Food Engineering Progress
Vol. 7, No. 4. pp. 195~201 (2003.11)

총 설

Active Packaging Systems for Preventing Oxidation

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Abstract

The rapid growth of the food packaging field is powered by the ever growing health conscious consumers and demand for fresher and higher quality foods. Active packaging technologies provide solutions for extending products shelf life with specially altered packaging systems. Among the several shelf life enhancer systems, active packaging system for preventing oxidation is discussed in this paper. Oxidation is generally regarded as the main factor in the development of rancidity of fats and oils. The oxidative processes result in the food becoming unacceptable for consumers. Such oxidation is inhibited by exclusion of oxygen and by the presence of antioxidants. First of all, oxygen scavengers made up of substances which chemically or enzymically react with oxygen were developed to remove oxygen. The commercial oxygen scavengers such as “ageless sachet”, “platinum catalyst”, and “glucose/oxidase enzyme” have been greatly discussed in their action mechanisms and applications. The use of antioxidants in packaging manufacture has so far been limited to stabilizing the polymer during the processing or retarding the change of polymer's physical properties during storage when UV irradiated. However, a further benefit derived from incorporation of an antioxidant into the polymer is more interesting for its ability to retard lipid oxidation of the packaged food via slow migration of an antioxidant from the polymer to food. In view of which, in this paper we will review some oxygen scavenger systems as well as antioxidant-impregnated or antioxidant-coated polymer packaging material.

Key words: active packaging, antioxidant-impregnated film, antioxidant-coated film, oxidation

Introduction

The food packaging is a rapidly growing field in order to satisfy today's consumers who are health conscious than ever before and are demanding foods that is fresher and of higher quality. There is a continuous growing need for the research and development into food preservation by extending its shelf life while providing the high quality of food. At the initial stage of active packaging, controlled atmosphere packaging (CAP) and modified atmosphere packaging (MAP) were introduced into the food packaging market for improving the shelf life and nutritional quality of it's contents. CAP usually refers to storage in which the composition of the atmosphere has been altered with respect to the proportions of O_2 and/or CO_2, and in which the proportion of these gases are carefully controlled, usually within ±1% of the desired value. MAP does not differ in principle from CAP, except that the control of the gas concentration in less accurate. The first practical attempt for conventional CAP or MAP was hypobaric package of vegetable and fruit for retardation respiration, reducing the auto-catalytic production and reducing decay caused by microorganism. However, active packaging is a more advanced concept of CAP or MAP. The key concept of active packaging is the controlling of permeability of undesirable gases and water vapor as well as the controlled releasing of other compounds which have preservative effect on the food by continuous interaction between packaging film itself and the food. The active packaging, which is commercially used as gas scavengers or emitters, was shown in Table 1. They involve the specific control of the concentration of oxygen, carbon dioxide, ethanol,

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Table 1. The commonly used active packaging system (data from Sacharow, 1988).

Method	Variations	Products
Oxygen scavenger	1-Powdered iron oxide 2-Ferrous carbonate 3-Iron/sulfur 4-Metal(platinum) catalyst 5-Glucose/oxidase enzyme 6-Alcohol oxidase	cookies, cured meats, pizza crusts, bread rice cakes
Carbon dioxide scavenger/ emitter	1-Powered iron oxide/calcium hydroxide 2-Ferrous carbonate/metal halide	coffee, fresh meats/ fish
Preservative releaser	1-BHA/BHT 2-Sorbates 3-Mercurial compounds 4-Zeolite system	produce, meat, fish, bread, cereals, cheese
Ethanol emitter	1-Alcohol spray 2-Encapsulated ethanol	cakes, bread, fish, buns, tarts
Moisture absorber	1-PVA blanket	fish, meat poultry
Temperature control	1-Non-woven plastics 2-PET containers 3-Foams	prepared entrees, meats, poultry, fish

ethylene or water vapor in sealed packages. Among them, oxygen scavenger and antioxidant emitting system are very important in protecting oils, fats and fat soluble components such as vitamins, carotenoids and other nutritive ingredients. Therefore, it would be useful to provide a short review about oxygen scavenger systems as well as antioxidant-impregnated or antioxidant-coated polymer films.

Oxygen Scavengers System

oxygen scavengers are made up of substances which chemically or enzymically react with oxygen. They actively remove oxygen from the atmosphere enclosed in the food package. In this way, they preserve oxygen sensitive goods more efficiently than gas flush or vacuum packaging techniques that do not have any action after the sealing of the package. The elimination of oxygen in the headspace of the package reduces problems due to mold growth, oxidation of oils and fats, discoloration or change in tastes.

