

## Characterization and Enhancement of Package O<sub>2</sub> Barrier against Oxidative Deterioration of Powdered Infant Formula

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**Abstract** Powdered infant formula is susceptible to oxidation in the presence of oxygen. Even though the product is usually packaged in nitrogen atmosphere, the oxygen ingress through the package layer may occur in case of flexible pouches and affects the oxidation of the product. O<sub>2</sub> barrier of the package is thus important variable to protect the product from oxidative deterioration. O<sub>2</sub> barrier property was investigated for aluminum-laminated small pillow packs of 3.5×17.5 cm. Storage temperature and combination of primary and secondary packages were evaluated as variables affecting the barrier for conditions of empty pouch flushed with nitrogen. Apparent oxygen transmission rate of the primary package exposed to air was  $2.32 \times 10^{-3}$  mL (STP) atm<sup>-1</sup> d<sup>-1</sup> at 30°C and its temperature dependence could be explained by activation energy of 28.5 kJ mol<sup>-1</sup> in Arrhenius relationship. The additional secondary package of nylon/PE film containing 20 primary packages was ineffective in modulating package O<sub>2</sub> transmission and was only marginally helpful when combined with oxygen scavenger. The same was true in suppressing the product oxidation when the primary package was filled with 14 g of the formula.

**Keywords** Oxygen transmission, Oxidation, Temperature, Secondary package, Nitrogen flushed package

### Introduction

Infant formula powder is labile to lipid oxidation due to high fat concentration above 20%<sup>1,2</sup>. Access to the product of oxygen permeated through the package or present inside the package at initial filling determines the oxidation rate and degree limiting its shelf life. So, barrier of the package against oxygen is important to protect the infant formula powder from lipid oxidation.

In order to protect oxidation-labile products such as powdered infant formula from oxidation, many technologies have been developed to increase the oxygen barrier or reduce oxygen concentration of the package. These include high gas barrier material, oxygen scavenger, secondary packaging and so on. High gas barrier plastic films such as aluminum-laminated structure can prevent the oxygen permeation in the flexible pouches. However, with these pouches, there is still possibility of oxygen permeation through the heat-seal area<sup>3</sup>. Oxygen scavengers are helpful to help to remove or decrease the level of oxygen present inside the package<sup>4</sup>. Secondary packaging may work as another extra barrier to protect the primary pack-

aging from oxygen ingress.

These days, small size packages of single serve are available for improved convenience of feeding. Because these small packages of the infant formula product have high proportion of surface or seal area, they may be vulnerable to oxygen permeation or oxidative deterioration. Thus it is required to evaluate the oxygen barrier of these packages and examine the potential of tools enhancing the barrier when needed.

Therefore this work determined oxygen permeability of the commercially available small pillow packs and investigated potential of possible tools to reduce the permeability or exposure to oxygen. As the tools for extra protection, use of the secondary packaging and the oxygen scavenger was examined.

### Materials and Methods

#### 1. Measurement of O<sub>2</sub> transmission for small pillow packs

Small size pillow packs (dimension: 3.5×17.5 cm) usually used for containing 14 g product were used for measuring O<sub>2</sub> transmission. The film structure consisted of 4 layers of polyethylene terephthalate (PET) 12 μm/polyethylene (PE) 25 μm/aluminum foil (Al) 7 μm/polyethylene 65 μm. The empty pillow packs flushed with nitrogen in an industrial facility (Maeil Dairies Co., Ltd., Pyeongtaek, Gyeonggi-do, Korea) were

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moved immediately to the laboratory and stored at 20, 30 and 40°C under exposure to the normal atmospheric condition of 21% oxygen. Their average free volume measured by immersing them in water was 32 mL. These packs were taken out periodically to measure their oxygen concentration by a gas analyzer (Checkmate 3, PBI Dansensor, Ringsted, Denmark).

