t e d d i e n e s a n d t 		T h e a n t i o x i d a n t s f r o m b a r l e y h u s k s h a v e b e e n s h o w n t o b e e f f e c t i v e i n s l o w i n g l i p i d h y d r o l y s i s a n d i n c r e a s i n g o x i d a t i v e s t a b i l i t y o f h a l i b u t	P e r e i r a d e A b r e u e t a l. (20 11a)
----------	---	--	--	---	--	---	--	--	--

EV OH	G r e e n t e a e x t r a c t	Q u e r c e t i n. A s c o r b i c a c i d . F e r u l i c a c i d	D P P H. •	W a t e r. E t h a n o l 10%(v, v). E t h a n o l 95% (v/v) . B r i n e d s a r d i n e s		P e r o x i d e v a l u e. T B A R S	E V O H f i l m s w e r e i m m e r s e d i n t h e t h r e d i f f e r e n t s i m u l a n t s a t 37°C , f o r 30 d a y s	U V- V i s s p e c t r o s c o p y	T h e r e l e a s e o f a s c o r b i c a n d f e r u l i c w a s h i g h e r i n a q u e o u s s i m u l a n t s a n d t h e r e l e a s e o f q u e r c e t i n a n d g r e e n t e a e x t r a c t w a s h i g h e r i n e t h a n o l i c s i m u l a n t. T h e f i l m w i t h g r e e n t e a e x t r a c t w a s t h e m o s t e f f e c t i v e	L ó p e z - d e- D i C a s t i l l o, G ó m e z- E
----------	---	--	------------------------	--	--	---	--	--	---	---

EV OH		Catechin. Quercetin	DP PH•	Water. Ethanol 10%(v/v). Ethanol 95% (v/v) · Isooctane. Fried peanuts		Peroxide value. Hexanal analysis (GC/MS). HPLCFL determination of the 2,5dihydroxybenzoic acid formed		Both bioactive antioxidants were extracted by ethanol. In aqueous and alcoholic food simulants their release was greater in the case of the catechin containing samples	López - de- Castillo, Pérez, et al. (2012)
----------	--	------------------------	-----------	--	--	---	--	---	--

LD PE /P P		α - toco pherol. β - toco pherol. γ - toco pherol. δ - toco pherol	95% etha nol (v/v) . Linol eic acid	Conjug ated dienes (deter mined by UV spectro scopy in linoleic acid simula nt)	The fil m wa s im me rse d in eth an ol 95 % at 40°C , an d in lin olei c aci d un der rot ary sha kin g an d at 40°C	HPL C- DAD (for both simu lants)	Toco pher ol relea se was slow er in LDP E/P P blen d films , corre spon ding to lowe r toco pher ol diffu sivit y and bette r antio xida nt effec tiven ess	Zh u et al. (20 12)
---------------------	--	--	--	---	---	--	--	---------------------------------

Note: ABTS•+, 2,2'-azino-bis (3-ethylbenzothiazoline); AO, antioxidant; BHA, butylated hydroxyanisole; BHT, butylated hydroxytoluene; DPPH•, 2,2-diphenyl-1-picrylhydrazyl; ESR, electron spin resonance spectroscopy; EVOH, ethylene-vinyl alcohol copolymer; HDPE, high-density polyethylene; HPLC-DAD, high-performance liquid chromatography coupled to diode array detector; HPLC-Fl, high-performance liquid chromatography coupled to fluorescence detector LDPE, low-density polyethylene; LLDPE, linear low-density polyethylene; m-PE, metallocene polyethylene; ORAC, oxygen radical absorption capacity assay; PE, polyethylene; PP, polypropylene; PET, polyethylene terephthalate; RP-HPLC, reverse phase high-performance liquid chromatography; SPE, solid-phase extraction; SPME, solid-phase microextraction; and TBARS, thiobarbituric acid reactive substances assay.

Table 3. Biodegradable and/or edible films.

Type of polymer	Polymeric matrix	Source of AO or AO added directly	Food matrix or food simulants used	Methods to determine the antioxidant activity of the active films	Method to determine specific antioxidant compounds	Method to determine the oxidation protection effect of the active film in food or food simulants	Results	Other properties of the active film besides antioxidant activity	Reference
-----------------	------------------	-----------------------------------	------------------------------------	---	--	--	---------	--	-----------

Coating polymer	EVA	Nisin and/or α -tocopherol	Milk cream. Model emulsion (66% water, 32% paraffin oil with 2% emulsifier)			TBARS	Nisin incorporation conferred antimicrobial properties and α -tocopherol incorporation retarded lipid oxidation. The combined inclusion could provide both functions	Antimicrobial activity	Lee et al. (2004)
-----------------	-----	-----------------------------------	---	--	--	-------	---	------------------------	-------------------

Edible film	Milk protein-based films	Essential oils: oregano and /or pimento	Beef	Folin-Ciocalteu (total phenolic content) DPD colorimetric method	TBARS	Oregano-based films stabilized lipid oxidation and pimento-based films demonstrated the highest antioxidant activity	Antimicrobial activity	Oussalah et al. (2004)
-------------	--------------------------	---	------	--	-------	--	------------------------	------------------------

Edible film	Tuna-fish gelatin	Murta extracts (Ugnimoli nae Turcz). Two ecotypes: SG and SC		DPPH • SDS-linoleic acid FRAP. Folin Ciocalteu (this method was applied just to aqueous extracts of murta leaves)		Films containing murta extracts had the antioxidant capacity increased five-fold. Films containing SC had higher antioxidant capacity, but the mechanical properties decreased due to a higher content of polyphenols		Gómez Guillén et al. (2007)
-------------	-------------------	--	--	---	--	---	--	-----------------------------

Edible film	Gelatin-based film with plant extracts or chitosan	Rosemary and oregano extracts	Smoked sardine (Sardinia pilchardus)			Peroxide index. Free fatty acids. TBA. RS. Total phenols. FRA. P. TVB-N	The active edible films decreased lipid oxidation levels and increased the phenol content of the muscle	Antimicrobial activity (gelatin-chitosan based films)	Gómez-Estaca et al. (2007)
-------------	--	-------------------------------	--------------------------------------	--	--	---	---	---	----------------------------

Table 3. Continued.

