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Changes in the gaseous H_2S barrier properties of damaged silicate coated nylon 6 films

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The damage imposed on SiO_x deposited nylon 6 films as a result of abrasion with a cotton cloth and Gelboflex testing was examined by evaluating the rate at which copper plates, which were enveloped by the damaged films, were corroded by H_2S. Abrasion with a cotton cloth caused some micro-cracking of the SiO_x layer and the permeation rate of H_2S approached that of the uncoated nylon 6 film. Damage to the SiO_x layer by twisting and crushing progressed gradually with the number of Gelboflex test cycles and correspondingly the corrosion rate of the copper plates increased. Comparison of the corrosion rates of the copper plates kept in the pouches made of various commercial films with those obtained for the damaged SiO_x deposited nylon 6 films showed a clear relationship between the H_2 permeation rate of the films and the corrosion rate of the copper plates by H_2S. © *2003 Kluwer Academic Publishers*

1. Introduction

Transparent high barrier films utilized for the packaging of foods, confectioneries, toiletries, and electronics have been manufactured by the coating of thin ceramic layer, such as SiO_x and Al_2O_3, on flexible plastic films by vacuum deposition technique [1–11]. Effects of the vacuum deposition condition and evaporation material of SiO_x layer on the barrier properties of SiO_x deposited nylon 6 films have been reported by the authors [2, 3]. However, the superior barrier property of plastic films coated with the ceramic layer may be deteriorated by the damage accompanying abrasion, bending, twisting and stretching, which are commonly subjected to the films in the converting processes and daily usage. 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 [4, 5].

In this study, change in the barrier property of SiO_x deposited nylon 6 films accompanied by the damage introduced by abrasion and twisting were examined. Generally the barrier property of the plastic films are examined by the measurements of oxygen and water vapor permeation rates. However 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 in various deformations. Change in H_2S permeation rate was compared with that of H_2 permeation rate.

2. Experimental

2.1. Packaging films

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 biaxally oriented nylon 6 film (EMBLEM-ON, Unitika Co., Ltd) using a heating system of an electron beam. The mixture of Si and SiO_2 was used as an evaporation source. The thickness of the deposited SiO_x layer is about 40 nm. This film is known as a high barrier film whose H_2 and O_2 permeation rates are 7.2×10^{-4} and 1.67×10^{-5} $m^3/m^2 \cdot day \cdot MPa$, respectively as compared with an undeposited nylon 6 film whose H_2 and O_2 permeation rates are 7.7×10^{-3} and 2.56×10^{-4}, respectively.

TABLE I H_2 permeation rates through SiO_x-ON and the various commercial films utilized in this study

Specimen	H_2 permeation rate ($\times 10^{-4}$ m^3/ $m^2 \cdot day \cdot MPa$)	Composition (thickness)
SiO_x-ON	7.2	SiO_x deposited oriented nylon 6 (15 μm)/LLDPE (60 μm)
ON	77	Oriented nylon 6 (15 μm)/LLDPE (60 μm)
PVDC-ON	41	PVDC coated oriented nylon 6 (17 μm)/LLDPE (60 μm)
PET	196	PET (12 μm)/LLDPE (60 μm)
OPP	3,400	Oriented PP (20 μm)/cast PP (50 μm)
SiO_x-PET	2.2	SiO_x deposited PET (12 μm)/cast PP (60 μm)

Five other kinds of commercial general purpose and high barrier films laminated with either linear low density polyethylene (LLDPE) or cast PP (CPP) were also used for comparison. General purpose films include oriented polypropylene (OPP: Fukusuke Industrial Ltd.), poly(ethylene terephthalate) (PET: Unitika Co. Ltd., EMBLET), 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.) films. Detailed information and H_2 permeation rates of SiO_x deposited nylon 6 and these commercial films are listed in Table I.

2.2. Damaging of SiO_x deposited nylon film

2.2.1. Abrasion

SiO_x deposited nylon films were fixed over a smooth plastic plate in 200 mm wide and 360 mm long with a deposited surface outside. Another plastic plate in 140 mm wide and 100 mm long weighing 230 g was covered with a standard cotton cloth for staining of color fastness test (JIS L0803, muslin No.3) as an abrading material. This plate covered with the cotton cloth was placed on a SiO_x deposited nylon film with a normal load of 161 Pa. Predetermined cycles of abrasion were given to SiO_x layer by moving the sliding plate in one direction at 100 mm/min. Only the part of film on which the sliding plate passed were used as test specimens.