Chemical system

Mitsubishi produces an oxygen absorber called “ageless” which chemically scavenges oxygen. This is a sachet filled with powdered iron oxide which is placed in the food package itself. The sachet is very permeable to oxygen and the chemical reaction consists of oxidizing iron to the ferric state. A residual level of 0.01% oxygen in the modified atmosphere of the package is achievable (Abe and Kondoh, 1989). The nominal chemical reaction is: $4\ Fe + 3\ O_2 \rightarrow 2\ FeO_3$.

The amount of iron that needs to be used depends on the initial level of oxygen in the headspace, the amount of dissolved oxygen that is in the food, and the film permeation rate (Labuza and Breene, 1989). Nakamura and Hoshino (1983) have calculated the stoichiometric basis for the reaction of iron with oxygen at atmospheric pressure and different relative humidities. The reaction is very complex, but in general, 1 gram of iron can react with 0.0136 moles of oxygen which is equivalent to 0.336 L.

This system is currently used for many foods such as bread, cake, cookies, pastry, cured or smoked meats, dried tea, cheese, potato chips, dried egg, spices, nuts, coffee, and chocolates. Nakamura and Hoshino (1983) showed that white bread wrapped with a sachet in a polypropylene film can be kept for more than 45 days without any appearance of molds while it became moldy in 4-5 days without any sachet. However, this method has its limitations. It can be used only when the water activity of the food is high enough so that the iron will oxidize. Furthermore, there is always the risk that the toxic pouch may be accidently consumed, regardless of the warning label written: “do not eat”. The Japanese company selling the “Gerber baby cereal foods” has eliminated this risk by incorporating sachet inside the package itself.

Other oxygen scavengers have also been developed. American Can Co. developed a scavenger film that used a platinum or palladium catalyst as a reaction oxygen with hydrogen (Zimmerman, *et al*., 1974). Waletzko and Labuza (1976) showed this to be very effective in extending the shelf-life of intermediate moisture foods for the space program or in the military food caches. Oxygen levels as low as 0.001% were maintained over a 6 month period of time. However, mass commercial use of this system was not viable with the cost of the film being 30 times greater than that of foil alone.

The Carnation Co. has a patent which uses a sulfite salt and copper sulfate as the catalyst for scavenging oxygen. Sodium sulfite and the copper must be intimately mixed and ground and then formed into pallets under high pressure. The reaction is SO^{-3} to SO^{-4}. The advantages of this is that the palletized particles can react without the presence of water because of their intimate contact. In addition, since they can be ground to a fairly fine particles size, they should be easily incorporated into a film.

Enzyme System

Glucose/oxidase enzyme may be used to control the level of oxygen in food package. Basically, it transfers the two hydrogens from the -CHOH group of the glucose to a molecule of oxygen. This results in the formation of a glucono-delta-lactone molecule and a molecule of hydrogen peroxide. The lactone is then oxidized by water to gluconic acid. Reed (1966) has summarized the commercial applications of this system. One use is the elimination of oxygen from bottle beer and wine. However, it is used mainly in the industrial preparation of dried or frozen whole eggs to degrade the glucose they contain. The glucose, if not removed, reacts with egg proteins during preparation giving it a brown color and producing off-flavors. The enzyme is currently added directly to egg magma. Further research is being carried out to impregnate the surface of packaging materials with the enzyme (Borque, 1984).

Besides glucose oxidase, ethanol oxidase which oxidizes ethanol to acetaldehyde has potential to control the level of oxygen in food package. This reaction has the advantages in that it is extremely rapid and can react in a wide water activity range. However, due to no kinetic data available for this enzyme, it is not easy to predict the exact amount of enzyme to prevent an off odor in the package. In addition, considerable acetaldehyde would be formed which would give the food a yogurt-like odor.

Type of Antioxidants

The term “antioxidant” is generally applied to those compounds that interrupt the free-radical chain reactions involved in lipid oxidation. Generally, antioxidants are classified into five types: (i)primary antioxidants; (ii) oxygen scavengers; (iii) secondary antioxidants; (iv) enzyme antioxidants; (v) chelating agents or sequestrants (Table 2). These antioxidants can again be devided into two groups, natural and synthetic. Generally, antioxidants are used for the prevention of oxidation of lipid and fats via a direct and indirect indroducing method. The direct method refers to the process where the antioxidants are directly introduced into the foodstuffs. The latter, indirect, refers to the method where the antioxidants are impregnated into the packaging material from where the antioxidants then migrate to the foodstuffs. The migration rates and amounts of antioxidants are varied according to the characteristics of polymer films, the interaction between polymer films and antioxidants, and the type of impregnated antioxidants.

