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Films and edible coatings containing antioxidants – a review

Filmes e coberturas comestíveis contendo antioxidantes – uma revisão

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Summary

The incorporation of natural antioxidants into films and edible coatings can modify their structure, improving their functionality and applicability in foods, such as in fresh-cut fruits. This paper reviews the more recent literature on the incorporation of antioxidants from several sources into films and edible coatings, for application in fruits and vegetables. The use of synthetic antioxidants in foods has been avoided due to their possible toxic effects. Instead, a wide range of natural antioxidants (such as essential oils and plant extracts, as well as pure compounds, like ascorbic acid and α-tocopherol) have been incorporated into edible films and coatings to improve their bioactive properties. Films and coatings containing added antioxidants help to preserve or enhance the sensory properties of foods and add value to the food products by increasing their shelf life.

Key words: *Bioactive compounds; Natural additives; Functionality; Essential oil; Extracts.*

Resumo

A incorporação de antioxidantes naturais em filmes e coberturas comestíveis pode modificar sua estrutura, melhorando sua funcionalidade e aplicação em alimentos, tais como as frutas. Este artigo apresenta uma revisão da literatura mais recente sobre a incorporação de antioxidantes, de diversas fontes, em filmes e coberturas comestíveis aplicados em frutas e vegetais. A utilização de antioxidantes sintéticos em alimentos tem sido evitada em razão do seu possível efeito tóxico. Assim, inúmeras categorias de antioxidantes naturais – tais como óleos essenciais, extratos de plantas e compostos puros, como ácido ascórbico e α-tocoferol – têm sido adicionadas a filmes e coberturas comestíveis, para melhorar suas propriedades bioativas. As embalagens aditivadas com antioxidantes podem preservar ou melhorar as qualidades sensoriais dos alimentos sobre os quais são aplicadas e agregar valor a produtos alimentares pelo aumento de sua vida de prateleira.

Palavras-chave: *Compostos bioativos; Aditivos naturais; Funcionalidade; Óleo essencial; Extratos.*

1 Introduction

The greatest hurdle of the food industry is the limited shelf life of food products, a consequence of oxidation reactions such as degradation, enzymatic browning, and oxidative rancidity (SOLIVA-FORTUNY and MARTÍN-BELLOSO, 2003). One approach to reduce food deterioration is to use edible films and coatings.

Edible films or coatings constitute thin layers of material that are suitable for consumption and which act as a barrier against different agents (water vapor, oxygen, and moisture). They help to improve the quality and extend the shelf life of fresh and processed foods. The addition of active compounds, such as antioxidants, to these films and coatings can enhance their functional properties and make them potentially applicable in food preservation (SÁNCHEZ-GONZÁLEZ et al., 2011). Indeed, antioxidants can bind free radicals to protect materials against oxidation processes, regardless of the action mechanism (POKORNÝ, 2007a).

Many researchers have studied how incorporation of antioxidants affects the functional properties of different biopolymer films and coatings. Antioxidant agents from natural sources, such as plant extracts (AKHTAR et al., 2012; ZENG et al., 2013; LI et al., 2014), essential oils (BONILLA et al., 2013; RUIZ-NAVAJAS et al., 2013; PERDONES et al., 2014), and other components with antioxidant activity, like α-tocopherol (fat-soluble antioxidant)(BLANCO-FERNANDEZ et al., 2013; JIMÉNEZ et al., 2013), ascorbic acid (BASTOS et al., 2009; PÉREZ et al., 2012; DE'NOBILI et al., 2013), or citric acid (ATARÉS et al., 2011; ROBLES-SÁNCHEZ et al., 2013), have been widely studied individually or in combination, to replace synthetic antioxidants, such as BHA or BHT.

Results presented by the aforementioned authors have suggested that incorporation of antibrowning agents into edible coatings maintains the quality properties of the food. Nevertheless, the overall quality and the antioxidant activity resulting from this incorporation have not been widely studied.

This work aimed to review the information available on the use of edible films and coatings as carriers of antioxidant compounds to improve the quality, safety, and functionality of fruits. It will identify the state-of-the-art of this innovative approach to food technology as well as discuss perspectives in this area.

2 Antioxidants: compounds, action mechanisms, and assays

Antioxidants comprise substances that can protect materials (not only foods) against autoxidation irrespective of the action mechanism (POKORNÝ, 2007a). These compounds can be classified as primary or secondary antioxidants, depending on the action mechanism. Some antioxidants exhibit more than one action mechanism, being often referred to as multiple-function antioxidants (REISCHE et al., 2002).