Type of polymer	Polymeric matrix	Source of AO or AO added directly	Food matrix or food simulants used	Methods to determine the antioxidant activity of the active films	Method to determine specific antioxidant compounds	Method to determine the oxidation protection effect of the active film in food or food simulants	Results	Other properties of the active film besides antioxidant activity	Reference
-----------------	------------------	-----------------------------------	------------------------------------	---	--	--	---------	--	-----------

Edible film	Fish skin-based gelatin	α -tocopherol or BHT	Lard	DPPH •		TBARS. Peroxide value	Antioxidative activity of fish skin gelatin films incorporated with α -tocopherol increased with increasing storage time. Films with α -tocopherol demonstrated a preventive effect on lard oxidation	Jongjareonrak et al. (2008)
-------------	-------------------------	-----------------------------	------	--------	--	-----------------------	---	-----------------------------

Edible film	Chitosan Carboxymethyl cellulose Casein	Olive, rosemary, onion, capicum, cranberry, garlic, oreganum and oreganum + carvacrol 5%	Butternut squash (Cucurbita moschata). Roman lettuce (Lactuca sativa L.). Butter lettuce (Lactuca sativa)	Peroxidase activity. Polyphenoloxidase activity		Chitosan enriched with rosemary and olive improved the antioxidant protection of minimally processed squash, showing the possibility of preventing oxidation in fruit and vegetables		Ponce et al. (2008)
Edible film	Plasticized soy protein isolates films	Mexican oregano (Lippia graveolens)		DPPH · Electrochemical generation of H ₂ O ₂		The oregano SPI films exhibited antioxidant properties in a concentration dependent fashion		Pruneda et al. (2008)

Edible films	Tuna-skin gelatine. Bovine-hide gelatin	Oregano or rosemary extracts		Folin-Ciocalteu. FRAP. ABTS	HPLC-DAD (identification of polyphenols in extracts of rosemary and oregano)		The antioxidant capacity of both gelatins can be increased by adding oregano and rosemary polyphenol-rich extracts		Gómez-Estaca et al. (2009)
--------------	---	------------------------------	--	-----------------------------	--	--	--	--	----------------------------

Table 3. Continued.

Type of polymer	Polymeric matrix	Source of AO or AO added directly	Food matrix or food simulants used	Methods to determine the antioxidant activity of the active films	Method to determine specific antioxidant compounds	Method to determine the oxidation protection effect of the active film in food or food simulants	Results	Other properties of the active film besides antioxidant activity	Reference
-----------------	------------------	-----------------------------------	------------------------------------	---	--	--	---------	--	-----------

<p>Synthetic biodegradable plastic</p>	<p>Cellulose acetate films with different concentrations of the polymer</p>	<p>L-ascorbic acid or L-tyrosine</p>	<p>Water</p>	<p>ABTS •+ (film samples contacted with ABTS •+ free radical solution for the determination of immobilised antioxidant activity)</p>		<p>ABTS •+ (film samples contacted with water simulant before the assay)</p>	<p>L-tyrosine-containing films demonstrated greater immobilised antioxidant activity than L-ascorbic active films and L-tyrosine released to water in a slower rate. The antioxidants conferred different morphological and mechanical properties to the</p>		<p>Gemili et al. (2010)</p>
--	---	--------------------------------------	--------------	--	--	--	--	--	-----------------------------

							films and the variation of the structural characteristics of the films allowed a controlled release of the antioxidants		
Edible film	Chitosan coating with or without cinnamon oil	Cinnamon essential oil	Rainbow trout (Oncorhynchus mykiss)			Peroxide value. TVB-N. TBARS	Chitosan incorporated with cinnamon oil prolonged the shelf life of trout	Antimicrobial activity	Ojagh et al. (2010)

Edible films	Chitosan	Indian gooseberry extract		Folin - Ciocalteu β -carotene bleaching method		The release characteristics, swelling and functional group interaction of the antioxidant films, as assessed by FTIR spectroscopy, were found to be affected by the drying methods and conditions, as well as the concentration of the extract	Antimicrobial activity	Mayachew and Devasthina (2010)
--------------	----------	---------------------------	--	--	--	--	------------------------	--------------------------------

Edible film	Chitosan	Green tea extract		DPPH • Folin Ciocalteu		Antioxidant activity was 15-fold higher in chitosan films containing green tea extract than chitosan control films	Siripatrawan and Hartono (2010)
-------------	----------	-------------------	--	------------------------	--	--	---------------------------------

Table 3. Continued.

