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식품포장의 항산화제 첨가 플라스틱의 용도

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The Applications of Antioxidant Impregnated Polymers to Food Packaging

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요 약

플라스틱 포장재의 주요 기능은 식품을 수송, 보관과정에서 안전하게 보존하는 것이다. 식품과 플라스틱 포장재 간의 반응은 식품의 품질과 안전성 문제에 있어서 성당한 이슈가 되고 있는데 이는 주로 플라스틱에 남아있는 잔류용제, 단량체, 첨가물 등이 식품으로 전이되는 문제들이다.

플라스틱 포장재에 항산화제를 첨가하는 것은 필름의 열화는 물론 포장된 식품, 특히 유지가 많은 제품의 산화를 막을 수 있다. 현재 BHT와 같은 항산화제를 플라스틱 포장재에 적용하는 것이 상업화되어 제품의 유통기간을 연장시키는 방법으로 사용되고 있다. Alpha tocopherol은 가장 중요한 자유기 제거제의 하나로 생물 시스템에는 잘 알려져 있는데 이것을 포장재에 사용함으로써 생산자와 소비자 모두 매우 긍정적인 반응을 보이고 있다. Alpha tocopherol은 폴리올레핀계 레진에 적용되어 BHT를 대체하고 있다.

이 연구는 포장재와 제품간의 증발-흡착 메카니즘을 이용한 항산화제의 효과와 그 적용, 그리고 이러한 메카니즘을 예측할 수 있는 분석기법을 설명하였다.

Abstract

The main function of plastic materials in food packaging is to preserve a food for safe transportation and storage. The interactions between food and plastic materials in food packaging have become increasingly important for food quality and safety because monomer, low molecular weight components, or additives of plastic packaging materials can migrate into a food. The use of antioxidants in plastic materials can help protect the degradation of film itself and retard the oxidation of a packaged food containing lipid, through the migration of antioxidant from the packaging to a product via an evaporation / sorption mechanism. Nowadays, antioxidant (BHT) impregnated plastic materials are used for commercial food packaging application with the intention of achieving an extended shelf life of food in USA.

Alpha tocopherol, as one of the most important free radical scavengers, has been well known in biological systems. Moreover, the potential use of alpha tocopherol as an additive for polymers used in the packaging industry may offer the most positive perception from both consumers and manufacturers. Alpha tocopherol has been used as an antioxidant for polyolefin resins fabricated to both bottles and film and has applications in the food packaging industry as a replacement for BHT. Today, alpha tocopherol offers an attractive choice for use as an antioxidant in polymers.

This paper provides an overview of antioxidants effectiveness and applications for its use by the food packaging industry based on the evaporation-sorption mechanism of a packaged model product, where quality is associated with lipid oxidation. Important analytical techniques for predicting antioxidants interaction between the package system and product are discussed.

Key words : antioxidant, packaging, polymer, BHT

1. Lipid Oxidation in Food System

Oxidation of food products is a major factor in the development of off-flavors due to oxidative chemical changes of lipids. Lipids are one of the major constituents in many food systems.

The main cause of lipid degradation involves oxidative and hydrolytic reactions. The oxidative reaction, referred to as autoxidation, can occur from progressive reactions with atmospheric oxygen to produce free radicals. Here, autoxidation is an autocatalytic reaction, where the rate of oxidation increases with reaction time. In such a case, the oxidation induction period or the initiation step is a slow process and then increases as the oxidation reaction progresses (Chan, 1987). These oxidative reactions induce unstable physical and chemical changes in the stored food product. Frankel (1991) described the autoxidative mechanism that leads to the formation of free radicals to produce off-flavors from polyunsaturated edible oils. The hydrolytic reactions occur by the reaction of lipase enzymes, which act on the triglyceride ester linkage, resulting in the hydrolysis of lipids. Controlling temperature conditions can minimize the oxidation and hydrolytic reactions associated with enzymatic activity.

The oxidation of lipids is catalyzed by the presence of light, trace metals, lipoxygenase enzymes, or the effect of heat to initiate the production of free radicals. The free radicals react with oxygen to yield the primary products of lipid hydroperoxides. Unsaturated fatty acids are susceptible more specifically to oxygen attack leading to the free-radical mechanism. The hydroperoxides formed from the reaction of unsaturated fatty acids with oxygen are also catalyzed by the action of lipoxygenase (Jadhav, et al., 1996).

