Chapter 12
Natural Ingredients as Additive for Active Antioxidant Food Packaging

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Abstract Active packaging materials have been developed to interact with the packed products and to extend their shelf life. When regarding antioxidant active packaging, it also has the advantage of allowing lower antioxidant addition to the food product. Although many synthetic antioxidant have already been used as antioxidant additives for polymers, recent studies have demonstrated that natural antioxidants are promising sources of additives. In this chapter, some aspects related to natural antioxidants have been reviewed and a few natural antioxidant sources, used as additive for active antioxidant food packaging materials, have been discussed.

Keywords Antioxidant • Active packaging • Natural additives

12.1 Introduction

Packaging materials are traditionally used to hold, protect, and sell food products. The protecting layer has the aim of preserving quality in order to minimize physical, chemical, and biochemical alterations that might contribute to the product degradation. The food industry, seeking for competitive advantages, search for safe and high-quality products. In this matter, packaging systems have been studied with the objective to interact with the packaged food, helping to extend shelf life (Azeredo et al. 2000). Such packaging materials are called "active packagings." The term "active" has been applied for the first time to food by Ted Labuza, in 1987, in a Scottish Conference about the nutritional impact of processed foods

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G.P.P. Lima and F. Vianello (eds.), *Food Quality, Safety and Technology*,
DOI 10.1007/978-3-7091-1640-1_12,

(Rooney 2005) and the article that literally applied the term "active packaging" was first published in December of 1986, entitled "Alcan Micro Match: an active packaging system" by Smith, J.D. (Mendes 2010).

Among the most important active packaging materials is the antioxidant packaging, which has a protective effect against the oxidation of the packed product (Vermeiren et al. 1999; López-de-Dicastillo et al. 2012). Its utilization in food can also allow the production of food with lower antioxidant addition (Rooney 1995; Soares and Hotchkiss 1998; Hayashi et al. 2006; Souza et al. 2011), helping to avoid allergies related to food preservative ingestion (Ahvenainen 2003).

Among the many existing antioxidant additives, those from natural sources have been cited as promising substitutes for synthetic additives in packaging materials (Hayashi et al. 2006; Grisi et al. 2008; Souza et al. 2011). In this work, some aspects related to natural antioxidants have been considered and a few natural antioxidant sources, used as additive for active antioxidant packaging of food materials, have been discussed.

12.2 Natural Antioxidants

Halliwell and Gutteridge (1995) defined antioxidants as "any substance that, when present at low concentrations compared with that of a substrate that can be oxidized, significantly delays or inhibits oxidation of that substrate," but later defined them as "any substance that delays, prevents or removes oxidative damage to a target molecule" (Halliwell 2007).

The antioxidant activity can be effective through various ways: as inhibitors of free radical oxidation reactions (preventive oxidants), by inhibiting formation of free lipid radicals; by interrupting the propagation of the autoxidation chain reaction (chain breaking antioxidants); as singlet oxygen quenchers; by synergism with other antioxidants; as reducing agents, converting hydroperoxides into stable compounds; as metal chelators, transforming metal pro-oxidants (iron and copper derivatives) into stable products; and finally as inhibitors of pro-oxidative enzymes (lipo-oxygenases) (Kancheva 2009; Carocho and Ferreira 2012).

The oxidative deterioration of fats and oils in foods is responsible for rancid odors and flavors, with a consequent decrease in nutritional quality and safety, caused by the formation of secondary, potentially toxic compounds. The addition of antioxidants is required to preserve food flavor and color, and to avoid vitamin destruction. Among synthetic antioxidants, the most frequently used to preserve food are butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), propyl gallate (PG), and tert-butyl hydroquinone (TBHQ). Reports reveal that BHA and BHT could be toxic, and their high manufacturing costs, along with the increasing consciousness of consumers with regard to food additive safety, created a need for identifying a more natural, and probably safer, antioxidant alternative (Moure et al. 2001; Bonilla et al. 2012).

The replacement of synthetic antioxidants by natural ones may have benefits due to health implications and functionality of food systems, such as solubility in both oil and water, which is of interest for application in emulsions (Moure et al. 2001). Vegetable materials contain many compounds with antioxidant activity. Several plants (seeds, fruits, leaves, and roots) and derivatives have been studied as sources of potentially safe natural antioxidants for the food industry. Among the antioxidant components most thoroughly investigated from vegetables sources, polyphenols, flavonoids, carotenoids, vitamins, organic acids, and tocopherols are the most studied (Kaur and Harish 2001; Oliveira et al. 2011).