Type of polymer	Polymeric matrix	Source of AO or AO added directly	Food matrix or food simulants used	Methods to determine the antioxidant activity of the active films	Method to determine specific antioxidant compounds	Method to determine the oxidation protection effect of the active film in food or food simulants	Results	Other properties of the active film besides antioxidant activity	Reference
-----------------	------------------	-----------------------------------	------------------------------------	---	--	--	---------	--	-----------

Edible film	Chitosan	Rosemary extract	Fresh-cut peaches			Polyphenol oxidase activity analysis. Folin Ciocalteu	A combination of pure oxygen pretreatment and chitosan coating incorporated with rosemary extracts may be a potential method to maintain cut-fruit quality and diminish browning, softening and decay		Xiao et al. (2010)
-------------	----------	------------------	-------------------	--	--	---	---	--	--------------------

Edible films	Chitosan HP MC	Bergamot essential oil	Muscatel table grapes			DPPH, Folin Ciocalteu	The most recommended coating for Muscatel table grape is the chitosan containing bergamot oil since, despite only contributing slightly to the sample colour, it showed the highest antimicrobial activity and the greatest control of the respiration rates, with a	Antimicrobial activity	Sánchez González et al. (2011)
--------------	----------------	------------------------	-----------------------	--	--	-----------------------	--	------------------------	--------------------------------

							reasonably good control of water loss during storage		
Edible film	Gelatin-based film	Cinnamon essential oil	Rainbow trout			TVB-N. TBAR S. Free fatty acids. Sensory evaluation	Cinnamon-encrusted coating can prolong trout shelf life through lipid oxidation inhibition	Antimicrobial activity	Andevari and Rezaei (2011)
Edible film	Fish-skin gelatin film	Lemongrass essential oil	Sea bass slices (Lates calcarifer)			TVB-N. TBAR S	The active film retarded lipid oxidation at 4°C in sea bass and could be used as an active packaging	Antimicrobial activity	Ahmad et al. (2012)

Table 3. Continued.

Type of polymer	Polymeric matrix	Source of AO or AO added directly	Food matrix or food simulants used	Methods to determine the antioxidant activity of the active films	Method to determine specific antioxidant compounds	Method to determine the oxidation protection effect of the active film in food or food simulants	Results	Other properties of the active film besides antioxidant activity	Reference
Composite of biodegradable biopolymer (chitosan) and synthetic biodegradable polymer (PVA)	Chitosan and PVA	Mint extract, pomegranate peel extract		DPPH · Folin Ciocalteu			The addition of natural extracts to bioactive biopolymers has great potential for being developed into functional packaging material	Antimicrobial activity	Kana et al. (2012)

Edible film	Chitosan	Zataria multiflora Boiss essential oil (ZEO). Grape seed extract (GSE)		DPPH-reducing power assay . Folin Ciocalteu			Chitosan incorporated with ZEO or with GSE are good antioxidant films		Moradi et al. (2012)
-------------	----------	--	--	---	--	--	---	--	----------------------

Biopolymer	Cellulose	Green tea extract, clove, cinnamon, thyme and ginger oils	Soybean oil	β -carotene-linoleate bleaching broth method DPPH-		Peroxide value. Free fatty acids	Cellulose films either containing cinnamon oil, clove oil or green tea extract demonstrated a possible application in active packaging as antioxidant film	Phoopuritam et al. (2012)
------------	-----------	---	-------------	--	--	----------------------------------	--	---------------------------

Edible films	Chitosan	Green tea extract	Pork sausages		HPLC-PDA (determination of polyphenolic compounds in the green tea aqueous extract)	TBARS. Colour and texture measurements. Sensory evaluation	Chitosan film incorporating green tea extract retards lipid oxidation and microbial growth, prolonging the shelf life of sausages	Antimicrobial activity	Siripatrawan and Noipha (2012)
--------------	----------	-------------------	---------------	--	---	--	---	------------------------	--------------------------------

Table 3. Continued.

Type of polymer	Polymeric matrix	Source of AO or AO added directly	Food matrix or food simulants used	Methods to determine the antioxidant activity of the active films	Method to determine specific antioxidant compounds	Method to determine the oxidation protection effect of the active film in food or food simulants	Results	Other properties of the active film besides antioxidant activity	Reference
-----------------	------------------	-----------------------------------	------------------------------------	---	--	--	---------	--	-----------

Composite edible film	Barley bran proteoglycan (BBG)	Grape seed extract (GSE)	Salmon			TBA RS. Peroxide value	Packaging with the BBG GSE film resulted in a lower peroxide value and TBA RS during storage. The composite film is effective in protecting salmon from lipid oxidation	Antimicrobial activity	Song et al. (2012)
-----------------------	--------------------------------	--------------------------	--------	--	--	------------------------------	---	------------------------	--------------------

Biodegradable composite	<i>k</i> -carrageenan composite film	Satureja hortensis essential oil	Folin-Ciocalteu . DPPH•	Antioxidant effect was greatly improved when the proportion of added <i>S. hortensis</i> essential oil was 3%	Antimicrobial activity	ShojaeAliabadi et al. (2013)
-------------------------	--------------------------------------	----------------------------------	-------------------------	---	------------------------	------------------------------

Note: ABTS•+, 2,2'-azino-bis (3-ethylbenzothiazoline); AO, antioxidant; BBG, barley bran protein-gelatin; BHT, butylated hydroxytoluene; DPD, *N, N*-diethyl- *p*-phenylenediamine colorimetric method; DPPH•, 2,2-diphenyl-1-picrylhydrazyl; EVA, ethylene-vinyl acetate copolymer; FRAP, ferric-reducing ability of plasma assay; FTIR, Fourier transform infrared spectroscopy; GSE, grape seed extract; HPLC-DAD, high-performance liquid chromatography coupled to diode array detection; HPLC-PDA, high-performance liquid chromatography coupled to photodiode array detection; HPMC, hydro-xypropylmethyl-cellulose; PVA, polyvinyl alcohol; SC, Soloyo Chico; SDS, sodium dodecyl sulphate; SG, Soloyo Grande; SPI, soy protein isolate; TBARS, thiobarbituric acid reactive substances assay; TVB-N, total volatile base nitrogen; and ZEO, *Zataria multiflora* Boiss essential oil. (*Lippia graveolens*) which demonstrated good AO properties.

Chitosan (poly- β -(1-4)-D-glucosamine), a deacetylated product of chitin, is a biopolymer with a wide range of applications. Due to it being biodegradable, compostable and non-ecotoxic, it possesses excellent potential for use in biodegradable active packaging (Mayachiew & Devahastin 2010; Lago et al. 2011). Chitosan has antimicrobial activity due to its effectiveness at inhibiting the growth of Gram-positive and Gram-negative bacteria, yeasts and moulds (Siripatrawan & Harte 2010).