Also, for the case of food systems with relatively low amounts of unsaturated fats, oxidative rancidity can still play a role as the main influence of deterioration of food quality during storage. The off-flavors arising in a food system with higher amounts of unsaturated fatty acids can be absorbed in the lipid, since most of the off-flavor compounds are lipophilic, volatile compounds

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(Roozen, et al., 1994).

The main concerns involving the oxidation of a stored food product occur due to the lipid oxidation, and are typically addressed by controlling the environmental conditions of product storage, which include: temperature, relative humidity, and light. The incorporation of antioxidants into food products also helps to extend the product shelf life, by retarding oxidation processes under normal storage conditions. The oxidative process in food systems containing unsaturated fatty acids can be retarded by adding antioxidants, either directly to the food products or by incorporating them into the packaging materials (Coulter, 1988).

2. Mechanism of Lipid Oxidation

The mechanism of lipid oxidation has been well defined by a number of studies (Chan, 1987; Frankel, 1984) and can be described as an autocatalytic chain reaction that can be viewed as involving three major steps, namely:

initiation, (2) propagation, and (3) termination. The oxidative mechanism is influenced by several factors such as oxygen, light, heat, heavy metals, and enzymes.

Below, each step of the autoxidation mechanism is discussed briefly.

Initiation: $RH \longrightarrow R\cdot + \cdot H$

$$RH + O_2 \longrightarrow R\cdot + \cdot OOH$$

Propagation: $R\cdot + O_2 \longrightarrow ROO\cdot$

$$ROO\cdot + RH \longrightarrow ROOH + R\cdot$$

Termination: $R\cdot + R\cdot \longrightarrow RR$

$$R\cdot + RO\cdot \longrightarrow ROR$$

$$R\cdot + ROO\cdot \longrightarrow ROOR$$

The initiation step occurs when a labile hydrogen is abstracted from the unsaturated lipid (RH) to produce the alkyl radical (R•). In the propagation step, oxygen reacts rapidly with the alkyl radical to form the peroxyl radical (ROO•). The peroxyl radical reacts with a hydrogen atom abstracted from another unsaturated lipid molecule to form an unstable hydroperoxide (ROOH), and another free alkyl radical (R•). The decomposition of hydroperoxides (ROOH) leads to the formation of aldehydes and esters, and other secondary products. In the initial stages of the propagation step, one begins to observe the deterioration of product flavor. In the termination step, the chain reaction can be stopped by the formation of non-free radical reaction products. This same trend is reflected in the length of the induction period for lipid oxidation, which was determined by Maskan (1993) from storage stability studies using an accelerated shelf-life testing procedure.

An alternative mechanism of lipid oxidation involves the reaction of singlet oxygen with the double bond of a fatty acid. The reaction between a lipid and oxygen typically proceeds with the lipid molecule in a singlet electronic state, and the oxygen molecule in a triple state (Bradly and Min, 1992), which is the common ground state energy level for oxygen. For initiating the autoxidation reaction involving the singlet lipid with the triple oxygen directly, a high activation energy is required for the reaction to proceed (Jadhav, et al., 1996). Therefore, an initiator such as a sensitizer, high temperature, or a lipoxygenase enzyme plays an important catalytic role to provide the capability of altering triplet oxygen to singlet oxygen for lipid oxidation. Singlet oxygen can react at the end of the double bond of a lipid and yield a hydroperoxide (Raws and Vansanten, 1970). Singlet oxygen is generated by the transfer of energy from a sensitizer such as chlorophyll or myoglobin with ultraviolet light. Ultraviolet light, as the main factor, is required for this oxidation mechanism to occur. (Frankel, 1984).