Antioxidant-Impregnated or Anioxidant-Coated Polymer Film

In food packaging, antioxidants impregnated into the packaging material may have a dual function to protect the polymer from oxidative degradation during processing and to delay protect the onset of oxidation of the packaged foodstuff during storage. In the former case, Jipa *et al* (1997) showed the inhibition of thermal and irradiation oxidation of low density polyethylene (LDPE) in the presence of a number of phenols such as 1-pyrenol and phenanthrol isomers. Mallegol *et al*

Table 2. The classification of antioxidants and its action mechanism.

Type	Action mechanism	Antioxidants
Primary antioxdants	those compounds, mainly phenolic substances, that terminate the free radical chains in lipid oxidation.	natural and synthetic tocopherols, akyl gallates, BHA, BHT, TBHQ, etc.
Oxygen scavengers	react with oxygen, and can thus remove it in a closed system.	acorbic acid(Vitamin C), ascorbyl palmitate, erythorbic acid(D-isomer of ascorbic acid) and its sodium salt, etc
Secondary antioxidants	function by decomposing the lipid hydroperoxides into stable end products.	dilauryl thiopropionate and thiodipropionic acid
Enzymic antioxidants	function either by removing dissolved/headspace oxygen, e.g. with glucose oxidase, or by removing highly oxidative species from food system, e.g. with superoxide dismutase.	glucose oxidase, superoxide dismutase, catalase, glutathione peroxidase, etc.
Chelating agents or sequestrants	chelate metallic ions such as coppper and iron that promote lipid oxidation through a catalytic action.	citric acid, amino acid, EDTA, etc.

(2001a, 2001b) showed that the α-tocopherol is comparable to or better than BHT in preventing the oxidation of high density polyethylene (HDPE) exposed to *v*-rays. Irganox 1010 (-3', 5'-di-*tert*-butyl-4'-hydroxyl-phenyl) has a poorer antioxidant activity in ã-irradiated HDPE at 30^{o}C. Commercially, Irganox and Ionox (complex high molecular weight compounds) are mainly functioned as an antioxidant stabilizer of PE and PP films because polyolefins need the addition of stabilizers, primarily antioxidants, to preserve their chemical and physical mechanical properties. Schwope *et al* (1987) have reported considerably less migration of Irganox as compared to BHT in corn oil from LDPE films. Marcato *et al* (2003) reported on the migration of primary antioxidants, Irganox 1010 and Irgafos 168, from different polymeric materials into oily vehicles. The migration of Irganox 1010 and Irgafos 168 varied according to the polymer crystallinity grade and structure.

A further benefit derived from incorporation of an antioxidant into the polymer is that it can also retard lipid oxidation of the packaged food via volatilization from the packaging surface followed by diffusion into the food. Antioxidants which have been suggested for use in active packaging are butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), ascorbic acid and α-tocopherol. Tawfix and Huyghebaert (1999) evaluated the effect of different factors including (i) type of packaging material (glass, polyethyleneterephthalate, polyvinylchloride, polypropylene, and polystyrene), (ii) antioxidants in the plastics (BHA and BHT) on the stability and quality of market vegetable oils. The results showed that both BHA and BHT were migrated from plastics films to vegetable oils during storage. However, The rate of oxidation was not reduced by antioxidant migration for it was not enough amount to prevent the oxidation of oily food during storage. Sharma *et al* (1990) studied the effect of PE film with BHA and BHT or without them on the storage stability of refined sunflower oil and groundnut oil at 37^{o}C. They concluded that changes in peroxide value and thiobarabituric acid were significantly less in the presence of plastic films than in control samples. When Kiritsakis (1984) studied the oxidative stability of olive oil stored in glass and PE, he concluded that glass bottles provide better protection from oxidation than PE plastic bottle do. Kaya *et al* (1993) studied the effect of permeability on the shelf-life of sunflower and olive oils by measuring their peroxide values. Kleen *et al* (2002) investigated the incorporation of BHA into zein-based films for stabilizer of lipids against oxidation. Incorporation of 4000 ppm of BHA into the zein-based films eliminated peroxide formation during accelerated UV storage conditions.