Polyphenols are secondary plant metabolites and confer both desirable and undesirable food qualities to fruits and vegetables. They are ubiquitous in plant material and sometimes present as esters and glycosides, possessing antioxidant activity as chelators and free radical scavengers, with special impact over hydroxyl and peroxyl radicals, superoxide anions, and peroxynitrites. One of the most studied and promising compounds, belonging to the hydroxybenzoic group, is gallic acid, which is also the precursor of many other tannins, while cinnamic acid is the precursor of all the hydroxycinnamic acids (Krimmel et al. 2010).

Flavonoids and related compounds occur in many plant and fruits. They belong to an antioxidant group of compounds, composed of flavonols, anthocyanins, isoflavonoids, flavanones, and flavones. Their antioxidant properties are conferred on the phenolic hydroxyl groups, attached to aromatic ring structures, and they can act as reducing agents, hydrogen donators, singlet oxygen quenchers, superoxide radical scavengers, and even as metal chelators. They are also able to activate antioxidant enzymes, reduce α-tocopherol radicals (tocopheroxyls), inhibit oxidases, mitigate nitrosative stress, and increase levels of uric acid and other low molecular weight molecules. Some of the most important flavonoids are catechin, catechin-gallate, quercetin, and kaempferol (Prochazkova et al. 2011).

Carotenoids are a group of natural pigments that are synthesized by plants and microorganisms, but not by animals. They are frequently used as natural coloring materials, but they also possess antioxidant activity, especially in the presence of light. The main antioxidant property of carotenoids is against singlet oxygen. They can be separated into two vast groups: the carotenoid hydrocarbons, known as the carotenes, which contain specific end groups, such as lycopene and β-carotene, and oxygenated carotenoids, known as xanthophylls, such as zeaxanthin and lutein (Carocho and Ferreira 2013).

Many studies have evidenced the antioxidant potential of natural plants, vegetables, oils, fruits, teas, etc., and in Table 12.1 a list of some natural compounds with antioxidant activity is presented.

Studies about the use of these natural antioxidants, as food additives, have increased in last years, and results are encouraging.

Table 12.1 Antioxidants from natural sources

Sources of active compounds	References
Mango/acerola	Investigation on the antioxidant activity of leaves, peels, stems bark, and kernel of mango (*Mangifera indica* L.) (Sultana et al. 2012)
	Agronomic characterization and antioxidant potential of fruit from clones of the acerola plant (Cunha et al. 2012)
Palm oil/açaí	Phenolic acid analysis and antioxidant activity assessment of oil palm (*E. guineensis*) fruit extracts (Neo et al. 2010)
	Açaí (*Euterpe oleraceae*) “BRS Pará”: A tropical fruit source of antioxidant dietary fiber and high antioxidant capacity oil (Rufino et al. 2011)
Oregano oil/yerba mate tea	Sensory attribute preservation in extra virgin olive oil with addition of oregano essential oil as natural antioxidant (Asensio et al. 2012)
	Antioxidant activity of yerba mate extracts: Interactions between the individual polyphenols (Valerga et al. 2013)
Wine/jabuticaba	Prediction of total antioxidant capacity of red wine by Fourier transform infrared spectroscopy (Versari et al. 2010)
	Jaboticaba peel: Antioxidant compounds, antiproliferative and antimutagenic activities (Leite-Legatti et al. 2012)
Cocoa/coffee	Comparison of the antioxidant activity of commonly consumed polyphenolic beverages (coffee, cocoa, and tea) prepared per cup serving (Richelle et al. 2001)

12.3 Antioxidant Food Packaging

Incorporation of antioxidants into packaging films has become very popular, since oxidation was recognized as one of the main causes of food spoilage. Oxidation alters the taste (rancidity) and nutritional quality (loss of vitamins and essential fatty acids) of foods, and generates reactive and toxic compounds, which may represent a danger to consumers (Laguerre et al. 2007).

Synthetic antioxidants are the most used antioxidant additives to prevent/retard the oxidation process. Such additives recently received a great deal of interest due to toxicological concerns, prompting an increased interest in natural antioxidants, such as those derived from fruits, vegetables, plants, and others (Bonilla et al. 2012).

Recently, researches about the applications of natural antioxidants in active packaging have being cited in the literature, as reported in Table 12.2.

