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Antioxidant Packaging as Additional Measure to Augment CO_2-enriched Modified Atmosphere Packaging for Preserving Infant Formula Powder

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Abstract Al-laminated packaging film incorporating ascorbic acid or tocopherol at inner food contact layer was tested in the potential to improve antioxidative preservation of powdered infant formula under CO_2-enriched atmosphere. Product of 200 g was packaged with the packaging film containing 0.3% antioxidant in sealant layer of low density polyethylene and stored at 30°C for 286 days with periodic measurement of package atmosphere and product's quality attributes. The CO_2-flushed package resulted in shrinkage of tight contact between the product and the film not allowing gas sampling of package atmosphere after 140 days. Package of tocopherol-incorporated film allowed some ingress of oxygen after 112 days presumably due to its weakening of heat-seal area. The increased oxygen concentration in the tocopherol-added film package led to the concomitant increase of peroxide value, an index of lipid oxidation. On the other hand, packaging of ascorbic acid-added film pouch could suppress lipid oxidation marginally in consistent manner compared to control package without any antioxidant.

Keywords Ascorbic acid, Tocopherol, Modified atmosphere packaging, Oxidation, Carbon dioxide

Introduction

Infant formula powder based on dairy ingredients is labile to oxidation because of its low moisture and high lipid content[1]. Oxygen-excluded packaging is widely used for inhibiting oxidation of the fatty powder product. Modified atmosphere of pure nitrogen or mixture of nitrogen and carbon dioxide is commonly filled into the packages of the powder products[2-4]. However, operation of modified atmosphere packaging (MAP) cannot usually attain complete removal of oxygen in the package and leaves low level of oxygen in the package causing oxidation to a low but unfavorable level. Oxygen concentration of 1% was found to result in significant flavor loss of foam-dried whole milk at 26.7°C[5]. Oxygen concentration above 1.5% is often met initially in MAP products of O_2-exclusion[6]. Thus antioxidant packaging incorporating antioxidant in the polymer material can be effective to inhibit the oxidation of fatty foods and scavenge some oxygen from the headspace as additive tool to strengthen the MAP[7]. As an example, tocopherol incorporated polyethylene layer was reported to protect whole milk powder from oxidation by slow release into the product[8, 9]. A variety of antioxidant packaging materials have been developed to preserve oxidative foods by including natural antioxidant such as ascorbic acid, catechin and quercetin in polymer matrix[10]. So properly designed antioxidant packaging in oxygen-excluded MA has potential to improve further the storage stability of the infant formula powder. As another factor in MAP, high CO_2 concentration has been reported to enhance the activity of bifidobacteria added for health-promoting function in manufacturing process[11]. It would also be interesting to see the effect of antioxidant packaging under CO_2-enriched atmosphere in terms of chemical and biological quality preservation of the infant formula powder.

Therefore, this study tested ascorbic acid- and tocopherol-incorporated antioxidant films for preserving infant formula powder under MAP condition of 100% carbon dioxide.

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Materials and Method

1. Antioxidant films

Aluminum-laminated multilayer films were fabricated with low density polyethylene (LDPE) sealant layer containing ascorbic acid or tocopherol at 0.3% w/w. To include antioxidant in the inner layer, ascorbic acid (purity: 99.0%, Northeast Pharmaceutical Group Co., Shenyang, China) or tocopherol (purity: 99.3%, DSM Nutritional Products Ltd., Kaiseraugst, Switzerland) as food additive grade was added first in extrusion process for LDPE master batch at 10% w/w concentration under industrial production condition at Samhwa Corporation

(Chungju, South Korea). The master batch was combined with linear low density polyethylene pellets in a single screw extruder under industrial production condition (Yuhan Chemical Co., Yangju, Korea) to produce 50 μm thick film with the antioxidant concentration of 0.3%. Finally, the film with antioxidant was laminated to a film consisting of aluminum (Al, 6 μm) and nylon (15 μm) layers following industrial practice at factory of Taebang Patec Co. (Yangju, South Korea). The non-antioxidant Al-laminated multilayer film with plain inner-layer (polyethylene terephthalate 12 μm/polyethylene 25 μm/Al 7 μm/LDPE 65 μm) procured from Uwrapco Co. (Ansan, South Korea) was also used for control packaging.

2. Packaging and storage test of infant formula powder

Infant formula powder product in nitrogen flushed cans (750 g, Maeil Co., Ltd., Pyeongtaek, Gyeonggi-do, South Korea) was transported to the laboratory and used for repackaging in pouches of antioxidant films. Composition of the infant formula powder was carbohydrate of 53%, lipid of 22%, protein of 18%, ash of 4% and moisture of 3% according to the manufacturer.