The rate of loss of BHT (synthetic) from multilayer coextrusion film structures was much greater than the rate of loss of α-tocopherol (natural) under the same storage conditions (Bailey, 1995). Similar results were obtained by Wessling *et al* (1998) for BHT and á-tocopherol impregnated LDPE film in contact with fatty foods and fatty food stimulating liquids. In addition, Lee (1999) found that the effect of a BHT impregnated laminate film structure was greater than the effect of an á-tocopherol impregnated laminate film structure in inhibiting lipid oxidation of a model food product during 45°C storage. However, Ho *et al* (1994) have shown α-tocopherol to be more effective at lower levels than those required for synthetic antioxidants such as Irganox 1010 and BHT in reducing the off-flavor from blow molded HDPE bottles. Furthermore, due to growing concern regarding unfavorable migrants, natural form of antioxidants to that of a synthetic as a polymer stabilizer is drawing highlighted interest. Wessling *et al* (1999) investigated the retention of α-tocopherol in LDPE and PP film in contact with diverse food products with varying fat and alcohol content. Generally, both the LDPE and the PP films showed good retention of α-tocopherol in contact with the various foods and food-simulating liquids. However, different food characteristics, such as contact phase properties, and fat, alcohol and acid contents, seemed to influenced the retention of α-tocopherol in the LDPE material (Table 3). Unlike LDPE, PP did not show any interaction with the ingredients of food. The α-tocopherol content in the PP film remained more or less unaffected (Table 4). Therefore, LDPE seems to offer the possibility of active transfer of α-tocopherol to products with a high fat or alcohol content. In PP, on the other hand, the α-tocopherol remained in the film and might be able to scavenge permeating oxygen from the outside at the surface of a packaged food. LDPE films incorporat-ing α-tocopherol-impregnated LDPE films were found to have an enhancing effect on the stability of a linoleic acid emulsion stored in contact with films at 6°C (Wessling *et al.*, 2000). However, the optimum concentration of α-tocopherol should be considered with respect to a positive effect on the oxidation stability, but an adverse effect on LDPE polymer characteristics such as impact resistant, tear strength and elongation. Armitage *et al* (2002) evaluated the antioxidant activity of egg albumen coating with natural antioxidants such as fenugreek, rosemary, and α-tocopherol in diced raw and diced cooked poultry breast meat. The cooked egg albumen coated samples showed malondialdehyde (oxidative compound) content changes of 1.56×10^{-7} M for 4 d of refrigeration, compared to 1.59×10^{-6} M change in the cooked control. Raw control changes of 1.97×10^{-6} M versus 1.67×10^{-6} M for raw rosemary coated samples. In raw and cooked studies, egg alumen coating only showed most effective against lipid oxidation. Lee *et al* (2003) tested oxidative deterioration with α-tocopherol coated paper in a binder of vinyl acetate-ethylene copolymer. α-Tocopherol migrated into an o/w type emulsion and reached an equilibrium level of about 6%.

Future Perspectives

So far, the functional polymer film which continuous release antioxidant into foodstuffs have been developed under the following two basis; (i) antioxidants-impregnated polymer film (ii) polyolefins polymer film coated with antioxidants in the plastic binding medium. (Han and Floros, 1997; Wessling *et al.*, 1999;

Table 3. α-Tocopherol content (%) in the LDPE film after storage at 4°C in contact with the various foods and food-stimulating liquids (data from Wessling *et. al.*, 1999).

Storage time (weeks)	Mayonnaise	Cream	Low-fat milk	Tap water	Orange juice	95% v/v ethanol	95% v/v ethanol +α-tocopherol	White wine
0	100	100	100	100	100	100	100	100
1	69	91	91	64	96	20	100	92
2	46	81	93	34	107	2	99	95
3	51	79	NA	33	103	NA	86	107
4	43	77	80	31	95	1	93	103

NA: not analysed

Table 4 α-Tocopherol content (%) in the PP film after storage at 4°C in contact with the various foods and food-stimulating liquids (data from Wessling *et. al.*, 1999).

Storage time (weeks)	Mayonnaise	Cream	Low-fat milk	Tap water	Orange juice	95% v/v ethanol	95% v/v ethanol +α-tocopherol	White wine
0	100	100	100	100	100	100	100	100
1	96	104	87	92	99	99	119	99
2	88	100	89	88	105	93	113	91
3	95	97	90	NA	NA	97	112	95
4	101	104	99	95	101	100	121	93

NA: not analysed

Devlieghere *et al*., 2000; Hong *et al*., 2000; Kim *et al*., 2000; An *et al*., 2000; Ha *et al*., 2001). However, due to the heat involved in the film fabricating process, degradation of antioxidant is inevitable in the above mentioned cases. In addition, migration of the remaining antioxidant is deterred due to the entrapment that occurs in the complex matrix system of the polymer. Hence, the very few antioxidants that succeed to reach the foodstuffs are of such low proportions that can not act as an antioxidant. These occurrences, however, can not be offset by increasing just the adding level of antioxidants due to the negative effect on the mechanical and the physical properties of the film. Therefore, a whole new concept of composit structured polymer film needs to be developed with its focus on controlling the rate of migration. One alternative is a composite polymer film coated with the edible biopolymer prepared from various proteins and polysaccharides such as methyl cellulose, high-amylose starch, collagen, wheat gluten, soy protein, whey protein and zein.

Acknowledgements

This work was supported by the Korea Science and Engineering Foundation (Project # R01-2002-000-00154-0).

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