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General paper

Changes in the Barrier Properties to Gaseous H₂S Accompanying Elongational and Bending Deformations Imposed on Silicate Deposited Nylon 6 Films

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Abstract: The changes in the barrier properties due to the damage imposed on the SiO_x deposited nylon 6 films accompanying various deformations such as bending and elongation were examined by evaluating the corrosion rate of the copper plates by H_2S kept in the pouches made of the damaged films. After application of elongational deformation of as high as 2 % or less, only slight corrosion of the copper plates, almost similar to those of the copper plates kept in the pouches made of undeformed films, was observed. After application of elongational deformations of 3 % or more, the corrosion of the copper plates was more distinct and proceeded significantly with time. Bending deformation given to the SiO_x deposited nylon films also deteriorated the barrier property to H_2S when the radius of curvature at the bent part was small. Comparison of the corrosion rates of the copper plates kept in the pouches made of films also deteriorates of the copper plates kept in the pouches made of films and undeformed commercial films shows a clear relationship between the H_2 permeation rate of the films and the corrosion rate of the copper plates by H_2S .

Key words: SiO_x deposited film, Vacuum deposition, Nylon film, Elongation, Bending, H_2S permeation rate, H_2 permeation rate

1. INTRODUCTION

Transparent high barrier films utilized for the packaging of foods, confectioneries, toiletries, and electronics have been manufactured by the coating of a thin ceramic layer, such as SiO_x and Al_2O_3 , on flexible plastic films [1-3, 10-22]. However the superior barrier property of ceramic coated plastic films may be degraded by the damages accompanying the stretching and bending processes, which are commonly subjected to the films in the conversion processes and during daily usage [4-6]. Changes in the surface morphology and the barrier property of SiO_x-deposited nylon 6 films accompanying various deformations were also investigated by the present authors [7-9]. Among these deformations, only elongational and bending deformations are well defined in magnitude while the magnitudes are rather ambiguous in other deformations such as abrasion and flexing in Gelboflex tests [23].

In this study, changes in the barrier property of SiO_x deposited nylon 6 films accompanied by the damage introduced by elongation and bending were examined. Generally the barrier property of the plastic films is examined by the measurements of oxygen and water vapor permeation rates. However hydrogen permeation rate of the films has attracted a considerable attension recently to the industrial researchers who have been developing a fuel cell. Further it is important to know the resilience of so called high barrier films when exposed to

corrosive and poisonous gases such as hydrogen sulfide H_2S . This paper will report the rate of corrosion by H_2S of copper plates packed in pouches made of SiO_x -deposited nylon 6 films damaged by elongational and bending deformations. Change in permeation rates of H_2S obtained were compared with that of H_2 permeation rates.

2. EXPERIMENTAL

2.1. Materials

SiO_x-deposited biaxially oriented nylon 6 film (SiO_x-ON) (MOS-NO, Oike Industrial Co.,Ltd.) was used as a sample. This film was manufactured by the vacuum deposition of a SiO_x layer on a biaxially oriented nylon 6 film (EMBLEM-ON, UNITIKA Co.,Ltd) using the heating system of an electron beam. The mixture of Si and SiO₂ was used as an evaporation source. The thickness of the deposited SiO_x layer was determined to be 40 nm by measuring the light transmittance at 320 nm and by measuring the weight of burned ash.

Five other kinds of commercial general purpose and high barrier films were also used for comparison. The general purpose films include oriented polypropylene (OPP) (U-1, To-Cello Co., Ltd.), poly(ethylene terephthalate) (PET) (EMBLET, UNITIKA Co., Ltd.), and oriented nylon 6 (ON) (EMBLEM-ON, UNITIKA Co., Ltd). High barrier films include polyvinylidene chloride coated oriented nylon 6 (PVDC-ON) (EMBLEM-DCR, UNITIKA Co., Ltd.) and SiO_x- deposited PET (SiO_x-PET) (MOS-TH, Oike Industrial Co., Ltd.). These commercial films were laminated with either linear low-density polyethylene (LLDPE) or cast polypropylene (CPP). It is known that H_2S and H_2 gases easily permeate through the LLDPE and CPP layers. Thicknesses of sample films and laminated layer are listed in Table 1.