Film pouches of 15 × 16 cm were prepared from different films and used for containing 200 g of infant formula. Modified atmosphere condition of 100% carbon dioxide was flushed into the pouches, which were then heat-sealed. Package volume measured immediately after sealing by immersing the pouch in water was 320 mL on average, which provided estimate of free volume as 162 mL by applying true density of the infant formula (1.26 kg L^{-1}) determined from com-positional data and the density values of its components (1.38, 0.93, 1.55, 0.72 and 1.00 kg L^{-1} for protein, fat, carbohydrate, ash and moisture, respectively)[12]. The packages were stored in dark condition at 30°C for 286 days with periodic measure-ment of package atmosphere and product quality for the taken-out sample products.

The package gas composition in O_2 and CO_2 concentrations was measured by a gas analyzer (Checkmate 3, PBI Dansensor, Ringsted, Denmark). As an oxidative quality index, peroxide value (POV) of the lipid in infant formula was measured by a method of Jo et al.[13] to be presented in unit of meq/kg of lipid matter. As a chemical quality attribute, pH was measured for blended solution of 5 g powder in 50 mL distilled water by using a pH meter (Model 920A pH Meter, Orion Research Inc., Boston, USA). Titratable acidity was determined in lactic acid concentration by titrating the same solution by 0.1 N NaOH (up to the end point of pH 8.3). BL agar (KisanBio, Seoul, South Korea) added with sheep blood was used for counting probiotic bifidobacteria. Samples in dilutions were plated on BL agar plates and incubated under anaerobic condition at 37°C for 3 days. Cell viability was expressed in colony forming units (CFU) per gram sample. All the measurements were done at least in replicates and mean values were reported in graphs. Statistical significance of difference among treatments was examined by Duncan's multiple range test at $\alpha = 0.05$ when needed. Standard deviations were also added for gas concentrations in graphical presentation.

Result and Discussion

1. Package gas composition

CO_2 flushing operation could attain initial CO_2 concentration of 96%. CO_2 flushed packaging resulted in very low O_2 concentration (<0.5%) initially (Fig. 1). O_2 concentration increased very slightly during the initial storage and later stayed at relatively constant level (0.8-1.4%) for all the packages over 84 days, and CO_2 concentration experienced slight initial decrease before reaching the stable level in the same period. This change of O_2 and CO_2 concentrations would have come from release of O_2 occluded in the product and dissolution of CO_2 onto the product. Porous dairy powder product is known to retain oxygen inside its structure which is later be released into the headspace[6]. Infant formula powder has been reported to absorb carbon dioxide because of high fat

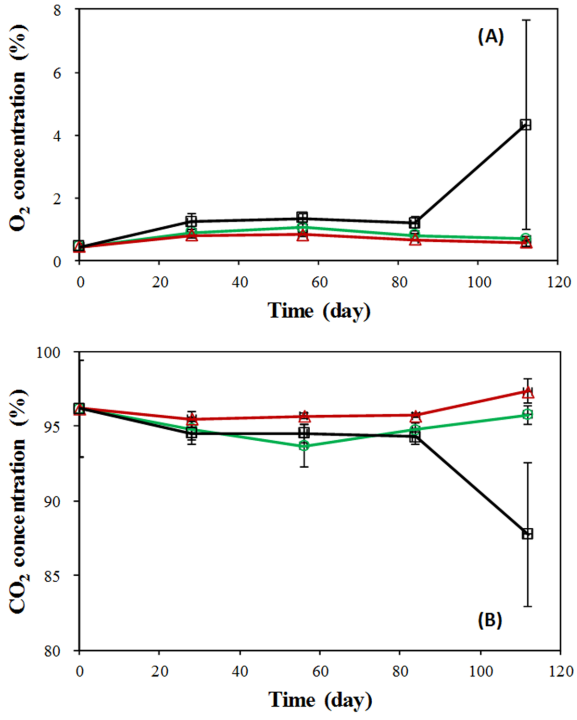

Fig. 1. Changes in (A) oxygen and (B) carbon dioxide concentration of different film packages of infant formula powder at 30°C. Vertical bars are standard deviations. CO_2-flushed packages shrunk tightly to the product after 140 days allowed gas sampling and concentration measurement only up to 112 days of storage. ○: control; Δ: ascorbic acid-incorporated film; □: tocopherol-incorporated film.

content to decrease its concentration or partial pressure in the package[14].