Sanches-Silva et al. (2012) have prepared chitosan from shrimp by-products. The fraction rich in chitin obtained after fermentation of shrimp products was depigmented (using a mixture of petroleum ether-acetone-water), deproteinised (with proteolytic enzymes), demineralised (with HCl), blanched (with sodium hypochlorite), and dried (in an oven at 105°C). Afterwards, chitin was converted into chitosan by deacetylation with NaOH and dried. The chitosan was washed with water until reaching a pH close to neutral after each treatment and, finally, particle size was reduced with a hammer mill.

Chitosan films were prepared at different concentrations (1%, 2% and 3%w/w) by casting by dissolving chitosan in acetic acid aqueous solution 1%(w/v), with (1%, w/w) or without glycerol. Subsequently, the solutions were kept under stirring until complete dilution and poured onto flat plates. Finally, they were dried in an oven at 40°C for 12 h in order to allow solvent evaporation.

With respect to monolayer films carried out by extrusion, chitosan (with two different particle sizes, 180 and 300 μ m) at different concentrations (2%(w/w),5%(w/w),6%(w/w), 8%(w/w) and 10%(w/w)), was mixed with polyamide 6 (PA 6) to obtain blends pellets. Subsequently, these were processed in an extruder with a specific screw for PA 6. Thus different plastic films of the blends were obtained.

Specific migration tests of chitosan were carried out in all films by full immersion of 6 cm² plastic film in 10 ml of food simulant. Two food simulants were used: distilled water and ethanol 95%(v/v) in aqueous solution. Migration tests were carried out at 40°C during 10 days. Subsequently, the food simulant was allowed to cool at RT and then evaporated in a rotary evaporator. The residue was then hydrolysed with 20 ml of HCl(8M) and derivatised with 9-fluorenylmethyl chloroformate. For each film, three independent chromatographic analyses (using an ultra-performance liquid chromatograph, LOQ of glucosamine hydrochloride = 10 μ gml⁻¹) were carried out. Although chitosan is not permitted in the manufacture of plastic FCMs, specific migration tests of glucosamine (which indirectly measure the migration of chitosan because chitosan is formed by glucosamine units) were carried out. No specific migration of glucosamine was quantified for all films except for casting films with 1%, 2% and 3%(w/w) of chitosan without glycerol. Therefore, it was concluded that the addition of a plasticiser (glycerol) was effective at avoiding the migration of glucosamine from the casting films to ultrapure water. The specific migration levels of glucosamine from the casting films increased with the amount of chitosan added. The glucosamine migration levels found in the films prepared by casting without glycerol exceeded the overall limit of migration (10mgdm⁻²), indicating that they could not be used in contact with aqueous foodstuffs, when the chitosan is added to the packaging with the aim of exhibiting a function in the packaging. However, if the chitosan was permitted in active food packaging materials, its migration could be desired and the SML permitted could be higher. In order to check if the other films (films prepared by extrusion and film prepared by casting with glycerol) could be used as food packaging, other SM tests should be used. For instance, the specific migration of ϵ -caprolactam in the case of films prepared by extrusion or glycerol in the cases of casting films prepared with this plasticiser. Although it has also been reported to have some AO activity, the addition of AOs to chitosan has been tested in order to obtain films with both actions (Table 3). For instance Ojagh et al. (2010) have incorporated cinnamon oil (*Cinnamomum zeylanicum* L.) into chitosan films and they were able to inhibit successfully the lipid oxidation and microbial growth of refrigerated rainbow trout fillet. Abdollahi et al. (2012) incorporated nanoclay and rosemary essential oil into chitosan film. The nanoclay (montmorillonite) was added with the aim of improving the water vapour barrier and mechanical properties (tensile strength and elongation) of the film.

One of the categories of foods for which edible films have received more attention is perishable food like freshcut fruits. Edible films can enhance their limited shelf life because they reduce their loss of firmness and the cutsurface browning of fresh-cut fruits (Xiao et al. 2010).

Conclusions

Nowadays, it is possible to reduce food oxidation without adding AOs to the food. An extensive bibliographic review on food packaging with incorporated natural AOs was carried out. Special attention was given to the natural AOs incorporated in active food packaging, and in the activity tests carried out in both packaging and packed foods to evaluate the efficiency of these new materials.

Recently, besides the great improvement in food packaging materials in order to increase food shelf life with the addition of natural AOs, the tendency is to incorporate these compounds in biodegradable/compostable packaging or edible films (used as coatings on foodstuffs) to decrease the impact of packaging in the environment because of their biodegradability and also to reduce food loss, which, in turn, impacts less on the environment (sustainability). Newer materials are emerging day by day and it is essential to study their properties, as well as their safety and effectiveness, in order to evaluate which food products are more suitable to be packed by each material.

Funding

Tânia Albuquerque is grateful for a research grant [grant number BRJ/DAN-2012] funded by the National Institute of Health Dr Ricardo Jorge, I.P. This work was supported by Project Number PTDC/AGR-TEC/3366/2012 with the acronym Rose4Pack (Biodegradable active packaging with rosemary extract (*Rosmarinus officinalis* L.) to improve food shelf life) and funded by the Foundation for Science and Technology (FCT) and COMPETE Programme [grant number FCOMP-01-0124-FEDER-028015].