The qualitative data presented in most studies (Frankel, et al., 1989, Hallberg, et al., 1991, Gardner, 1985) shows that hexanal is the major adehyde formed from autoxidation of polyunsaturated fatty acids. Quantitatively, hexanal has also been identified as one of the major oxidation products, resulting from autoxidation of linoleic acid (Schieberle and Grosch, 1981; Henderson, et al., 1980). The quantification of hexanal in low fat food products, as a measure of oxidative rancidity, is a simple and effective analytical method, since hexanal is a stable compound and less reactive in the low fat model food product than other secondary products. When the hexanal level increases above a certain concentration in dehydrated and low-fat foods containing linoleic acid, quality deterioration by lipid oxidation is indicated.

3. Antioxidants

Antioxidants are a major class of compounds (21 Code of Federal Regulations (CFR) 170.3) that prolong the onset of deterioration, rancidity, or discoloration of food products, which occur due to oxidation, as defined by the United States Food and Drug Administration (FDA) (Dziezak, 1986).

Antioxidants function by retarding or inhibiting the initiation, and propagation reactions in the free radical autoxidation process associated with lipid oxidation.

Such a reaction scheme is shown below.

$$R\cdot + AH \longrightarrow RH + A\cdot$$
$$ROO\cdot + AH \longrightarrow ROOH + A\cdot$$

Here, the antioxidant (AH), which has a phenolic hydroxyl structure, can donate a hydrogen atom to a free radical (R•) or a peroxyl radical (ROO•) of the lipid, thus terminating the propagation step. Reaction of a hindered phenolic antioxidant with a free radical forms a free phenoxy radical (A•), which is stabilized by the electron delocalization in the aromatic ring.

Antioxidants of the hindered phenolic type are classified as either synthetic or a natural product. Currently, the application of α-tocopherol to a food product directly or indirectly is increasing, as the trend toward the use of natural antioxidants increases (Shahidi and Wanasundara, 1995). This affords a greater biological benefit and reduces health risk, even though synthetic antioxidants applied to food products are effective and inexpensive (Landvik et al., 1996).

Many food manufactures tend to substitute synthetic antioxidants with foods containing natural antioxidant substances (Marshell, 1974). In general, the use of antioxidants for a food product directly is limited to 200-300 ppm(w/w) of butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), and tertiary butylhydroquinone (TBHQ), or 200-500 ppm of the gallates, for the stabilization of fats and oils (Madhavi and Salunkhe, 1996).

Porter (1977) evaluated both natural and synthetic phenolic antioxidants in a dry model system that had linoleic acid monolayers on activated silica gel. BHA was found to be highly effective, even though a monohydric compound. Shahidi and Wanasundara (1995) reported that canola extracts and some of the flavonoids (morin, myricetin, quercetin, and rutin) were more effective than BHA and BHT in preventing the oxidation of canola oil. The antioxidant molecule may react with the free hydroperoxide radicals. The free antioxidant radicals are produced after the active free radicals are deactivated. The antioxidant free radicals are more stable and can undergo oxidation to quinones or combine with other free radicals.

α-Tocopherol shows a good ability to inhibit lipid oxidation or to extend the induction period of free radical oxidation, as well as to slow the propagation step of the autoxidation process (Widicus and Kirk, 1981; Pershen, et al., 1995).

4. Antioxidants for the Polymer Plastic Film

Currently, polymeric packaging materials are widely used due to commercial advantages of their cost and good control of their physical and mechanical properties. Among the polymeric food contact materials, a commercial HDPE has shown high usage in food packaging such as for milk bottles, drinking water bottles, and as a package for edible oil containing fatty acid components (Till, et al., 1982). Polyolefins have incorporated antioxidants to maintain the stability of the polymer to oxidation during processing and at environmental conditions, as well as to retard the oxidation of packaged food products. The oxidation of polyolefins is related to the degree of chain branching in the polymer. The oxidative degradation of polyolefins in the presence of oxygen, during melt processing at high temperatures, may be related to the packaging article's inability to withstand a stress associated with aging or deteriorating effects (Birley, 1991).

The use of α-tocopherol to prevent oxidative reactions in extrusion processing for HDPE bottles and LDPE film packaging at high temperatures has shown the effectiveness of α-tocopherols performance as an antioxidant, through sensory evaluations. Its application at low temperatures has also been determined (Zambetti, 1995). Laermer and Nabholz (1990) evaluated α-tocopherol as a highly effective melt stabilizer, alone at low concentrations and in synergistic mixtures with other secondary antioxidants, including phophites (such as TNPP, Hostanox PAR204, Weston 619) and thioesters (such as DSTDP) in polypropylene. The melt and color stabilization observed for a series of mixtures of tocopherol with phosphite and thioester antioxidants with polypropylene and polyethylene showed such mixtures to have excellent stability properties, as compared with other antioxidants (Laermer and Zambetti, 1992).