Apparent O<sub>2</sub> transmission rate (OTR) or permeability was determined from the oxygen concentration history following the relationship of transient phase<sup>5</sup>:

$$\ln\left[\frac{0.21 - P_{O_2,i}}{0.21 - P_{O_2}}\right] = \frac{RT}{V}\left[\frac{A\bar{P}_{O_2}}{L}\right]t \quad (1)$$

where  $\bar{P}_{O_2}$  is permeability coefficient of the film (mol mm atm<sup>-1</sup> day<sup>-1</sup> m<sup>-2</sup>),  $P_{O_2,i}$  is initial O<sub>2</sub> partial pressure of package (atm),  $P_{O_2}$  is O<sub>2</sub> partial pressure of package at the time,  $t$  (atm),  $A$  is surface area of the film (m<sup>2</sup>),  $V$  is package volume (L),  $L$  is thickness of the film (mm),  $R$  is 0.082 atm L K<sup>-1</sup> mol<sup>-1</sup> and  $T$  is temperature (K). Lumped parameter of  $A\bar{P}_{O_2}/L$  in unit of mol atm<sup>-1</sup> d<sup>-1</sup> was calculated from the history of  $P_{O_2}$  as apparent OTR of the primary package and then presented in unit of mL (STP) atm<sup>-1</sup> d<sup>-1</sup> for shelf life estimation.

## 2. Application of secondary packaging condition for protection against oxygen and oxidation

Two kinds of plastic film (62 μm thick nylon/PE film and 68 μm thick oriented polypropylene (OPP)/cast polypropylene (CPP) film) were used as the secondary packaging of 22.0×19.5 cm size with or without O<sub>2</sub> scavenger. Each secondary package contained 20 primary packs, and three oxygen scavengers (1.8 g of each sachet, TPG Ltd., Gimpo-si, Gyeonggi-do, Korea) were inserted as an extra variable. The secondary package was placed in a paper box (6.8×12.4×18 cm) like the commercial sale unit. Firstly N<sub>2</sub>-flushed empty primary packages of pillow packs were wrapped with heat-sealed secondary package and stored at 30°C with measurement of O<sub>2</sub> concentration. Primary package without secondary packaging was used as control treatment. Secondly the primary packages containing 14 g of powdered infant formula each were submitted to the same treatments of secondary packaging. The infant formula in primary packages manufactured by Maeil Dairies Co., Ltd. (Pyeongtaek, Gyeonggi-do, Korea) was transported to the laboratory within one week after production. The product composition of the infant formula powder was carbohydrate of 55%, lipid of 22%, protein of 16.5%, ash of 3.5% and moisture of 3% according to the manufacturer. Nylon/PE film is understood to have the lower gas permeability than OPP/CPP film.

During the storage at 30°C, package's O<sub>2</sub> concentration and product's peroxide value (POV) were measured. POV of the lipid in infant formula was measured using a method modified slightly from Cesa *et al.*<sup>6</sup> and Mu *et al.*<sup>7</sup>. First, 0.5 g of lipids extracted with n-hexane (Samchun, Pyeongtaek, South Korea)

was dissolved in 25 mL of a mixture of chloroform (Daesung Co., Siheung, South Korea) and glacial acetic acid (Samchun Co., Pyeongtaek, South Korea) (2:3, v/v). The extract was added with 1 mL of saturated potassium iodide (Alfa Aesar, Haverhill, Massachusetts, USA) solution, shaken gently for 1 min and then left under darkness for 10 min. The solution was combined with 30 mL of distilled water and 1 mL of 1% starch indicator (Alfa Aesar, Haverhill, Massachusetts, USA) in order to be finally titrated by 0.01N sodium thiosulfate solution. Color change from dark to clear was used as end point of titration. Blank test was conducted with the same procedure using 0.5 mL of distilled water instead of 0.5 g of lipids. The POV was given in unit of meq/kg of lipid matter.