According to Reische et al. (2002), primary antioxidants are free radical acceptors that delay or inhibit the autoxidation initiation step or interrupt the autoxidation propagation step. Secondary antioxidants slow the oxidation rate through numerous mechanisms, but they cannot convert free radicals to more stable products.

Antioxidants can be natural or synthetic. Synthetic antioxidants that have received approval for use in foods include butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG), octyl gallate, dodecyl gallate, ethoxyquin, ascorbylpalmitate, and tertiary butyl hydroquinone (TBHQ) (ANDRÉ et al., 2010). Tocopherols, tocotrienols, ascorbic acid, citric acid, carotenoids, and enzymatic antioxidants are natural antioxidants commonly added to foods (FINLEY et al., 2011). Although these natural antioxidants present some drawbacks (lower antioxidant activity as compared with synthetic antioxidants and the presence of other substances that can negatively affect the sensory properties of the product, among others), they offer many advantages, including the fact that consumers readily accept them. Besides the number of natural antioxidants that are currently available and accepted by health authorities, food components that can be used as flavorings, positively affect sensory properties and act as preservation agents which are easily accessible (POKORNÝ, 2007b).

The antioxidant capacity has been extensively studied and different methods have been suggested due to the growing interest to discover new sources of bioactive compounds and their protective effects. However, the quantitative in vitro capacity of an antioxidant may depend on pH, solvent, oxidation levels, and other reaction conditions (FRANKEL and FINLEY, 2008). Assessment of the free radical scavenging potential of a substance is an important method to determine its antioxidant activity (POKORNÝ, 2007a). Among the methods that detect electron or radical scavenging are the DPPH assay (2,2-diphenyl-1-picrylhydrazyl), the ABTS assay (2,2’-azinobis3-ethylbenzothiazoline-6-sulfonic acid), and the FRAP assay (ferric reducing antioxidant power) (BERGER et al., 2011).

The DPPH assay is a simple and highly sensitive method. DPPH consists of a nitrogen free radical; a proton radical scavenger such as a hydrogen donating antioxidant can quench DPPH, to generate its nonradical form (DPPH-H). The antioxidant effect of a compound is proportional to the disappearance of DPPH in the samples. Concerning the FRAP assay, it gives fast, reproducible results. This assay affords the antioxidant capacity of the target compound in the assayed samples on the basis of the FRAP ferric ion reduction to ferrous iron. The ABTS assay, it is applicable in both aqueous and lipid phases. ABTS discoloration provides information on the antioxidant activity of the natural products. The discoloration can be measured on the basis of the reduction of the radical cation, as the percentage inhibition of the absorbance at 734 nm (MOON and SHIBAMOTO, 2009).

The rapid ORAC assay provides results that often coincide with the total phenols as determined by the Folin-Ciocalteu reagent (BERGER et al., 2011). The phenolic content can function as an indicator of the antioxidant capacity; it finds application in the preliminary screening of any product intended as a natural source of antioxidants in functional foods (VIUDA-MARTOS et al., 2011). On the other hand, high phenolic content can indicate polyphenol oxidase activity, which underlies oxidative processes, such as fruit browning.

Enzymatic reactions that change the color of products impact the commercialization of fresh-cut fruits. In addition, cutting the fresh fruit can modify it in undesirable ways, to alter the flavor and smell as well as the firmness of fruit tissues (MARTÍN-BELLOSO et al., 2007). These changes originate from the enzymatic browning that occurs after peeling and cutting of the fruit in the presence of oxygen, a result of the polyphenol oxidase activity mentioned above. To tackle this problem, it is necessary to employ a browning inhibitor; e.g., an antioxidant, to prevent development of a brown coloration (ZAMBRANO-ZARAGOZA et al., 2013).

3 Application of antioxidant films and coatings

One way to control fruit browning is to immerse the sample in antioxidant solutions after peeling or cutting. This methodology relies on modified atmosphere packaging and storage at low temperature, to increase product shelf life (BALDWIN et al., 1995). Films and edible coatings can also enhance the shelf life of fresh-cut fruits. Further addition of antioxidants to the formulation of films and coatings can improve the preservative function, inhibit browning, and reduce the undesirable effects of nutrients oxidation (PASTOR et al., 2011; BONILLA et al., 2013).

Before adding antioxidants to films and coatings, it is necessary to evaluate not only their antioxidant capacity, but also how they influence (i) the properties of the materials into which they are being incorporated, such as the retention power, and (ii) the characteristics of the food product, like flavor, color, and chemical modifications. Tables 1, 2 and 3 present the composition, added antioxidant, method of measurement, and the main results of several studies on antioxidant films and coatings.