While this state of package atmosphere became stabilized later for control package and package of ascorbic acid-incorporated film, that of tocopherol-incorporated film showed abrupt increase in O_2 concentration and decrease in CO_2 concentration with high variability after 112 days. Considering that Al-laminated film is perfect gas barrier, the changes in O_2 and CO_2 concentrations are thought to have resulted from gas permeation through the seal-area of the pouches. It has been reported that significant gas permeation may occur through heat-seal area in plastic pouch packages[15]. It may be reasoned that incorporation of tocopherol in polyethylene seal-layer would have weakened the hermetic barrier property of the heat-seal in the film pouch. It is noted that package of tocopherol-incorporated film also had slightly higher O_2 concentration even before 84 days. Probably there might have been some weakening of the sealing in the of tocopherol-incorporated film layer and have been aggravated with extended storage (in 112 days). This weakened sealing may have resulted from interaction with CO_2 gas dissolved into the plastic layer. High gas permeation of tocopherol-loaded LDPE film seal caused by CO_2-flushed condition has not been reported elsewhere. This study reporting the apparently compromised phenomenon of gas barrier did not reach the elucidation of mechanism. Effect of tocopherol incorporation in sealant layer of packaging on the seal property needs further investigation particularly with interactive influence of CO_2. Incorporation of tocopherol only food contact layer except the sealing area may work as a way to resolve the problem of degraded sealing quality for tocopherol-incorporated film. For the packages of control and ascorbic acid-incorporated film there would have been a little oxygen permeation through the sealing area, which raised oxygen concentration only very slightly during the storage (< 1%).

Even with its high gas permeation at 112 days, there seemed to be retained seal integrity for package of tocopherol-incorporated film, which could be confirmed by pronounced shrinkage producing tight contact between product and packaging film in 140 day storage. The package shrinkage was also observed similarly for control package and package of ascorbic acid-incorporated film. The visual shrinkage was greater with tocopherol-incorporated film package. The tightened shrinkage of these packages is presumed to have occurred due to high dissolution of CO_2 gas into the fatty formula product. It was reported previously that significant amount of CO_2 can be dissolved in the powdered dry infant formula[14]. The high solubility of CO_2 gas in food matrix is known to induce significant degree of package contraction when the fatty or aqueous food is packaged with small headspace gas of high CO_2 concentration[16]. The tightened shrinkage worked to deplete free volume completely and did not allow the sampling of gas samples from any CO_2-flushed packages after 140 days, which is the reason why Fig. 1 presents oxygen and carbon dioxide concentrations only up to 112 days. Still packages stored for the later period were taken out to measure the product quality affected by the package variables.

2. Quality changes depending on packaging film

Progress of lipid oxidation in the infant formula powder packaged with different films is given in POV change by Fig. 2. During initial storage of very low POV level up to 56 days, the packages of two antioxidant films showed slightly but significantly lower POV than control package. Then tocopherol-incorporated film package started to increase in the product POV at 84 days and continued the POV increase until reaching 32 meq/kg at 231 days, showing significantly higher oxidation than the other two packages in the later storage. Pronounced POV increase of the product in tocopherol-incorporated film package was observed to initiate at 112 days when its oxygen concentration also started to increase (Figs. 1 and 2). Then the subsequent POV rise went in parallel with increase of package oxygen concentration. From this finding it may be reasoned that product oxidation have been onset and progressed mainly by oxygen permeated though the sealing area of the package. Similarly, oxidation of cream powder packaged in low oxygen condition at 30°C has been reported to be influenced dominantly by the oxygen permeated through plastic stopper rather than the initial oxygen concentration[17]. Thus, current state of tocopherol-added film is deemed not to be suitable for antioxidative preservation of the product.

On the other hand, package of ascorbic acid-incorporated film could suppress the oxidation through the whole storage period of 286 days: ranging from initial POV of 1.7 meq/kg to the value 3.0 meq/kg at 286 days. Its POV range is significantly lower than that of control package product in range of 1.7 to 5.5 meq/kg over most of storage period (except storage times of 112, 231 and 286 days) (Fig. 2). Even though

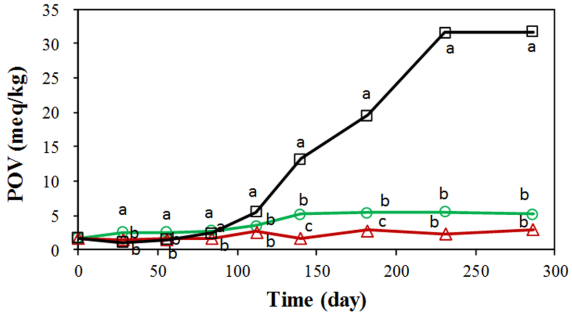

Fig. 2. Effect of different packaging films on POV changes of infant formula powder stored at 30°C. ○: control; Δ: ascorbic acid-incorporated film; □: tocopherol-incorporated film. Different letters on the same storage time means significant difference from other treatments at $\alpha = 0.05$.