References

- Abdollahi M, Rezaei M, Farzi G. 2012. A novel active bionanocomposite film incorporating rosemary essential oil and nanoclay into chitosan. *J Food Eng.* 111:343-350.
- Ahmad M, Benjakul S, Sumpavapol P, Nirmal NP. 2012. Quality changes of sea bass slices wrapped with gelatin film incorporated with lemongrass essential oil. *Int J Food Microbiol.* 155:171-178.
- Al-Malaika S, Suharty N. 1995. Reactive processing of polymers: mechanisms of grafting reactions of functional antioxidants polyolefins in the presence of a coagent. *Polymer Degrad Stabil.* 49:77-89.
- Almenar E, Del Valle V, Catalá RN, Gavara R. 2007. Active package for wild strawberry fruit (*Fragaria vesca* L.). *J Agric Food Chem.* 55:2240-2245.
- Andevari GT, Rezaei M. 2011. Effect of gelatin coating incorporated with cinnamon oil on the quality of fresh rainbow trout in cold storage. *Int J Food Sci Technol.* 46:2305-2311.
- Appendini P, Hotchkiss JH. 2002. Review of antimicrobial food packaging. *Innov Food Sci Emerg.* 3:113-126.
- Arrua D, Strumia MC, Nazareno MA. 2010. Immobilization of caffeic acid on a polypropylene film: synthesis and antioxidant properties. *J Agric Food Chem.* 58:9228-9234.
- Arvanitoyannis IS, Bosnea L. 2004. Migration of substances from food packaging materials in foods. *Crit Rev Food Sci.* 44:63-76.
- Arvanitoyannis IS, Kotsanopoulos KV. 2014. Migration phenomenon in food packaging. Food-package interactions, mechanisms, types of migrants, testing and relative legisla-

tion-a review. Food Bioprocess Technol. 7:21-36.
Astray G, Gonzalez-Barreiro C, Mejuto JC, Rial-Otero R, SimalGandara J. 2009. A review on the use of cyclodextrins in foods. Food Hydrocolloid. 23:1631-1640.
Bentayeb K, Rubio C, Batlle R, Nerín C. 2007. Direct determination of carnosic acid in a new active packaging based on natural extract of rosemary. Anal Bioanal Chem. 389:1989-1996.

Bentayeb K, Vera P, Rubio C, Nerin C. 2009. Adaptation of the ORAC assay to the common laboratory equipment and subsequent application to antioxidant plastic films. Anal Bioanal Chem. 394:903-910.
Bolumar T, Andersen ML, Orlien V. 2011. Antioxidant active packaging for chicken meat processed by high pressure treatment. Food Chem. 129:1406-1412.

Camo J, Beltrán JA, Roncalés P. 2008. Extension of the display life of lamb with an antioxidant active packaging. Meat Sci. 80:1086-1091.
Camo J, Lorés A, Djenane D, Beltrán JA, Roncalés P. 2011. Display life of beef packaged with an antioxidant active film as a function of the concentration of oregano extract. Meat Sci. 88:174-178.

Chen C, Pearson AM, Gray JI. 1992. Effects of synthetic antioxidants (BHA, BHT and PG) on the mutagenicity of IQ-like compounds. Food Chem. 43:177-183.

Colon M, Nerin C. 2012. Role of catechins in the antioxidant capacity of an active film containing green tea, green coffee, and grapefruit extracts. J Agric Food Chem. 60:9842-9849.

Contini C, Katsikogianni MG, O'Neill FT, O'Sullivan M, Dowling DP, Monahan FJ. 2012. PET trays coated with citrus extract exhibit antioxidant activity with cooked turkey meat. LWT - Food Sci Technol. 47:471-477.

Cooper I. 2007. Plastics and chemical migration into food.. In: Barnes KA, Sinclair CR, Watson DH. Chemical migration and food contact materials. Cambridge: CRC Press - Woodhead Publishing Limited; p. 228-250.

Curcio M, Puoci F, Iemma F, Parisi OI, Cirillo G, Spizzirri UG, Picci N. 2009. Covalent insertion of antioxidant molecules on Chitosan by a free radical grafting procedure. J Agric Food Chem. 57:5933-5938.

Dainelli D, Gontard N, Spyropoulos D, Zondervan-van den BE, Tobbäck P. 2008. Active and intelligent food packaging: legal aspects and safety concerns. Trends Food Sci Tech. 19:S103-S112.

European Commission. 2002. EU directive 2002/72/EC relating to plastics materials and articles intended to come into contact with foodstuffs. Off J Eur Comm L. 220:18-55.

European Commission. 2004. Regulation (EC) No. 1935/2004 of the European Parliament and of the Council of 27 October 2004, on materials and articles intended to come into contact with food and repealing Directives 80/509/EEC and 89/109/EEC. European Commission. Off J Eur Comm L. 338:4-17.

European Commission. 2006. Directive 2006/52/EC of the European Parliament and of the Council of 5 July 2006 amending Directive 95/2/EC on food additives other than colours and sweeteners and Directive 94/35/EC on sweeteners for use in foodstuffs. Off J Eur Comm L. 204:10-22.

European Commission. 2006. Commission Regulation (EC) No. 2023/2006 on good manufacturing practice for materials and articles intended to come into contact with food. Off J Eur Union. L. 384:75-78.

European Commission. 2009. Commission Regulation (EC) No. 450/2009 on active and intelligent materials and articles intended to come into contact with food. Off J Eur Comm L. 135:3-11.

European Commission. 2011. Commission Regulation (EU) No. 10/ 2011 of 14 January

2011 on plastic materials and articles intended to come into contact with food. Off J Eur Comm L. 12:1-89.

FDA. Code of Federal Regulations. 2013. Title 21: Food and Drugs. Chapter I - Food and Drug Administration, Department of Health and Human Services, Part 182 Substances generally recognized as safe [Internet]. Subpart D. Chemical Preservatives. 182.3890. Office of the Federal Register: Washington, DC; [cited 2013 Nov 21]. Available from: www.fda.gov

Franz R, Störmer A. 2008. Migration of plastic constituents. In: Piringer OG, Paner AL, editors. *Plastics packaging interactions with food and pharmaceuticals*. 2nd edition. Weinheim: Wiley - VCH Verlag GmbH & Co. KGaA; p. 349-415.