Sample	Film	Lamainated layer
SiO _x -ON	SiO _x deposite nylon 6	LLDPE
	15 µm	60 µm
ON	Oriented nylon 6	LLDPE
	15 µm	60 µm
PVDC-ON	PVDC coated nylon 6	LLDPE
	17 µm	60 µm
OPP	Oriented PP	Cast PP
	20 µm	50 µm
SiO _x -PET	SiO _x deposited PET	LLDPE
	12 µm	60 µm
PET	PET	LLDPE
	12 µm	60 µm

Table 1. Composition of sample films used in this study.

2.2. Application of Various Deformations to SiO_x-Deposited Nylon Film

2.2.1. Elongation

Rectangular specimens 40 mm in width and 100 mm in length were cut out of SiO_x -ON films. These specimens were stretched by a tensile tester (Autograph IM-100, Shimadzu Corporation) at a tensile speed of 0.5 mm/min up to the predetermined strains at 22°C. The stretched films were kept in a desiccator to avoid further elongation caused by the absorption of moisture before being laminated.

2.2.2. Bending

 SiO_x -ON films120 mm in width and 60 mm in length were wound tightly with the deposited surface inside on steel rods with various diameters from 1 to 4 mm and kept for 30 hours. The films were kept in a desiccator after unwinding.

2.3. Lamination of Deformed Film

SiO_x-ON films deformed in various ways were laminated with 50- μ m-thick linear low-density polyethylene (LLDPE) over a SiO_x-deposited surface with a dry lamination method. A polyester/polyurethane type adhesive (TM-215/CAT-10L, Toyo Morton Co.,Ltd.) was applied on the SiO_x-deposited surface with a Meyer bar coater and dried with hot air. Then LLDPE films (TUX-FCS, To-Cello Co.,Ltd.) were laminated on the SiO_x-ON films by pressing with a roll.

2.4. Sample Preparation

Rectangular pouches 30 mm long and 40 mm wide

were made of damaged SiO_x-ON and other commercial laminated films. An impulse heat sealer (Type M200-4, Fuji Impulse Co., Ltd.) which has a heater of 4 mm width was used to seal three edges of the pouches. A rectangular copper plate 25 mm \times 15 mm in area and 1 mm in thickness was put in each pouch and the pouches were sealed with the sealer after removing the air in the pouches.

2.5. Exposure to H₂S Gas

The pouches thus prepared were placed in a 12 liter desiccator. After the air in the desiccator was evacuated by a vacuum pump, H_2S gas (>99.99%, Sumitomo Seika Chemical Co.,Ltd.) was blown into the desiccator slowly up to the level of atmospheric pressure. The pouches were kept in the desiccator for various periods of time at 26°C.

2.6. Evaluation

The degree of permeation of H_2S gas through sample films was evaluated by examining the change in the appearance of the copper plates and the reflectance at the copper surfaces. H_2 permeation rates through the sample films were also determined.

2.6.1. Spectral Reflectance

The reflectance at the surface of copper plates was measured by a spectrophotometer (Color-Eye 3100; Gretag Macbeth Co.,Ltd.) in the spectral range from 360 nm to 740 nm with a wavelength interval of 20 nm. Measurements were carried out according to ISO-7724-1, 2, and 3 regulations to indicate the color by the system of Commission Internationale de l'Eclairage (CIE) Lab [24-28]. The copper surfaces were illuminated with pulse xenon sources conditioned to illuminant D65 with an optical configuration at 2 degrees for an aperture size of 5 mm x 10 mm. The color of the copper surface was indicated by the reflectance at 620 nm [29] and the psychometric lightness L^* . L^* stipulates the attribute concerning the relative lightness of the surface color on the basis of the normally white object color illuminated on the same condition and represents the coordinate corresponding to the lightness in CIE 1976 $L^*a^*b^*$ color space which is prescribed by CIE as a method of measuring the object color.