Tocopherols incorporated into polymeric packaging afford commercial advantages to the polymer system and to commercial applications of the polymer. Polymers stabilized with-tocopherol were found to have fewer taste and odor problems, as well as better color stability, than those with typical commercial polymer antioxidants. Further, there is a reduction of contamination risk from the packaging components, and good thermal stability during processing (Laermer et al., 1994). At accelerated stability tests, HDPE/EVA liner packaging films with various concentrations of tocopherol added, showed a noticeable reduction of flavor loss from a packaged cereal product at 37℃, over a three month storage period (Laermer et al., 1994). Ho and Yam (1994) reported that HDPE drinking water bottles containing tocopherol had less odor and higher acceptability than these containing the antioxidants, Irgonox 1010 or BHT, through sensory evaluation of the off-flavor problem. This problem can be identified with the following possible factors associated with odor threshold, namely: molecular weight, and polarity of the compounds released from the polymer, such as ketones and aldehydes. Lin (1996) observed that cereal product packaged in pouches without antioxidant showed a significantly higher level of hexanal, as compared to the rate of oxidation of cereal product packaged in antioxidant (α-tocopherol, BHT) impregnated structures, following the 20th week of storage (23℃/50%RH). The hexanal levels detected in cereal product packaged in α-tocopherol impregnated pouches and BHT impregnated pouches showed no significant difference, over a 44 week storage period at ambient conditions (23℃/50%RH).

5. The Mechanism of the Migration of Antioxidants from the Packaged Film Structures to a Contained Product.

Antioxidant migration from a packaging film structure into a contained food product can be described by the following basic mechanism. First, diffusion of antioxidant molecules contained within the void volume between the polymer chains through the polymer bulk phase to the polymer surface. Second, evaporation of antioxidant molecules from the surface of the packaging material to the internal package environment. Third, sorption of antioxidant molecules onto the surface of the packaged product. High molecular weight antioxidants would be expected to migrate slowly into the food product, as compared with low molecular weight migrants. The mechanism for the three step migration process is illustrated in Figure 1.

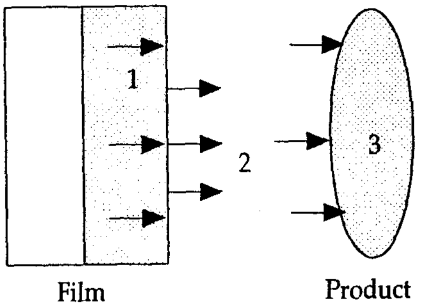

Figure 1. A three step migration process

Generally, migration from a polymeric packaging material can be described as either global or specific migration. These terms refer to whether the total mass of migrant is considered, or a number of restricted migrating components from the package into the contained food, under specified conditions, are being considered (Crosby, 1981).

The migration system can be divided into the three types based on migrant diffusion, such as described by Robertson (1993): (1) migration takes place only from the packaging surface regardless of the presence of a food product. (2) the presence of food may affect migration from the packaging surface; However, migration is not controlled by the food product, but by the rate of diffusion of the migrant through the polymer bulk phase. In this case a diffusion coefficient can be measured under the test conditions and during a specified contact time. (3) Migration is controlled by the food product at the packaging surface, and the food system plays an important role in the transfer of migrants from the film structure to the contained product. Here, penetration of the film structure by a component of the contacting food system can increase the rate of diffusion of the migrant from the packaging film.

The relationship describing the loss of antioxidants from the packaging film structure into the food product can be expressed by the rate of migration of the antioxidants. The migration rate of the antioxidant is affected by the following factors (Calvert and Billingham, 1979): the additive solubility, the diffusion coefficient of the additive, and additive volatility, which are discussed briefly below. (1) The solubility of antioxidants in the film structures. This is described by the solubility coefficient, which is determined by the morphology of the polymer and the chemical properties of the antioxidants. The temperature and vapor pressure also affect the solubility of antioxidants. (2) The diffusion coefficient of antioxidants within the film structures, describes how rapidly molecules are advancing through the polymer bulk phase and the time to reach steady state. The molecular size of the antioxidant affects the magnitude of the diffusion coefficient.