Antioxidants properties of protein-based films from fish skin gelatin, incorporated with different citrus essential oils, including bergamot, kaffir lime, lemon, and lime, were investigated. Films incorporated with lemon essential oil showed the highest ABTS radical scavenging activity and ferric reducing antioxidant power, among other modified films (Tongnuanchan et al. 2012).

Souza et al. 2011 developed several active films from starch cassava, containing mango and acerola pulps as antioxidant additives, using a response surface methodology for film characterization. The films were used to pack palm oil (maintained for 45 days of storage) under accelerated oxidation conditions (63 % relative

Table 12.2 Natural antioxidant additives for active packaging materials

Antioxidante natural	Based films	Packaged product	Results	References
Green tea extract	Chitosan Gelatin		The incorporation of aqueous green tea extract into chitosan films improved mechanical and water vapor barrier properties and enhanced polyphenolic content and antioxidant activity of the films The incorporation of GTE into gelatin films enhanced the total phenolic content, DPPH radical scavenging activity, and reducing power. However, DPPH radical scavenging activity and reducing power decreased during storage	Siripatrawan and Harte (2010) Wu et al. (2013)
Essential oils of pimento and oregano	Milk protein	Beef muscle	Oregano-based films stabilized lipid oxidation in beef muscle samples, whereas pimento-based films presented the highest antioxidant activity	Oussalah et al. (2004)
Marigold extract	Low-density polyethylene	Soybean oil	Spectroscopic, optical, and mechanical properties of the films were affected by the addition of the marigold extract. However, bags made of the films showed a positive effect on soybean oil stability when used as packaging	Colín-Chávez et al. (2012)
Barley husks	Low-density polyethylene	Blue shark muscle	The results confirm the efficacy of active packaging with a natural antioxidant derived from barley husks to slow the progress of lipid hydrolysis and increase oxidative stability in blue shark muscle	Pereira de Abreu et al. (2011)
Mango and acerola pulps	Starch	Palm oil	Although the film-forming procedure affected the	Souza et al. (2011)

(continued)

Table 12.2 (continued)

Antioxidante natural	Based films	Packaged product	Results	References
			antioxidant compounds, the results indicated that antioxidants were effective additives for protecting the packaged product	
Palm fruit	Cassava starch	Soybean oil	Results have indicated that the palm antioxidant compounds in the packaging material were preferentially oxidized, lowering the oxidation of the packed product	Grisi et al. (2008)
Cocoa/coffee	Cassava starch	Palm oil	Results have indicated efficacy when protecting the product in accelerated storage conditions. Besides the antioxidant effect, the resulting films also were colored by the cocoa and coffee pigments and flavored by their pleasant natural flavors	Silva (2009)
Barley husks	Low-density polyethylene	Blue shark muscle	The results confirm the efficacy of active packaging with a natural antioxidant derived from barley husks to slow the progress of lipid hydrolysis and increase oxidative stability in blue shark muscle	Pereira de Abreu et al. (2011)
Mustard meal	Xanthan gum	Smoked salmon	The composite coating improved the stability of smoked salmon against lipid oxidation without imparting a negative sensory quality to the salmon	Kim et al. (2012)

humidity and 30 °C) to simulate a storage experiment. Bio-based films were prepared (casting) by dispersing cassava starch (4 %), sucrose (1.4 %), inverted sugar (0.7 %), and mango and/or acerola fruit pulp (0–20 %) in distilled water, according to a (2^2) second-order experiment design (for a total of 11 experiments). It was noted that palm oil packed in bio-based films containing mango and acerola pulps showed a low peroxide index, when compared to the product packed in control films. The results indicated the efficacy of fruit pulps as antioxidant additives, acting to protect the packaged product. This effect can be considered concentration-dependent; palm oil packed in films with low pulp concentrations presented a higher oxidation value (IP = 64.27 %), when compared to packed in films with higher pulp concentrations, showing a lower PI value (IP = 31.62 %), during the same storage period. The increase of carotenoid content in the film showed a higher correlation with peroxide index (98.39 %) than polyphenols (56.99 %), confirming the efficacy of carotenoids incorporated into films in comparison to polyphenols. As mango pulp possesses a higher amount of carotenoids than acerola pulp, the product packed in films containing mango pulp showed less oxidation. It was observed by authors that the packaging material, rather than the packaged product, was oxidized, due to the active compound loss during storage. Figure 12.1 shows the mango and acerola antioxidant film and the surface response of the increase in the peroxide value of the packed oil after 45 days storage (63 % relative humidity and 30 °C), influenced by the mango and acerola pulp concentration as additive.