Gemili S, Yemenicioğlu A, Altinkaya SA. 2010. Development of antioxidant food packaging materials with controlled release properties. *J Food Eng.* 96:325-332.

Gómez-Estaca J, Bravo L, Gómez-Guillén MC, Alemán A, Montero P. 2009. Antioxidant properties of tuna-skin and bovine-hide gelatin films induced by the addition of oregano and rosemary extracts. *Food Chem.* 112:18-25.

Gómez-Estaca J, López-de-Dicastillo C, Hernandez-Muñoz P, Catalá R, Gavara R. 2014. Advances in antioxidant active food packaging. *Trends Food Sci Tech.* 35:42-51.

Gómez-Estaca J, Montero P, Gimenez B, Gómez-Guillén MC. 2007. Effect of functional edible films and high pressure processing on microbial and oxidative spoilage in coldsmoked sardine (*Sardina pilchardus*). *Food Chem.* 105:511-520.

Gómez-Guillén MC, Ihl M, Bifani V, Silva A, Montero P. 2007. Edible films made from tuna-fish gelatin with antioxidant extracts of two different murta ecotypes leaves (*Ugni molinae* Turcz). *Food Hydrocolloid.* 21:1133-1143.

Graciano-Verdugo AZ, Soto-Valdez H, Peralta E, Cruz-Zárata P, Islas-Rubio AR, Sánchez-Valdes S, Sánchez-Escalante A, González-Mendéz N, González-Ríos H. 2010. Migration of α -tocopherol from LDPE films to corn oil and its effect on the oxidative stability. *Food Res Int.* 43:1073-1078.

Granda-Restrepo DM, Peralta E, Troncoso-Rojas R, Soto-Valdez H. 2009. Release of antioxidants from co-extruded active packaging developed for whole milk powder. *Int Dairy J.* 19:481-488.

Granda-Restrepo DM, Soto-Valdez H, Peralta E, Troncoso-Rojas R, Vallejo-Córdoba B, Gámez-Meza N, Graciano-Verdugo AZ. 2009. Migration of α -tocopherol from an active multilayer film into whole milk powder. *Food Res Int.* 42:1396-1402.

Imaida K, Fukushima S, Shirai T, Ohtani M, Nakanishi K, Ito N. 1983. Promoting activities of butylated hydroxyanisole and butylated hydroxytoluene on 2-stage urinary bladder carcinogenesis and inhibition of gamma-glutamyl transpeptidase-positive foci development in the liver of rats. *Carcinogenesis.* 4:895-899.

Jongjareonrak A, Benjakul S, Visessanguan W, Tanaka M. 2008. Antioxidative activity and properties of fish skin gelatin films incorporated with BHT and α -tocopherol. *Food Hydrocolloid.* 22:449-458.

Kanatt SR, Rao MS, Chawla SP, Sharma A. 2012. Active chit-osan-polyvinyl alcohol films with natural extracts. *Food Hydrocolloid.* 29:290-297.

Koontz JL, Moffitt RD, Marcy JE, O'Keefe SF, Duncan SE, Long TE. 2010. Controlled release of α -tocopherol, quercetin, and their cyclodextrin inclusion complexes from linear low-density polyethylene (LLDPE) films into a coconut oil model food system. *Food Addit Contam Part A.* 27:1598-1607.

Lago MA, Rodríguez A, Sendón R, Sanches-Silva A, Costa HS, Sánchez-Machado DI, López-Cervantes J, Soto Valdez H, Aurrekoetxea GP, Angulo I, Paseiro Losada P. 2011. Compilation of analytical methods to characterize and determine chitosan, and main applications of the polymer in food active packaging. *CyTA - J Food.* 9:319-328.