The diffusive flux of antioxidants in a film structure can be expressed as the amount passing through a plane of unit area normal to the direction of flow during unit time.

$$F = M/A \cdot t \quad \cdots\cdots (1)$$

Fick's first law applies where the rate is directly proportional to the concentration gradient.

$$F = -D\,(\partial C/\partial X) \quad \cdots\cdots (2)$$

Where,

F= he flux (the rate of transfer of the diffusing substance per unit area)

M=the amount of the substance which passed through the film

A=area of surface at which diffusion occurs

C= he concentration of diffusing substance

X=the distance of diffusion

t =time

D=the coefficient of diffusion

For an infinite plane or sheet, across which diffusion occurs in a linear direction (x) of a thin membrane, in most cases, migration from a film structure into a food system can be expressed by Fick's second law (Equation 3).

$$(\partial C/\partial t) = D(\partial^2 C/\partial X^2) \quad \cdots\cdots (3)$$

The amount of antioxidant transferred per unit time, through a film structure with constant dimensions, can be represented by the transmission rate.

Factors affecting antioxidant diffusion within the film structure include the chemical nature of the film structure, the size of antioxidants, the thickness of the film structure (an inverse proportion), and environment conditions (temperatures, humidity).

(3) The loss rate of the antioxidants by volatilization from the film surface.

A mathematical model describing the loss of an antioxidant from the polymer to the environment in which the polymer is stored requires two parameter factors; namely: (1) a mass transfer constant, characterizing transfer across the boundary of polymer surface-air interface; and (2) a constant characterizing antioxidant mass transfer within the polymer bulk phase.

Han, et al. (1987) found that the loss of BHA from HDPE followed a first-order rate expression and described a method for the calculation of the diffusion coefficients (D) and the mass transfer coefficient (α) from sorption or desorption data for BHA and BHT in HDPE. The controlling parameter factor for mass transfer of the antioxidants was found to be volatilization rather than diffusion.

6. Isolation Techniques of Volatile Compounds Present in Food Systems

The off-flavor compounds related to various food products have a large number of different functional groups and chemical structures, which are derived from biochemical-metabolism or from external factors (Charalambous, 1992). Specifically, lipid oxidation leading to the unacceptability of a food product can be estimated by the development of unpleasant flavors. The major secondary oxidation products from linoleic acid, among a variety of fatty acids, are representative aldehyde type compounds, which include hexanal, pentanal, octenal, and decadienal etc. The aldehydes and vinyl ketones formed in the lipid phase of food products are mainly responsible for the off-flavors, due to their low threshold levels for human sensory response (Kochhar, 1993). Such volatile compounds are in low concentration and therefore must be concentrated from the food prior to instrumental analysis.

The volatile compounds resulting from the oxidation of food products can be isolated by static headspace, dynamic headspace, or distillation-solvent extraction techniques (Reineccius, 1984). The headspace sampling techniques were found to give accurate data for the level of volatile compounds derived from a food product. Gas chromatography/Mass spectrometry is an excellent method for analysis of volatile compounds, due to the high resolution and sensitivity afforded by this method.

7. Perspectives

In general, the fresh quality of food products is the most important factor for consumer. The use of antioxidant impregnated materials may be of value for oxidation sensitive products such as cereals, chips, and snacks to extend the shelf life for storage. Antioxidant impregnated materials can be also applied to the food contacted directly to its packaging such as butter, ice cream, liquid daily product, oil product including the fatty content, and drinking water stored in plastic materials which cause the development of off-flavors.

These applications benefit food manufactures as economic points of view for a long storage time involved prier to consumption. In addition, the use of an antioxidant minimizes oxidative degradation of a polymer, since its exposure to heat and oxygen during processing is unavoidable.

In consideration with regulatory and safety, it is important for the consumer to verify the antioxidants and their degradation products for food packaging applications.

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