## Results and Discussion

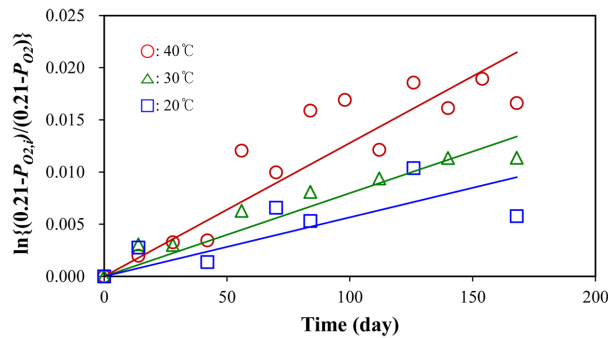
### 1. OTR of primary package

Fig. 1 shows oxygen concentration change of N<sub>2</sub>-flushed empty pillow packs of the primary package plotted according to Eq. (1). High temperature accelerated the ingress of oxygen into the package. For the small size pillow packs of 3.5×17.5 cm, OTR determined from the slope in Fig. 1 was 1.70×10<sup>-3</sup>, 2.32×10<sup>-3</sup> and 3.61×10<sup>-3</sup> mL (STP) atm<sup>-1</sup> d<sup>-1</sup> at 20, 30 and 40°C, respectively. Considering that aluminum-laminated film of the packs itself is not permeable to gases, the resultant OTR is thought to have been caused by the seal layer. OTR of this primary package is much lower compared to the reported one on barrier plastic pouches (0.372 mL atm<sup>-1</sup> d<sup>-1</sup> at 23°C)<sup>3</sup>, probably thanks to aluminum-laminated structure of the primary package. Temperature dependence could be explained by Arrhenius relationship (Eq. (2)) as shown in Fig. 2 and activation energy of 28.5 kJ mol<sup>-1</sup> could be obtained from the slope for explaining the temperature effect on the O<sub>2</sub> transmission:

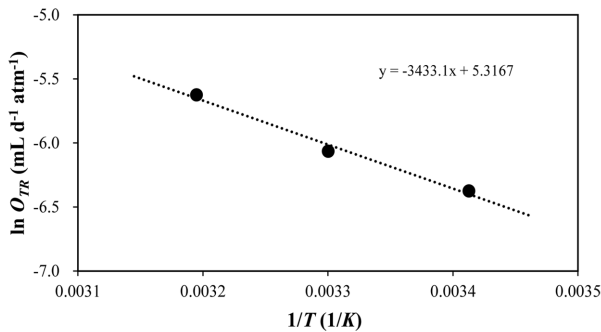
$$O_{TR} = O_{TR,o} \exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

where  $O_{TR}$  is apparent OTR given in lumped parameter of  $A\bar{P}_{O_2}/L$  at temperature  $T$  in K,  $O_{TR,o}$  is a constant and  $E_a$  is activation energy (J mol<sup>-1</sup>). This temperature dependence is close to that of O<sub>2</sub> permeability of polyolefin polymers ( $E_a$  of 30~38 kJ mol<sup>-1</sup>)<sup>9,10</sup>, which suggests the oxygen permeation occurs mainly through heat-seal area. There is possibility of increased O<sub>2</sub> permeation due to very small leaks on the seal area<sup>3,4</sup>.

Because Al foil-laminated film itself consisting of PET/PE/Al/PE layers cannot allow O<sub>2</sub> permeation as mentioned above, O<sub>2</sub> concentration increase in Fig. 1 leading to very low OTR is thought to occur due to the gas permeation through the heat-seal area of PE. OTR of 1.70×10<sup>-3</sup> mL (STP) atm<sup>-1</sup> d<sup>-1</sup> at 20°C given by the primary package was analyzed to provide shelf life of about 1.1 year, which was based on tolerable O<sub>2</sub> permeation limit of 0.146 mL at 20°C into the package of 1% O<sub>2</sub>



**Fig. 1.** O<sub>2</sub> concentration change of N<sub>2</sub>-flushed small pillow package.



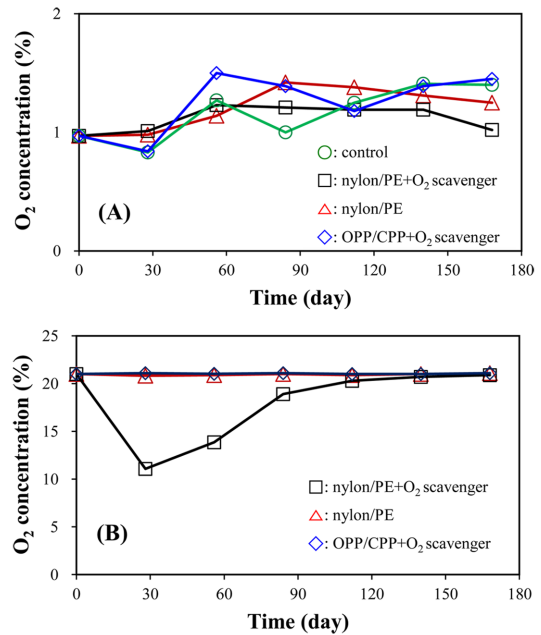
**Fig. 2.** Effect of temperature on oxygen transmission of the primary package.

concentration (0.01 atm) across O<sub>2</sub> concentration differential of 0.20 atm<sup>11</sup>).