2.2.2. Gelboflex

Flex resistance of flexible barrier films is generally determined by the Gelboflex tests according to the method described in ASTM-F392-93 [12]. Gelboflex tester used in this study is schematically illustrated in Fig. 1. This apparatus consists of 90 mm diameter stationary and movable mandrels spaced at a distance of 180 mm apart from face to face at the starting position. The film specimen is supported by the shoulders on the mandrels. The motion of the movable mandrel is controlled by a grooved shaft designed to give a twisting motion of 440° in the first 90 mm of the stroke of the movable mandrel, followed by a straight horizontal motion of 65 mm. The motion of the machine is reciprocal with a full cycle consisting of the forward and return strokes. The frequency of the reciprocating movement was 40 strokes/min.

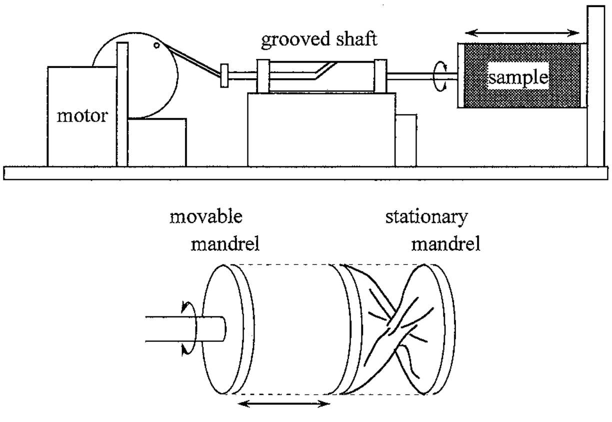

Figure 1 Schematic diagrams of Gelbotester and the mode of deformation.

2.3. Lamination of damaged films

SiO_x deposited nylon films damaged in various ways were laminated with 50 μm thick linear low density polyethylene (LLDPE) film over SiO_x deposited surface with a dry lamination method. Some of SiO_x deposited nylon films were laminated with LLDPE before giving various deformation for comparison. A polyester/polyurethane type adhesive (TM-215/CAT-10L, Toyo Morton Co., Ltd.) was applied on 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 deposited films by pressing with a roll.

2.4. Sample preparation

Rectangular pouches 30 mm long and 40 mm wide were made of SiO_x deposited nylon 6 and other 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 × 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 H_2S gas

The pouches 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.

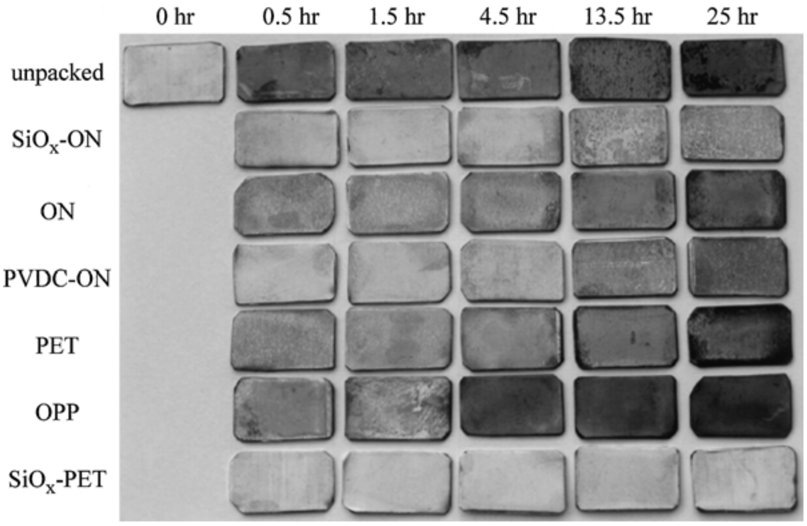

Figure 2 Appearance of copper plates packed in pouches made of various commercial films.

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 of the copper surfaces. H_2 permeation rates through the sample films were also determined.

2.6.1. Reflectance

The reflectance at the surface of copper plates was measured by a spectrophotometer (Color-Eye 3100; Gretag Macbeth Co., Ltd.) in a 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, 3 regulation to indicate the color by the system of CIE Lab [13–17]. 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 × 10 mm. The color of the copper surface was indicated by the reflectance at 620 nm and the psychometric lightness L^*.

2.6.2. H_2 permeation rate

The gas barrier property of the laminated films was evaluated by the measurement of the hydrogen gas permeation rate. The H_2 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 $m^3/m^2 \cdot day \cdot MPa$ for 100% H_2.