$$L^* = 116(Y/Yn)^{1/3} - 16.$$
(1)

Where Y/Yn > 0.01. Here the tristimulus value Yn defines the color of the normally white object-color stimulus and Y is the tristimulus value of the test specimen. Values of Y/Yn less than 0.01 may be included if the normal formula is used for values of Y/Yn greater than 0.008856, and the following modified formula is used for values of Y/Yn equal to or less than 0.0088596:

$$L^* = 903.3(Y/Yn).$$
 (2)

2.6.2. H₂ Permeation Rate

The gas barrier property of the laminated films was evaluated by the measurement of the hydrogen gas permeation rate. The H₂ permeation rate was measured at 22°C and 0 % RH by the method according to ASTM D-1434-75 with an apparatus for measuring gas permeability (Type MC3, Toyo Machinery Corporation). All values were specified in m^3/m^2 ·day·MPa for 100 % H₂.

3. RESULTS AND DISCUSSION

3.1. Deformation by Elongation

Figure 1 shows the appearance of the copper plates packed in the pouches made of SiO_x -ON films subjected to elongational deformation. The copper plates directly exposed to H₂S were placed on the top. The brightness of the copper surface fades gradually with time and the color of copper changes into tarnish, dark, gray, blackish and finally into black. The change in color begins at an edge or section of the copper plate and spreads gradually over the entire surface.

It was found that at the elongational strains less than 2 %, the change in color of the copper plates kept in the pouches was similar to that of the copper plates kept in the pouches of the unstretched film. Above a 3 % strain, the change in color of copper plates was more marked. At a 10 % strain, the corrosion rate was so high that the change in color was almost the same as that of the copper plates exposed to H_2S directly.

Atomic force microscope (AFM) observation reported by the authors [9] revealed that for the elongational strain less than 2.5 %, SiO_x layer was stretched with the substrate without being damaged and no obvious cracks were observed. At strains higher than 3%, the SiO_x layer no longer followed the deformation of the nylon film and linear cracks perpendicular to the stretching direction were produced on the SiO_x layer.



Fig.1. Appearance of copper plates packed in pouches made of SiO_x-ON films damaged by elongation.

The changes in the reflectance at a wavelength of 620 nm and the psychometric lightness are plotted in Fig.2 as functions of the period of exposure to H_2S . It was clear from the changes in these properties that the corrosion of the copper plate proceeded more rapidly with the increase of elongational strain up to 5 %. However at a 10 % of strain, the corrosion proceeded significantly and even more severely than that of the copper plate kept in the pouch made of the undeposited film. These results indicate that cracks and voids were formed on the SiO_x layer and the substrate films became thinner at higher elongational strain level.

3.2. Deformation by Bending

Figure 3 shows the change in the appearance of copper plates packed in the pouches made of SiO_x -ON films after being wound on steel rods with various diameters. Within 1.5 hrs of exposure to H₂S gas, distinct changes were observed on the surface of copper plates irre-



Fig.2. Reflectance and psychometric lightness L^* of copper plates kept in the pouches made of elongated SiO_x-ON films.

spective of the severity of bending deformation. At 4.5 hrs of exposure to H_2S , the copper plate, which was kept in a pouch made of the film wound on the rod of 1 mm in diameter, lost its glossy surface. At 13.5 hrs, none of the copper plates retained their gloss. The degree of the corrosion of the copper surface was more significant when the films were wound on the rod with smaller diameter.

Surface morphologies of bent SiO_x -ON films were observed using AFM and reported by the authors [9]. The SiO_x layers on the films wound around rods with diameter less than 2 mm have linear cracks parallel to the winding direction at intervals of 2.0 μ m. When the diameter of the rod was larger than 3 mm, no obvious cracks were observed in the films.