- Lau O-W, Wong S-K. 2000. Contamination in food from packaging material. *J Chromatogr A*. 882:255-270.
- Lee CH, An DS, Lee SC, Park HJ, Lee DS. 2004. A coating for use as an antimicrobial and antioxidative packaging material incorporating nisin and α -tocopherol. *J Food Eng*. 62:323-329.
- López P, Sánchez C, Batlle R, Nerín C. 2007. Development of flexible antimicrobial films using essential oils as active agents. *J Agric Food Chem*. 55:8814-8824.
- López-de-Dicastillo C, Alonso JM, Catalá R, Gavara R, Hernández-Muñoz P. 2010. Improving the antioxidant protection of packaged food by incorporating natural flavonoids into ethylene-vinyl alcohol copolymer (EVOH) films. *J Agr Food Chem*. 58:10958-10964.
- López-de-Dicastillo C, Gómez-Estaca J, Catalá R, Gavara R, Hernández-Muñoz P. 2012. Active antioxidant packaging films: development and effect on lipid stability of brined sardines. *Food Chem*. 131:1376-1384.
- López-de-Dicastillo C, Nerín C, Alfaro P, Catalá R, Gavara R, Hernández-Muñoz P. 2011. Development of new antioxidant active packaging films based on ethylene vinyl alcohol copolymer (EVOH) and green tea extract. *J Agric Food Chem*. 59:7832-7840.
- López-de-Dicastillo C, Pezo D, Nerín C, López-Carballo G, Catalá R, Gavara R, Hernández-Muñoz P. 2012. Reducing oxidation of foods through antioxidant active packaging based on ethyl vinyl alcohol and natural flavonoids. *Packag Technol Sci*. 25:457-466.
- López-Rubio A, Almenar E, Hernandez-Muñoz P, Lagarón JM, Catalá R, Gavara R. 2004. Overview of active polymerbased packaging technologies for food applications. *Food Rev Int*. 20:357-387.
- Mayachiew P, Devahastin S. 2010. Effects of drying methods and conditions on release characteristics of edible chitosan films enriched with Indian gooseberry extract. *Food Chem*. 118:594-601.
- Mecking S. 2004. Nature or petrochemistry? - Biologically degradable materials. *Angewandte Chemie Int Ed*. 43:1078-1085.
- Moradi M, Tajik H, Rohani SMR, Oromiehie AR, Malekinejad H, Aliakbarlu J, Hadian M. 2012. Characterization of antioxidant chitosan film incorporated with Zataria multiflora Boiss essential oil and grape seed extract. *LWT - Food Sci Technol*. 46:477-484.
- Nerín C, Tovar L, Djenane D, Camo J, Salafranca J, Beltran JA, Roncalés P. 2006. Stabilization of beef meat by a new active packaging containing natural antioxidants. *J Agric Food Chem*. 54:7840-7846.
- Nerín C, Tovar L, Salafranca J. 2008. Behaviour of a new antioxidant active film versus oxidizable model compounds. *J Food Eng*. 84:313-320.
- O'Grady MN, Maher M, Troy DJ, Moloney AP, Kerry JP. 2006. An assessment of dietary supplementation with tea catechins and rosemary extract on the quality of fresh beef. *Meat Sci*. 73:132-143.
- Ojagh SM, Rezaei M, Razavi SH, Hosseini SMH. 2010. Effect of chitosan coatings enriched with cinnamon oil on the quality of refrigerated rainbow trout. *Food Chem*. 120:193-198.
- Oussalah M, Caillet S, Salmiéri S, Saucier L, Lacroix M. 2004. Antimicrobial and antioxidant effects of milk protein-based film containing essential oils for the preservation of whole beef muscle. *J Agric Food Chem*. 52:5598-5605.
- Ozdemir M, Floros JD. 2004. Active food packaging technologies. *Crit Rev Food Sci*. 44:185-193.
- Peelman N, Ragaert P, De Meulenaer B, Adons D, Peeters R, Cardon L, Van Impe F, Devlieghere F. 2013. Application of bioplastics for food packaging. *Trends Food Sci Tech*. 32:128-141.
- Peltzer M, Wagner J, Jimenez A. 2009. Migration study of carvacrol as a natural

antioxidant in high-density polyethylene for active packaging. *Food Addit Contam Part A*. 26:938-946.

Pereira de Abreu DA, Cruz JM, Paseiro Losada P. 2012. Active and intelligent packaging for the food industry. *Food Rev Int*. 28:146-187.

Pereira de Abreu DA, Maroto J, Rodríguez KV, Cruz JM. 2012. Antioxidants from barley husks impregnated in films of lowdensity polyethylene and their effect over lipid deterioration of frozen cod (*Gadus morhua*). *J Sci Food Agric*. 92:427-432.

Pereira de Abreu DA, Paseiro Losada P, Maroto J, Cruz JM. 2010. Evaluation of the effectiveness of a new active packaging film containing natural antioxidants (from barley husks) that retard lipid damage in frozen Atlantic salmon (*Salmo salar* L.). *Food Res Int*. 43:1277-1282.

Pereira de Abreu DA, Paseiro Losada P, Maroto J, Cruz JM. 2011a. Lipid damage during frozen storage of Atlantic halibut (*Hippoglossus hippoglossus*) in active packaging film containing antioxidants. *Food Chem*. 126:315-320.

Pereira de Abreu DA, Paseiro Losada P, Maroto J, Cruz JM. 2011b. Lipid damage inhibition in hake by active packaging film with natural antioxidants. *Packag Technol Sci*. 24:353-360.

Pereira de Abreu DA, Paseiro Losada P, Maroto J, Cruz JM. 2011c. Natural antioxidant active packaging film and its effect on lipid damage in frozen blue shark (*Prionace glauca*). *Innov Food Sci Emerg Technol*. 12:50-55.

Pezo D, Salafranca J, Nerín C. 2008. Determination of the antioxidant capacity of active food packagings by in situ gas-phase hydroxyl radical generation and high-performance liquid chromatography-fluorescence detection. *J Chromatogr A*. 1178:126-133.

Phoopuritham BP, Thongngam M, Yoksan R, Suppakul P. 2012. Antioxidant properties of selected plant extracts and application in packaging as antioxidant cellulose-based films for vegetable oil. *Packag Technol Sci*. 25:125-136.

Ponce AG, Roura SI, del Valle CE, Moreira MR. 2008. Antimicrobial and antioxidant activities of edible coatings enriched with natural plant extracts: in vitro and in vivo studies. *Postharvest Biol Technol*. 49:294-300.

Pruneda E, Peralta-Hernández JM, Esquivel K, Lee SY, Godínez LA, Mendoza S. 2008. Water vapor permeability, mechanical properties and antioxidant effect of Mexican oregano-soy based edible films. *J Food Sci*. 73:488-493.

Reddy MM, Misra M, Mohanty AK. 2012. Bio-based materials in the new bio-economy. *Chem Eng Prog*. 108:37-42.

Reddy MM, Vivekanandhan S, Misra M, Bhatia SK, Mohanty AK. 2013. Biobased plastics and bionanocomposites: current status and future opportunities. *Prog Polym Sci*. 38:1653-1689.

Restuccia D, Spizzirri UG, Parisi OI, Cirillo G, Curcio M, Iemma F, Puoci F, Vinci G, Picci N. 2010. New EU regulation aspects and global market of active and intelligent packaging for food industry applications. *Food Contr*. 21:1425-1435.

Rijk R. 2007. Chemical migration from active and intelligent packaging materials into food. In: Karen A, Barnes KA, Sinclair CR, Watson DH, editors. *Chemical migration and food contact materials*. Cambridge: CRC Press - Woodhead Publishing Limited; p. 371-394.