3. Results and discussion

3.1. Corrosion of copper by H_2S

Copper is sulfurated by H_2S gas and a layer of copper sulfide is formed on the surface. The following chemical reactions are considered to occur [18];

$$2Cu + H_2S \rightarrow Cu_2S + H_2 \uparrow$$

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$$Cu + H_2S \rightarrow CuS + H_2 \uparrow$$

Fig. 2 shows the appearance of the copper plates packed in the pouches made of various commercial films exposed to H_2S gas for various periods of time. The brightness of the copper surface faded gradually with time and the color of copper changed into tarnish, dark, gray, blackish and finally into black. The change in color began at an edge or section of the copper plate and spreaded gradually over the entire surface. Following colors correspond approximately to the respective wavelengths; violet 420 nm, blue 470 nm, green 520 nm, yellow 580 nm, yellowish red 610 nm and red 650 nm, respectively [19]. Since the color of fresh copper appears closely to be yellowish red or red, the reflectance at the wavelength from 600 to 660 nm supposedly indicates the color of copper itself [20]. In this report, we took a reflectance and a psychometric lightness L^* at 620 nm as indices of the corrosion of copper by H_2S.

The change in the spectral reflectance at the surface of copper plate packed in a pouch of polyvinylidene chloride coated nylon (PVDC-ON) exposed to H_2S gas is shown in Fig. 3. The reflectance at the wavelength from 600 to 660 nm decreased with the increasing exposure period to H_2S. These correspond to the change in color shown in Fig. 2, in which one can see the brilliant yellowish red gradually turned to tarnish and grayish as the sulfuration proceeded.

3.2. Damages of SiO$_x$ deposited nylon 6 film by abrasion

Fig. 4 shows the appearance of the copper plates packed in the pouches made of SiO$_x$ deposited nylon films damaged by abrasion. The changes in the reflectance at the wavelength of 620 nm and the psychometric lightness are plotted in Fig. 5 as functions of the period of exposure to H_2S. The change in the appearance of the copper surface occured more quickly and significantly with the repetition of the abrasion on the film surface. Furthermore, the spectral reflectance and the psychometric lightness decreased more significantly when the copper plates were kept in the pouches of abraded films. It seems that once SiO$_x$ layer was abraded with a

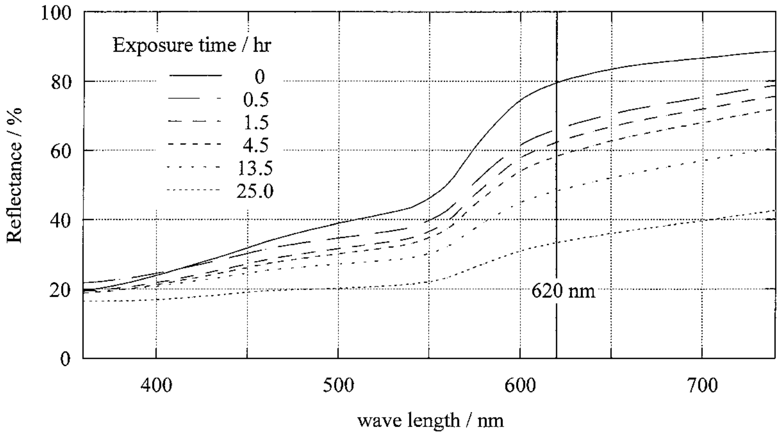

Figure 3 Change in the spectral reflectance at the copper surface kept in a PVDC-ON pouch.

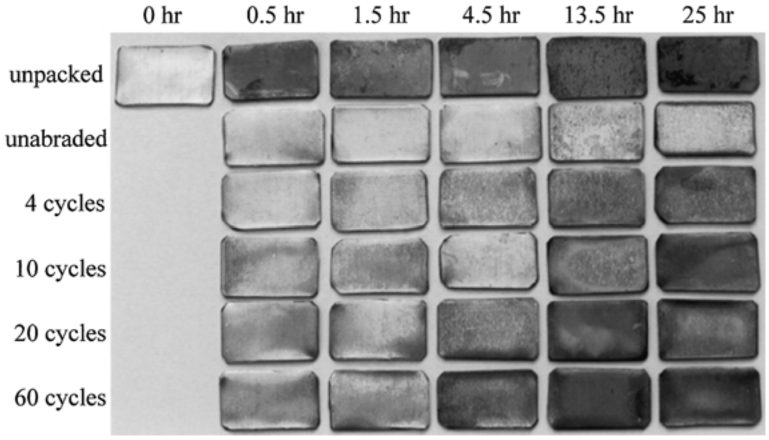

Figure 4 Appearance of copper plates packed in pouches made of SiO_xdeposited nylon 6 films damaged by abrasion.