3.1 Pure compounds

New trends in edible films and coatings have aimed to develop their functionality through incorporation of active compounds. An interesting alternative that may confer functional properties to such materials is to add the antioxidant as a pure compound, like ascorbic acid, citric acid, resveratrol, or tocopherol. These are generally the compounds of choice, because they constitute antioxidant models, supplement the diet, and protect the sensory and nutritive quality of the food itself (LEÓN and ROJAS, 2007).

The literature contains little information on how incorporation of compounds like resveratrol, ascorbic acid, α-tocopherol, butylated hydroxytoluene (BHT), and butylated hydroxyanisole (BHA), among others, affects film properties. However, their antioxidant activity (and in some cases their antimicrobial properties) has been extensively studied by physicochemical methods. For instance, ascorbic acid avoids enzymatic browning of fruits by reducing the o-quinones originating from the action of polyphenoloxidase enzymes. Unfortunately, after complete ascorbic acid oxidation to dehydroascorbic acid, quinones can accumulate again and undergo browning (ROJAS-GRAÜ et al., 2008).

As for the antioxidant activity of α-tocopherol, vanillin, BHT, BHA, phenol, propyl gallate, and sodium tripolyphosphate, only BHA is less active than resveratrol to inhibit lipid peroxidation (MURCIA and MARTÍNEZ-TOMÉ, 2001). Concerning the radical scavenging capacity of propyl gallate, ascorbic acid, α-tocopherol, and resveratrol, Soto-Valdez et al. (2011) reported that the latter is the best scavenger.

Table 1 shows recent studies about films and coatings containing pure antioxidant compounds and highlights the implications of adding antioxidants to the materials. In most of the cases, the antioxidant capacities of the films are proportional to the concentration of the active compound in the film, without notable activity loss during film formation and conditioning (PASTOR et al., 2011; NORONHA, 2012). Nonetheless, very diverse effects emerge upon addition of these compounds into a polymeric matrix, as verified by microstructural, mechanical, barrier, and optical properties, as well as antioxidant capacity (BASTOS et al., 2009; DE'NOBILI et al., 2013; JIMÉNEZ et al., 2013). On the other hand, effects like the cross-linking between the active compound and the polymer could also arise, to improve film properties. Acids, such as ascorbic and citric acids, and polymer chains, among others, reduce the oxygen permeability in films, which could protect the material against oxidation (ATARÉS et al., 2011; FABRA et al., 2011; HAN and KROCHTA, 2007).

It is crucial to evaluate compound stability in the films during storage. One way is to determine the percentage of antioxidant retention in the film under adverse light, relative humidity, and temperature conditions. Some works have verified that ascorbic acid is 100% retained after film casting; however, the degradation

Table 1. Coating and films incorporated with pure compounds.

Composition Film	Additive	Food	Method of measurement	Results	References
Chitosan Methylcellulose	Resveratrol	-	Antioxidant activity – DPPH assay	Composite films also exhibited antioxidant activity, which was proportional to the employed resveratrol concentration. No notable antioxidant activity loss of occurred during film formation and conditioning.	Pastor et al. (2013)
Low methoxyl pectin	Ascorbic acid	-	Ascorbic acid - Spectrophotometric method	Ascorbic acid degradation was less sensitive than film browning upon increasing storage relative humidity.	De'Nobili et al. (2013)
Corn starch	Oleic acid α-tocopherol	-	Antioxidant activity – ABTS assay	The antioxidant capacity of films containing only α-tocopherol was not statistically different at studied storage periods. However, incorporation of oleic acid decreased the antioxidant capacity partly because it promoted oxidation reactions, due to increased oxygen solubility.	Jiménez et al. (2013)
Chitosan	α-tocopherol	-	Antioxidant activity – DPPH assay	The films radical scavenging activity was similar to that exhibited by the freshly prepared α-tocopherol solution. However, the high α-tocopherol content conferred the film an oily aspect.	Blanco-Fernandez et al. (2013)
High methoxyl pectin	Ascorbic acid (AA)	-	Ascorbic acid - Spectrophotometric method	The initially determined AA concentration was 3.00 g of AA/100 g of film, which accounted for 100% AA recovery after casting. AA was the least stable in 80% methylated pectin, with higher retention in 50% and 70 % methylated pectin networks.	Pérez et al. (2012)
Sodium caseinate (NaCAS) Casein (CAS)	Tannic acid and catechin	-	Antioxidant activity – DPPH and ABTS assays	The CAS content in the film affected the initial radical-scavenging activity (RSA). During storage, RSA was satisfactorily stable. The surface RSA of NaCAS films containing phenolic compounds increased with storage time due to plasticizing and perhaps alteration of the NaCAS and CAS networks.	Helal et al. (2012)
Methylcellulose	Nanoparticles of poly-ε-caprolactone and β-carotene	-	Antioxidant activity – ABTS assay	The films developed with 70% β-carotene nanoparticles showed low antioxidant capacity. However, this activity was significantly ($p < 0.05$) higher than that of the control treatment using methylcellulose only.	Lino (2012)
Carboxymethylcellulose	α-tocopherol	-	Antioxidant activity – ABTS and DPPH assays	Release and antioxidant activity analyses showed higher values for the samples containing the lecithin formulation. The films had low values of α-tocopherol release in ethanol solution. The film matrix was stable over the analysis time.	Motta (2012)
Methylcellulose	Nanocapsules of poly-ε-caprolactone (NCs)	-	Antioxidant activity – ABTS and DPPH assay	For both assays, the film control had no radical scavenging activity. The results showed that the DPPH and ABTS scavenging activity of the films significantly increased ($p < 0.05$) with NCs concentration. The 70% NCs film exhibited the higher radical scavenging activity (DPPH - 56.21%, ABTS - 223.5 TEAC μMol/g).	Noronha (2012)