the relative effect of ascorbic acid-added film on antioxidative quality preservation of the product in Fig. 2 appears small, its potential to protect against oxidative deterioration is evident. It is noted that control package under CO_2-flushed condition had only small increase of POV, which would have been possible because of low level oxygen concentration (< 1.0%) kept though the storage time. Antioxidant effect of ascorbic acid-added film may have become more pronounced for the more vulnerable MAP conditions which often have higher residual oxygen concentration beyond 2%. Further study may be undertaken for assessing the explicit antioxidant preservation effect of the ascorbic acid-added film under commonly available MAP conditions. Highly oxidative product and severe storage conditions may be employed for the purpose.

Generally in the earlier storage up to 112 days the product pH tended to decrease from initial value of 6.73 and titratable acidity increased from 0.61% consistently for all the packages (Fig. 3). In the later period up to 286 days, pH was stabilized around 6.6 for the control and ascorbic acid-added film packages. And acidity was stayed around 0.7% for the two packages. However, tocopherol-added film package showed later changes of product pH and acidity reversed from its former tendency of change. Its titratable acidity change was in line with the pH change: acidity increase concomitant with pH decrease. The phenomenon of pH decrease and acidity increase observed mainly in earlier storage period is reasoned to occur from slow progress of CO_2 dissolution into the product as discussed before[11]. The reversed pH increase and acidity decrease after 112 days for tocopherol-added film package may be connected to CO_2 concentration decrease starting to decrease around this time (Fig. 1). Increased gas permeation of this package leading to the product lipid oxidation in the later storage would have worked to release carbon dioxide from the product reversing the acidity increase in the extended storage.

There were no significant differences in bifidobacteria count among the treatments due to scattering of the data. Only

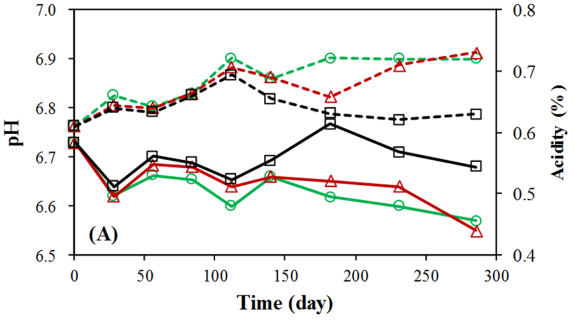

Fig. 3. Changes of pH (solid lines) and titratable acidity (dotted lines) of infant formula powder packaged with different films at 30°C ○: control; Δ: ascorbic acid-incorporated film; □: tocopherol-incorporated film

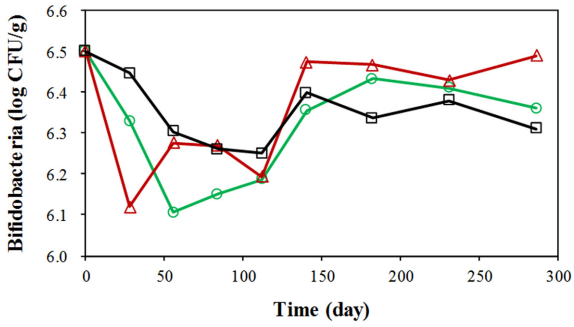

Fig. 4. Changes of bifidobacteria count of infant formula powder packaged with different films at 30 °C. ○: control; Δ: ascorbic acid-incorporated film; □: tocopherol-incorporated film.

non-significant tendency of slightly higher count was shown consistently in the later period of storage, particularly of ascorbic acid-added film package (Fig. 4). The reduced pH and increased acidity attained in the CO_2-flushed packages has been reported to enhance the survival of bifidobacteria[11]. Further bifidobacterial preservative effect by the antioxidant film cannot be observed at this point. There was limitation of covered treatments in this study to elucidate comprehensively interactive influences of package atmosphere and active packaging.

Conclusion

Packaging the powdered infant formula in ascorbic acid-added film pouch under CO_2 flushing could contribute to further suppression of lipid oxidation marginally in the extended storage compared to control package of plain film. Tocopherol-added film adversely affected the oxidative quality change of the product due to aggravated oxygen permeation presumed to occur in heat-seal area in the extended storage.

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