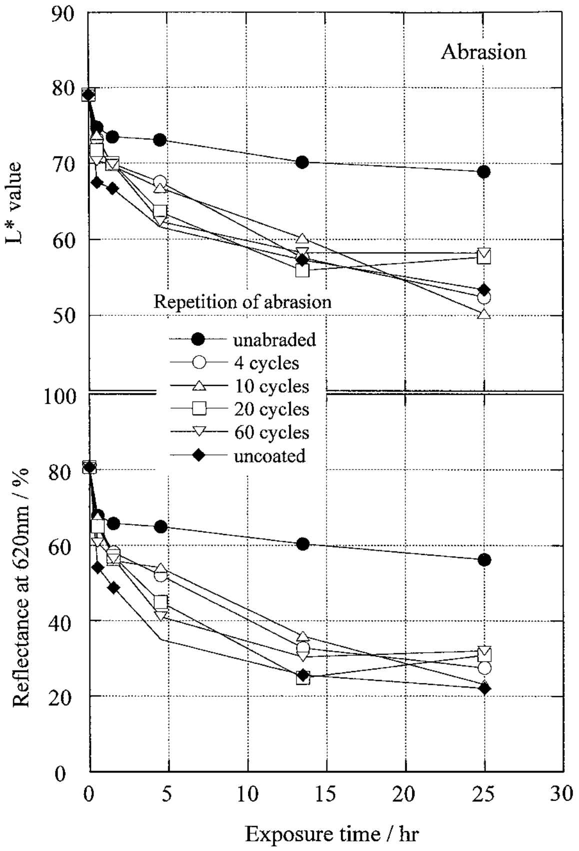

Figure 5 Changes in the reflectance at 620 nm and the psychometric lightness L^* for SiO_x deposited nylon 6 films abraded with a cotton cloth.

cotton cloth several times, some micro-cracks were formed and H_2S molecules easily permeated through the film.

The surface morphology of SiO_x layer and the H_2 permeation rate through the SiO_x deposited nylon 6 films damaged by abrasion have been reported elsewhere by the authors [4]. Abrasion by a sand paper completely ruined the gas barrier property of the film. Even mild rubbing with a cotton cloth several times significantly reduced the barrier property of the film. AFM observation revealed that there were a lot of irregular stripes to the abrasion direction on the SiO_x layer abraded with a cotton cloth more than 10 times and some micro-cracks were also found at the thinner parts of irregular stripes. Such change in the surface morphology extended to all surface area abraded. Although H_2 permeation rate of unabraded SiO_x deposited nylon 6 film is as low as 7.2×10^{-4} $m^3/m^2 \cdot day \cdot MPa$, it increased to 2.1×10^{-3} $m^3/m^2 \cdot day \cdot MPa$ by only 4 abrasion cycles and to about 3.4×10^{-3} $m^3/m^2 \cdot day \cdot MPa$ by 10 cycles. For 60 abrasion cycles, the H_2 permeation rate was almost the same as that of uncoated nylon 6 film.

Although H_2 permeation rate reported showed a clear dependence on the number of cycles of abrasion [4], the reflectance and the psychometric lightness obtained in this study indicate that once film was abraded some micro-cracks were formed and sufficient H_2S permeated through the abraded film to cause severe corrosion of the copper plate.