Table 1. Continued...

Composition Film	Additive	Food	Method of measurement	Results	References
Zein	Phenolic acids: gallic acid (GA); p-hydroxy benzoic acid; ferulic acids; Flavonoids:catechin (CAT); flavone; quercetin.		Total phenols – spectrophotometric method Antioxidant activity – ABTS assay	In films containing 1.5 and 3.0 mg.cm^{-2} phenolic, the total released GA was 1.6- and 1.9- fold higher than total released CAT, respectively. The trolox equivalent antioxidant capacity of total GA released from films containing 1.5 and 3.0 mg cm^{-2} phenolic compounds was 3.6- and 4.1-fold higher than those of total CAT released from the corresponding films, respectively.	Arcan and Yemenicioğlu (2011)
Calcium alginate-Capsul	Ascorbic acid	-	Ascorbic acid - Titration method	The antioxidant model was stable for five months when incorporated in these films stored at refrigeration in the dark and when stored at room temperature it was maintained for three months, thus suggesting that the film protected the antioxidant efficiently, mainly from the adverse conditions of light.	Bastos et al. (2009)
Whey Protein	Ascorbyl palmitate α-tocopherol	-	Oxygen permeability	The oxygen permeability of films obtained by Process 1 (the antioxidants were mixed using powder blending) was lower than that of films obtained by Process 2 (ethanol solvent-mixing). However, both the oxygen diffusivity and solubility were statistically the same in the two films.	Han and Krochta (2007)
Gellan gum	Ascorbic acid (AA)	-	Ascorbic acid - Spectrophotometric method	The initial AA concentration was 3.2% (w/w) on film basis and accounted for a retention that varied between 103 and 99% after film casting. The rate constants of non-enzymatic browning and acid ascorbic degradation increased with relative humidity.	León and Rojas (2007)
Coating					
Alginate	Ascorbic acid Citric acid	Mango	Ascorbic acid - HPLC β-carotene - HPLC Vitamin E - HPLC Phenolic compounds - HPLC Antioxidant activity - ABTS and DPPH assays	In fresh-cut mango, the addition of these antioxidants contributed not only to color retention but also to the antioxidant potential of fresh-cut mangoes. According to the results, it is possible to store fresh-cut Kent mango for 12 days at 4 °C, without any detrimental effects on nutritional and physicochemical quality.	Robles-Sánchez et al. (2013)
Cassava starch	Citric acid	Fresh-cut Mango	Respiration rate Weight loss β-carotene content Color parameters	This combination delayed the quality deterioration of fresh-cut mangoes, decreasing the fruit respiration rate and inhibiting the metabolic reactions associated with fruit ripening. Besides, it promoted a better preservation of mechanical properties and color characteristics during storage.	Chiumarelli et al.(2010)
Alginate, gellan or pectin	N-cetylcysteine Glutathione	Pears	Ascorbic acid - HPLC-UV Total phenolic content - Spectrophotometric method Antioxidant activity – DPPH assay	Significantly reduced vitamin C loss occurred for fresh-cut pears during more than one week. The total phenolic content was higher in samples containing the antioxidants than in the non-treated samples.	Oms-Oliu et al. (2008)

Table 2. Coating and films incorporated with essential oil.