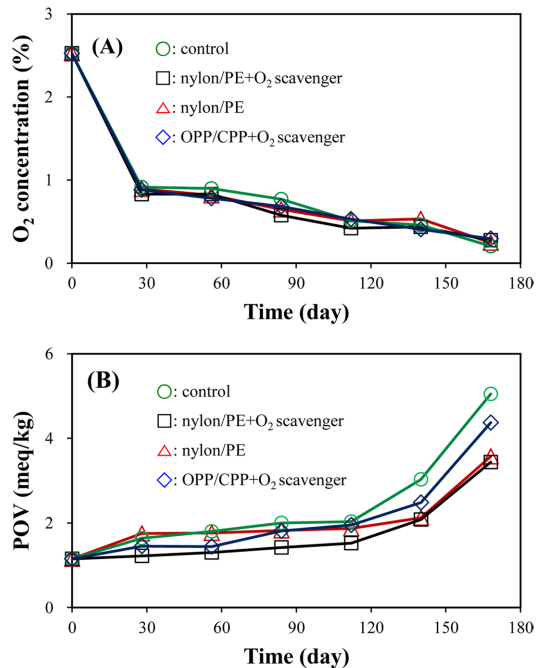
**2. Effect of secondary packaging on further protection against oxygen and oxidation**

As analyzed above, the current primary package can provide a shelf life of 1.1 year and longer shelf life would need extra barrier or means of oxygen removal. Secondary packaging of nylon/PE layer alone could not reduce the permeation into the primary package (Fig. 3(A)). Secondary packaging of more highly gas-permeable OPP/CPP film was not effective either even with O<sub>2</sub> scavenger. Only the secondary packaging with O<sub>2</sub> scavenger showed perceivably decreased O<sub>2</sub> concentration in the initial storage period of 28–84 days in the secondary package, which then disappeared gradually with the extended storage beyond 112 days (Fig. 3(B)). Adding lower barrier film bag of secondary package compared to the primary package was not effective against the oxygen ingress and presence of O<sub>2</sub> scavenger showed only very marginal effect in the oxygen blocking.

The same was true for the packages containing 14 g powder product each (Fig. 4). O<sub>2</sub> concentration was only slightly lower with secondary package of nylon/PE+O<sub>2</sub> scavenger compared



**Fig. 3.** (A) O<sub>2</sub> concentration change of N<sub>2</sub>-flushed empty pillow packs placed in secondary package and (B) O<sub>2</sub> concentration change in the outer secondary packaging.



**Fig. 4.** (A) O<sub>2</sub> concentration change of N<sub>2</sub>-flushed infant formula powder packages placed in secondary package at 30°C and (B) POV of the product packaged inside.

to the other treatments (Fig. 4(A)). The decrease of O<sub>2</sub> concentration seems to come along with reduced product oxi-

dition (Fig. 4(B)), which was also marginally lower with the treatment of secondary package of nylon/PE+O<sub>2</sub> scavenger than the other treatments. It is noted that secondary packaging is used for facilitating centralized packing of primary packages<sup>12)</sup>, even though special design may be used for protection against product oxidation<sup>13)</sup>.

## Conclusion

OTR of small size Al-laminated pillow packs used for 14 g powdered infant formula was determined as shelf life determining factor. Its magnitude and activation energy suggested that oxygen transmission to the package was dominated through the heat-seal area. Secondary packaging of nylon/PE comprising 20 primary packages did not give any further protection against O<sub>2</sub> permeation, and showed marginal effect of retarding O<sub>2</sub> ingress and product oxidation only when combined with oxygen scavenger.

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