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Review

Advances in antioxidant active food packaging

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

Introduction

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

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

Antioxidant active packaging

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

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

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

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

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

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

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

Antioxidant active packaging manufacture and application

There are basically two methodologies for producing antioxidant packaging systems:

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