Composition Film	Additive	Food	Method of measurement	Results	References
Quince seed mucilage	Oregano essential oil	-	Total phenols – spectrophotometric method Antioxidant activity – DPPH assay	The DPPH scavenging activity and total phenolic content of quince seed mucilage films augmented significantly ($p \leq 0.05$) with increasing oregano essential oil concentration.	Jouki et al. (2014)
Chitosan	Cinnamon leaf essential oil Oleic acid (OA)	-	Antioxidant activity – ABTS assay	All the films containing cinnamon showed higher antioxidant activity. The higher the cinnamon content in the dry film the greater the antioxidant power. OA addition did not significantly affect the antioxidant activity of cinnamon in the films. However, there was greater retention of the compounds from the cinnamon essential oil during film formation and handling when OA was present in the formulation.	Perdones et al. (2014)
Starch and chitosan	Basil essential oil and thyme essential oil	-	Antioxidant activity – ABTS assay	The antioxidant activity of the film containing thyme essential oil was higher than that of the film containing basil essential oil. The compounds lost their antioxidant capacity during film formation and the extraction procedure, probably due to their volatilization during film drying.	Bonilla et al. (2013)
Hake protein	Citronella, coriander, tarragon and thyme essential oils	-	Antioxidant activity – DPPH assay	Hake protein films exhibited some antioxidant activity, which was significantly improved upon addition of the essential oils. The films containing coriander and citronella oils considerably increased the DPPH radical-scavenging capacity.	Pires et al. (2013)
Fish skin gelatin	Root essential oils of ginger, turmeric and plai	-	Antioxidant activity - DPPH and ABTS assays	Films incorporated with turmeric and plai essential oils showed higher antioxidant activity than those incorporated with ginger, as attested by both DPPH and ABTS methods.	Tongnuanchan et al. (2013)
Chitosan	Essential oils of *Thymus moroderi* (TMEO) and *Thymus piperella (TPEO)*	-	Total phenols – spectrophotometric method Antioxidant activity - DPPH, FRAP, and FIC assays	At all the assayed concentrations, the TMEO films showed lower ($p < 0.05$) antioxidant activity than the TPEO films, as attested by both the DPPH and FRAP methods. The same behavior was observed for total phenols content.	Ruiz-Navajas et al. (2013)
Kappa-carrageenan	*Satureja hortensis* essential oil (SEO)	-	Total phenols – spectrophotometric method Antioxidant activity – DPPH assay	The results showed that the DPPH-scavenging activity and total phenols content of the films increased significantly ($P < 0.05$) with larger SEO concentrations, an effect that was greatly improved upon addition of 3% (v/v) SEO.	Shojaee-Aliabadi et al. (2013)

Table 2. Continued...

Composition Film	Additive	Food	Method of measurement	Results	References
Chitosan	*Zataria multiflora* Boiss essential oil (ZEO) Grape seed extract (GSE)	-	Total phenols - spectrophotometric method Antioxidant activity - DPPH and Reducing power assays	For the films incorporated with 10 gL^{-1} GSE, the phenols content was 17 times greater than that of the control. The results also showed that ZEO incorporation into GSE formulated films, significantly decreased the TP of the film ($P < 0.05$). Furthermore, the results revealed that chitosan+ ZEO and, to a greater extent, chitosan+ GSE contained more phenolics capable of quenching free radicals, to give more stable products.	Moradi et al. (2012)
Hake proteins	Thyme oil	-	DPPH radical-scavenging activity Reducing power	Hake protein films exhibited some antioxidant activity, improved by addition of 0.25 mL of thyme oil/g of protein.	Pires et al. (2011)
Sodium caseinate	Cinnamon essential oil Ginger essential oil	-	Antioxidant activity - accelerated test of oxidative rancidity	All the films effectively protected the sunflower oil against oxidation, probably due to their low permeability to oxygen at the low relative humidity of the surrounding atmosphere.	Atarés et al. (2010)
Coating					
Pectin	Cinnamon leaf oil	Peach	Antioxidant activity – DPPH and ABTS assays Total phenols – spectrophotometric method	The radical scavenging activity increased significantly ($p < 0.05$) as the added oil concentration rose. The coating treatments significantly affected ($p < 0.05$) the total phenolic and flavonoid content as well as the antioxidant capacity of fresh-cut peach.	Ayala-Zavala et al. (2013)
Pectin	Cinnamon leaf oil	Table grapes	Total phenolic and flavonoid contents – spectrophotometric method Antioxidant activity – DPPH and ABTS assays	Cinnamon leaf oil incorporated into pectin coatings significantly increased the antioxidant capacity of grapes.	Melgarejo-Flores et al. (2013)
Rice starch	Coconut oil	Tomatoes	Ascorbic acid -	Lipid addition to the starch film significantly controlled the ripening of tomatoes.	Das et al. (2013)
Cassava starch	Cinnamon bark essential oil Fennel essential oil	Fuji apple slices	Total phenols – spectrophotometric method Antioxidant activity – DPPH and FRAP assays	The coating containing cinnamon bark essential oil showed higher total phenols concentration and antioxidant activity than the other formulations.	Oriani et al. (2014)

Table 2. Continued...