Sánchez-González L, Pastor C, Vargas M, Chiralt A, GonzálezMartínez C, Cháfer M. 2011. Effect of hydroxypropylmethylcellulose and chitosan coatings with and without bergamot essential oil on quality and safety of cold-stored grapes. *Postharvest Biol Technol*. 60:57-63.

- Sanches-Silva A, Ribeiro T, Albuquerque TG, Paseiro P, Sendón R, Quirós AB, López-Cervantes J, SánchezMachado DI, Valdez HS, Angulo I, et al. 2012. Ultra-high pressure LC determination of glucosamine in shrimp byproducts and migration tests of chitosan films. *J Sep Sci.* 35:633-640.
- Sanches-Silva A, Ribeiro T, Albuquerque TG, Paseiro P, Sendón R, Quirós AB, López-Cervantes J, Sánchez-Machado DI, Valdez HS, Angulo I, et al. 2013. Ultra-high pressure LC for astaxanthin determination in shrimp by-products and active food packaging. *Biomed Chromatogr.* 27:757-764.
- Sanches Silva A, Sendón García R, Cooper I, Franz R, Paseiro Losada P. 2006. Compilation of analytical methods and guidelines for the determination of selected model migrants from plastic packaging. *Trends Food Sci Tech.* 17:535-546.
- Sánchez-Escalante A, Djenane D, Torrescano G, Beltrán JA, Roncalés P. 2001. The effects of ascorbic acid, taurine, carnosine and rosemary powder on colour and lipid stability of beef patties packaged in modified atmosphere. *Meat Sci.* 58:421-429.
- Shojaee-Aliabadi S, Hosseini H, Mohammadifar MA, Mohammadi A, Ghasemlou M, Ojagh SM, Hosseini SM, Khaksar R. 2013. Characterization of antioxidant-antimicrobial κ -carrageenan films containing *Satureja hortensis* essential oil. *Int J Biol Macromol.* 52:116-124.
- Siripatrawan U, Harte BR. 2010. Physical properties and antioxidant activity of an active film from chitosan incorporated with green tea extract. *Food Hydrocolloid.* 24:770-775.
- Siripatrawan U, Noipha S. 2012. Active film from chitosan incorporating green tea extract for shelf life extension of pork sausages. *Food Hydrocolloid.* 27:102-108.
- Siró I, Fenyvesi E, Szenté L, de Meulenaer B, Devlieghere F, Orgoványi J, Sényi J, Barta J. 2006. Release of alpha-tocopherol from antioxidative low-density polyethylene film into fatty food simulant: influence of complexation in beta-cyclodextrin. *Food Addit Contam.* 23:845-853.
- Song HY, Shin YJ, Song KB. 2012. Preparation of a barley bran protein-gelatin composite film containing grapefruit seed extract and its application in salmon packaging. *J Food Eng.* 113:541-547.
- Spizzirri UG, Iemma F, Puoci F, Cirillo G, Curcio M, Parisi OI, Picci N. 2009. Synthesis of antioxidant polymers by grafting of gallic acid and catechin on gelatin. *Biomacromolecules.* 10:1923-1930.
- Torres-Arreola W, Soto-Valdez H, Peralta E, Cardenas-Lopez JL, Ezquerro-Brauer JM. 2007. Effect of a low-density polyethylene film containing butylated hydroxytoluene on lipid oxidation and protein quality of sierra fish (*Scomberomorus sierra*) muscle during frozen storage. *J Agric Food Chem.* 55:6140-6146.
- Tovar L, Salafranca J, Sánchez C, Nerín C. 2005. Migration studies to assess the safety in use of a new antioxidant active packaging. *J Agric Food Chem.* 53:5270-5275.
- Veraart R. 2010. Compliance testing, declaration of compliance and supporting documentation in the EU. In: Rijk R, Veraart R, editors. *Global legislation for food packaging materials*. Weinheim: Wiley - VCH Verlag GmbH & Co. KGaA; p. 197-221.
- Veraart R, Coulier L. 2007. Compliance testing of chemical migration from food contact materials. In: Karen A, Barnes KA, Sinclair CR, Watson DH, editors. *Chemical migration and food contact materials*. Cambridge: CRC Press Woodhead Publishing Limited; p. 87-121.
- Wessling C, Nielsen T, Giacín JR. 2000. Antioxidant ability of BHT- and α -tocopherol-impregnated LDPE film in packaging of oatmeal. *J Sci Food Agric.* 81:194-201.
- Wessling C, Nielsen T, Leufvén A, Jägerstad M. 1998. Mobility of α -tocopherol and BHT in LDPE in contact with fatty food simulants. *Food Addit Contam.* 15:709-715.
- Wood WE. 2001. Improved aroma barrier properties in food packaging with cyclodextrins

[Internet]. TAPPI Polymers, Laminations and Coatings Conference; 367-377. [Cited 2013 Nov 18]. Available from: <http://www.tappi.org/69D6E5F3-35D0-4113-BE13-546A409AB4F8/FinalDownload/DownloadId-4331F7B1C8561E0C998ED8194B2643>

44/69D6E5F3-35D0-4113-BE13-546A409AB4F8/Downloads/unsorted/UNTITLED-plc0140pdf.aspx

Xiao C, Zhu L, Luo W, Song X, Deng Y. 2010. Combined action of pure oxygen pretreatment and chitosan coating incorporated with rosemary extracts on the quality of fresh-cut pears. *Food Chem.* 121:1003-1009.

Zhu X, Lee DS, Yam KL. 2012. Release property and antioxidant effectiveness of tocopherol-incorporated LDPE/PP blend films. *Food Addit Contam Part A.* 29:461-468.