Figure 4 shows the changes in the spectral reflectance and the psychometric lightness on the surfaces of copper plates with the period of exposure to H_2S . When the copper plate was packed in the pouch made of the undeposited nylon 6 film, these values suddenly decreased within a short period of exposure. However, those of the copper plates kept in the pouches made of undeformed and deformed films decreased slowly with time. At a longer exposure time, those values decreased more rapidly with time when the copper plate was kept in the pouches made of the films bent to a larger extent.

3.3. Comparison to Various Commercial Packaging Films

Five kinds of commercial general purpose and high barrier films were also used for comparison. The general purpose films included oriented polypropylene (OPP), poly(ethylene terephthalate) (PET), and oriented nylon 6 (ON). The high barrier films included polyvinylidene chloride coated oriented nylon 6 (PVDC-ON) and SiO_x deposited PET (SiO_x-PET). It may be interesting to plot the reflectance and the psychometric lightness L^* of the damaged SiO_x-ON and various commercial films as functions of H₂ permeation rates. Such a plot is shown in Fig.5. Since the atmosphere in the pouches made of damaged films may be saturated with H₂S at a longer



Fig.3. Appearance of copper plates packed in pouches made of SiO_x -ON films damaged by bending.

exposure time to H_2S , the reflectance and the psychometric lightness L^* measured at 0.5 hr of exposure were plotted. Both the reflectance and the psychometric lightness are inversely proportional to the logarithm of the H_2 permeation rate. However, those for the higher barrier films and general purpose films show different correlations to the H_2 permeation rate. SiO_x-ON films deformed by bending and those deformed by elongation up to 5 % were classified as high barrier films. Those values of the film elongated up to 10 % were classified as general purpose films.

It should be noted that the spectral reflectance and the psychcometric lightness drastically dropped when 10% of elongational deformation was given to a SiO_x-ON film, although SiO_x-ON films stretched 5% and 10% showed similar H₂ permeation rates. According to AFM observations [6] revealed that the SiO_x-ON film stretched 5% has a lot of linear cracks perpendicular to the stretching direction while that stretched 10% has linear cracks parallel to the stretching direction. Such disperpendicular to the stretching direction.



Fig.4. Reflectance at and psychometric lightness L^* of copper plates kept in pouches made of bent SiO_x-ON.

crepancy may be due to the difference in dimension of H_2 and H_2S molecules. SiO_x-ON film stretched 5% may have micro-cracks parallel to the stretching direction although they were not detected in AFM observation. Although H_2S molecules were not able to pass through these micro-cracks, H_2 molecules are so small that they passed through these micro-cracks easily.

4. CONCLUSIONS

We examined the damage imposed on SiO_x deposited nylon 6 films accompanied by elongation and bending. Change in the gas barrier property with the progress of damage was evaluated based on the corrosion rate of the copper plates kept in the pouches made of the damaged films and exposed to H₂S.

After application of elongational deformation of as high as 2 % or less, only slight corrosion of the copper plates, similar to that of the copper plates kept in the pouches made of undeformed films, was observed. After application of elongational deformations of 3 % or more, the corrosion of the copper plates was more distinct and proceeded significantly with time. Bending deformation given to the SiO_x deposited nylon films also degraded the





 \Box Damaged SiO_x deposited films by elongation

Fig.5. Reflectance and psychometric lightness L^* of copper plates kept in H₂S for 30 min as functions of H₂ permeation rate of the films.

barrier property to H_2S when the radius of curvature at the bent part was small.

Comparisons of the corrosion rate of the copper plates kept in the pouches made of various commercial high barrier and general purpose films and that obtained for the damaged SiO_x deposited nylon 6 films show a clear relationship between the H₂ permeation rate of the films and the corrosion rate of the copper plates by H₂S. Although SiO_x coated films deformed by bending and those deformed by elongation up to 5 % still fell into the category of the high barrier films, those film elongated up to 10 % fell into the category of general purpose films.

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