Composition Film	Additive	Food	Method of measurement	Results	References
Hydroxypropylmethylcellulose (HPMC)or chitosan (CH)	Bergamot essential oil	Table grapes	Total phenols – spectrophotometric method Antioxidant activity – DPPH assay	The coatings did not seem to reduce the rate of grape browning during storage, but they inhibited color development, thus improving the product appearance.	Sánchez-González et al. (2011)
Chitosan	Cinnamon oil	Sweet pepper	Vitamin C content - HPLC-UV Activities of superoxide dismutase (SOD), catalase (CAT) and peroxidase (POD)	At the end of storage, samples treated with chitosan-oil coatings maintained good sensory acceptability, whereas the sensory quality of control samples became unacceptable. The higher activities of scavenger antioxidant enzymes, including SOD, POD, and CAT, in treated peppers at the 35th day should contribute to the properties of the chitosan–oil coating.	Xing et al. (2011)
Sodium caseinate Chitosan Carboxymethyl cellulose	Oleoresins of rosemary, oreganum, olive, capsicum, garlic and cranberry	Romaine lettuce Butter lettuce Butternut squash	Antioxidant activity - peroxidase and polyphenoloxidase assays (spectrophotometric method)	Besides increasing the antimicrobial and antioxidant effectiveness, optimal additive concentration (2%) did not adversely affect the sensory acceptability.	Ponce et al. (2008)

Table 3. Coatings and films incorporated with extracts.

Composition Film	Additive	Food	Method of measurement	Results	References
Gelatin	Green tea extract (GET) Grape seed extract (GSE) Ginger extract (GE) Gingko leaf extract (GBE)	-	Antioxidant activity - DPPH and reducing power property assays	The addition of 1.0 mgmL^{-1} GBE made the film a better scavenger as analyzed by the DPPH assay. At the same time, the film containing GTE, GSP, and OPC had similar antioxidant property to that of the film incorporated with GBE.	Li et al. (2014)
Gelatin	Curcuma ethanol extract	-	Antioxidant activity – DPPH and ABTS assays	The DPPH and ABTS methods revealed significantly increased film antioxidant activity due to increased of curcuma ethanol extract concentration	Bitencourt (2013)
HPMC	Natural red compound -beetroot and purple carrot extract (NRC)	-	Antioxidant activity – ABTS assay	The NRC antioxidant activity decreased slightly during film preparation, but no significant change occurred during film casting or aging in the dark or under exposure to light.	Akhtar et al. (2012)
Alginate	Ginseng extract	-	Antioxidant activity - DPPH and reducing power property assays	The ginseng extract can be successfully incorporated into alginate films and retain excellent antioxidant activities, without changing the moisture content values.	Norajit et al. (2010)
Sole skin gelatin Commercial fish gelatin	Borage extract BHT α-tocoferol	-	Antioxidant activity - FRAP, ABTS, and Iron (II) chelation activity assays	The commercial gelatin with borage extract displayed the highest antioxidant activity. This compound seemed to be more promising than BHT and α-tocopherol.	Gómez-Estaca et al. (2009a)
Coating					
Rice starch	Coconut oil Green tea extract	Tomatoes	Antioxidant activity - DPPH assay Ascorbic acid (AA) - Titration method	The high AA content retention after 20 days of storage can be attributed to the effect of phenolic substances in the coating.	Das et al. (2013)
Konjac glucomann (KG)	Pineapple fruit extracts (PE) from peel, pulp and core	Rose apple	Total phenols – spectrophotometric method Polyphenol oxidase (PPO) – chromatographic method Peroxidase (POD) – spectrophotometric method	The pineapple fruit core extract more effectively retarded fruit browning as compared with the other extracts. Regarding browning inhibition from using KG + PE, this treatment led to the lowest PPO and POD activities and the highest total phenols content.	Supapvanich et al. (2012)
HPMC	Ethanolic extract of propolis	Table grapes	Total phenols – spectrophotometric method Antioxidant activity – DPPH assay	HPMC coatings prevented weight loss and browning of moscatel table grapes during cold storage, while improving their gloss and microbial safety and controlling the increase in oxygen consumption. Nevertheless, the incorporation of propolis did not significantly affect grape quality preservation during storage.	Pastor et al. (2011)
Chitosan	Rosemary extract	Pears	PPO activity – spectrophotometric method Total phenols – spectrophotometric method	A pure oxygen pretreatment combined with a chitosan coating that included rosemary afforded the lowest rates of browning, softening, and sensory degradation in the pear wedges after 3 days of storage at 20 °C. In addition, the combined treatment effectively reduced membrane permeability, vitamin C loss and weight loss by maintaining low pH and high L and h values in the fresh-cut pears.	Xiao et al. (2010)