A similar behavior was observed in films containing palm fruit pulp and its oil, as added antioxidants, which were used to pack soybean oil. In this case, a decrease in TC ranging from 79.90 to 99.60 % was observed during 90 days of storage (Grisi et al. 2008). Active polymers added to palm oil had presented the best antioxidant effect in packed oil (64 % RH, 30 °C). Authors noticed that increasing the palm fruit derivates' (extract and oil) addition decreased the final film total carotenoid content. However, when observing the total carotenoid content in the packed product, the higher was the antioxidant addition to the film, especially palm oil, the higher was the total carotenoid content. Results have indicated that, also in this study, the packaging material was oxidized, rather than the packaged product. Besides the presence of fibers, resulting from palm fruit addition, and oil incorporation, the polymer appeared with good transparency. Figure 12.2 shows the film appearance and transparency after palm fruit addition, and the surface response surface of the palm fruit extract vs. palm oil effect on the total carotenoid content (TC) of the packed product (soy bean oil) after 90 days of storage (63 % relative humidity and 30 °C).

12.4 Conclusions

Literature results have demonstrated that natural antioxidants can be incorporated, as additives, in conventional or biodegradable active packaging materials. Unfortunately, food and pharmaceutical industries have taken little advantage of such an innovation opportunity. A possible reason can be the lack of studies about large-scale production of such antioxidant materials.

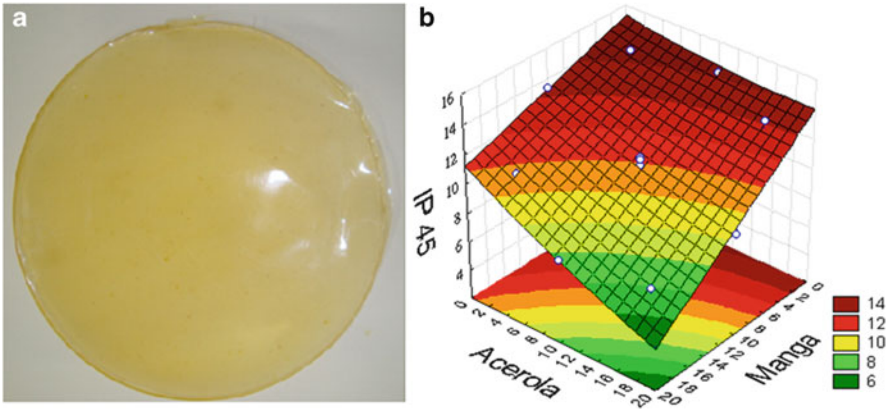

Fig. 12.1 (**a**) The film appearance and (**b**) the effect of mango and acerola addition as additive on the peroxide value increase of the packed oil after 45 days at storage (63 % relative humidity and 30 °C), Souza et al. (2011)

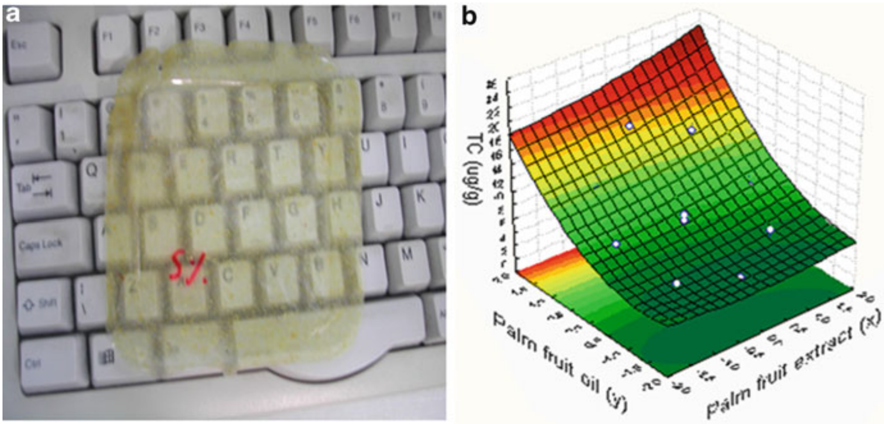

Fig. 12.2 (**a**) The palm fruit film appearance and (**b**) the response surface of the total carotenoid content in packed oil after 90 days at storage (63 % relative humidity and 30 °C), Grisi et al. (2008)

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