of this acid increases with higher relative humidity (LEÓN and ROJAS, 2007; DE'NOBILI et al., 2013). In contrast, Bastos et al. (2009) compared the influence of light and temperature, to conclude that both parameters are important during ascorbic acid degradation. Degradation becomes significantly faster upon a temperature rise of only 15 °C, whereas light impacts this reaction only slightly.

Results from different studies have pointed out that functional edible films containing added pure antioxidant are potentially applicable in food products that are sensitive to oxidative processes, to prolong their shelf life. Investigations have focused on improving several coatings and render them carriers of pure compounds. Such coatings have proven to efficiently maintain the quality properties of different foods (Table 1), but most of the employed antioxidants can still undergo rapid degradation due to oxidative processes (PIERUCCI et al., 2004).

Among the biopolymers used to formulate coatings, alginate, hydroxypropylmethylcellulose, pectin, and gellan are interesting options: they are odorless, tasteless, and biodegradable (KROCHTA and DE MULDER-JOHNSON, 1997). In the case of fruits and vegetables, the edible coatings carry antibrowning agents (SOLIVA-FORTUNY and MARTÍN-BELLOSO, 2003; CHIUMARELLI et al., 2010). Robles-Sánchez et al. (2013) and Oms-Oliu et al. (2008), who worked with minimally processed fruits, observed that the addition of antioxidants significantly impacts the overall quality of fresh-cut fruits. These compounds effectively reduce bioactive compounds loss (ascorbic acid, polyphenols), to keep the natural color of the fruits and increase their antioxidant potential.

3.2 Essential oils

Consumers have been demanding the use of fewer chemicals in minimally processed fruits and vegetables. Hence, the search for naturally occurring substances that can act as alternative antioxidants is essential. Antioxidants can prevent sensorial and nutritional quality loss and improve lipids stability, to lengthen the shelf life of food products (PONCE et al., 2008).

Essential oils are aromatic, natural antioxidant, and antimicrobial substances extracted from vegetables by physical means. They consist of a complex mixture of natural compounds; most of them contain a mixture of terpenes, terpenoids, phenolic acids, and other aromatic and aliphatic compounds, but their composition may vary depending on their origin. Because essential oils can lower lipid oxidation, their presence in food products could extend the shelf life (TONGNUANCHAN et al., 2013; PERDONES et al., 2014).

Essential oils exhibit great antioxidant potential and are classified as Generally Recognized as Safe (GRAS). However, some of their features – intense aroma, toxicity issues, and possible changes in the organoleptic properties of the food – have limited their use in food preservation. A strategy to solve this problem has been to incorporate essential oils into edible films and coatings. It is possible to minimize the required doses by encapsulating them into the polymer matrix, which limits their volatilization, controls their release (thereby reducing the negative impact of these ingredients), and preserves the quality and safety attributes of fresh-cut fruits and vegetables (SÁNCHEZ-GONZÁLEZ et al., 2011; BONILLA et al., 2013; RUIZ-NAVAJAS et al., 2013).

Table 2 lists many publications on essential oils incorporated into coatings or films prepared from biopolymers of several sources. Tongnuanchan et al. (2013) studied the antioxidant properties of the film prepared from fish skin gelatin incorporated with essential oils from roots (ginger, turmeric, and plai), to show that these films display higher antioxidant activity than the control film. Perdones et al. (2014) found that chitosan films containing cinnamon leaf essential oil exhibit higher antioxidant activity. Ruiz-Navajas et al. (2013) also produced chitosan films and used the DPPH and FRAP methods to demonstrate that films containing *Thymus piperella* essential oil present higher antioxidant activity than films containing *Thymus moroderi* essential oil. The antioxidant activity thus depends on the type of essential oils and results from the structural features of the molecules, mainly the reactivity of the hydroxyl groups present in the compounds. Concentration, temperature, light, substrate type, physical state of the system, and microcomponents acting as pro-oxidants or synergists also impact the antioxidant action. Furthermore, various antioxidants can interact with the film matrix in different ways, to release the free antioxidant in the essential oils through diverse mechanisms (ČÍŽ et al., 2010; TONGNUANCHAN et al., 2013).

Ponce et al. (2008) demonstrated that butternut squash containing chitosan coatings enriched with oleoresins improves the antioxidant protection of the fresh-cut squash, preventing the browning reactions and the consequent quality loss in fruits and vegetables without adversely affecting their sensory acceptability. However, the addition of antioxidants to films does not always enhance the antioxidant properties. Indeed, Atarés et al. (2010) described that incorporation of cinnamon and ginger essential oils into sodium caseinate films does not elicit any antioxidant effect as compared with the sodium caseinate film without essential oils, even though cinnamon essential oil alone possesses high antioxidant potential.

Besides their high antioxidant capacity, essential oils can also improve the water barrier properties of the film because they display the hydrophobic nature characteristic of lipids (ATARÉS et al., 2010). Several authors have reported that the antioxidant power of a biodegradable film containing essential oils is proportional to the amount of added essential oils; in other words, the antioxidant activity rises with increasing essential oil concentration in the film (GÓMEZ-ESTACA et al., 2009b; MORADI et al., 2012; SHOJAEE-ALIABADI et al., 2013; TONGNUANCHAN et al., 2013; JOUKI et al., 2014).

3.3 Extracts

Because synthetic antioxidants have raised some safety concerns and regulatory agencies have restricted their use as food additives, researchers have targeted films containing antioxidant agents from natural sources such as natural extracts (MURCIA and MARTÍNEZ-TOMÉ, 2001; DE'NOBILI et al., 2013). These extracts should also contribute to nutritional and quality aspects without impacting the food product integrity (GUILBERT et al., 1996).

Extracts like tea extracts (DAS et al., 2013; LI et al., 2014), fruit and vegetables extracts (AKHTAR et al., 2012; SUPAPVANICH et al., 2012), ginseng extract (NORAJIT et al., 2010), plant extracts (GÓMEZ-ESTACA et al., 2009b), and propolis (PASTOR et al., 2011) possess excellent antioxidant activity, can retard lipid oxidation, and improve the quality and shelf life of various food model systems in different ways (Table 3). The antioxidant activity of these extracts results mainly from phenolic compounds and their synergistic, antagonistic, and additive effects (KROCHTA and DE MULDER-JOHNSON, 1997). However, despite their strong scavenging activity and ability to protect food products, they are still less active than synthetic antioxidants.

Many authors have looked into the different functionalities of antioxidant extracts. Recently, fruit and vegetable extracts have been considered for application as natural bioactive additives for their coloring potential, pharmaceutical activities, and bioactivity, regarding aspects of hygiene, nutrition, and environmental consciousness (AKHTAR et al., 2012). Several studies on antioxidant and antiradical extracts that confer color to films have been published (GÓMEZ-ESTACA et al., 2009a, b; NORAJIT et al., 2010; AKHTAR et al., 2012; BITENCOURT, 2013; LI et al., 2014). In addition, it has been well documented that extracts exhibit coloring and antioxidant properties that, in some cases, enable good control against photo-oxidation through reduced light transmission, especially UV radiation (PASTOR et al., 2013; NORAJIT et al., 2010; LI et al., 2014).

In general, the physical properties of the film, like moisture content and water solubility, remain unaltered upon the addition of extracts, because the extract and the film matrix interact well. Li et al. (2014) analyzed gelatin-based film incorporated with tea extracts through FTIR and verified that the extracts establish hydrogen bonds with gelatin,to reduce free hydrogen. On the other hand, works have revealed that extract incorporation in films may generate a heterogeneous surface with numerous small pores (NORAJIT et al., 2010), which could account for the high water vapor permeability of the incorporated films.

In the same way that natural extracts can be successfully incorporated into biodegradable films, the use of edible coatings in fruits and vegetables could improve food quality and shelf life. However, light may degrade the active compound during storage and deteriorate optical properties like luminosity. Nevertheless, some papers have shown that this technology can better control weight loss and respiration rates, allowing for longer storage time as compared with samples without coating (PASTOR et al., 2011; SUPAPVANICH et al., 2012; DAS et al., 2013).

4 Conclusion

Coatings and films containing antioxidant agents constitute a natural and biodegradable alternative to chemical preservatives, by acting as protective barriers and extending foods shelf life. The addition of antioxidant compounds to edible films and coatings can increase food safety and quality by inhibiting deterioration reactions of the food materials.

Determination of the antioxidant capacity helps to evaluate the antioxidant potential status of the food tissue, which is a function of the type and amount of bioactive compounds present in the material. Research has indicated that applying edible coating containing antioxidants to fresh-cut fruits effectively reduces browning while increasing the antioxidant capacity of the coated or packed food.

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