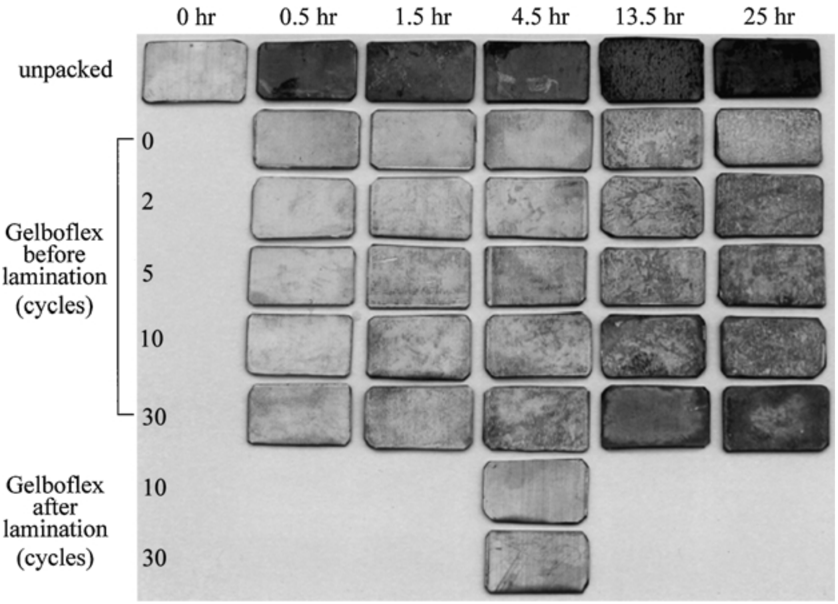

Figure 6 Appearance of copper plates packed in pouches made of SiO_x deposited nylon 6 films after Gelboflex tests.

3.3. Deformation by Gelboflex

The flexing action in the Gelboflex test consists of a twisting motion followed by a horizontal motion, thus, repeatedly twisting and crushing the film. Such flexing motion may deteriorate the barrier property of the film and pinholes may be formed in the film.

Fig. 6 shows the change in the appearance of copper plates packed in the pouches made of SiO_x deposited nylon films after Gelboflex tests. Fig. 7 shows the reflectance at 620 nm and psychometric lightness on the surfaces of copper plates. As the flexing cycles and the period of exposure to H_2S, the brilliant yellowish red of copper surface faded gradually and the color of copper became tarnished, grayish, gray, blackish and finally into black. This tendency was also observed in the changes of the spectral reflectance and psychometric lightness where these values decreased more quickly with the flexing cycles.

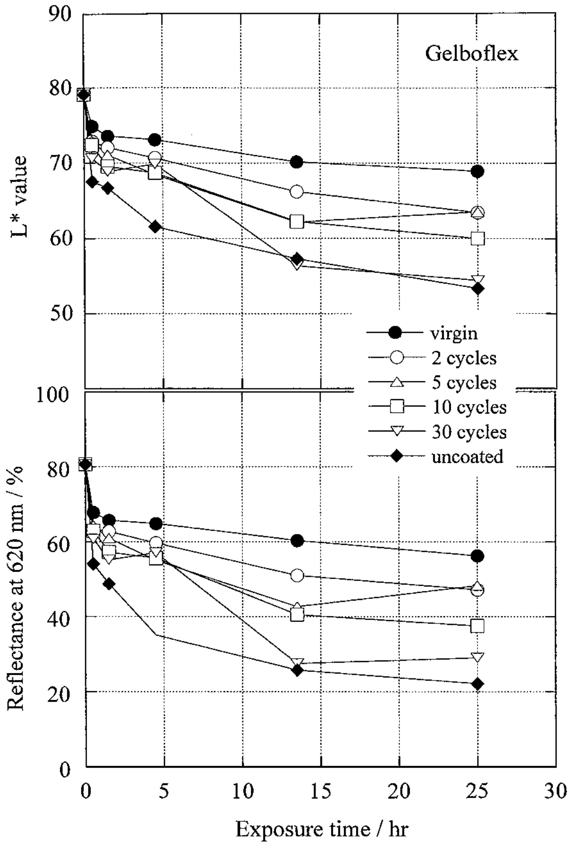

Figure 7 Changes in the reflectance at 620 nm and the psychometric lightness L^* for the SiO_x deposited nylon 6 films after Gelboflex tests.

AFM observation of the SiO_x deposited nylon 6 film after 30 Gelboflex cycles revealed that the damage by flexing formed locally [4]. Some of the part was filled with micro-cracks and other part was kept undamaged. The area and the extent of the damage seem to increase with the Gelboflex cycles and the barrier property deteriorated gradually. This is supported by the reflectance and the psychometric lightness which decreased at higher rates with time as the number of Gelboflex cycles increased. No macroscopic pinhole was formed within the number of Gelboflex tests carried out in this study.

Generally SiO_x deposited layer of the film is covered with other protective films. The effect of the lamination of LLDPE film on SiO_x layer on the severity of the damage during Gelboflex test was clearly seen in Fig. 8, where the reflectance and the psychometric lightness decreased more slowly with the number of Gelboflex cycles given to the SiO_x deposited film laminated with LLDPE.

3.4. Various commercial packaging films

Fig. 9 shows the reflectance and the psychometric lightness L^* at the surface of copper plates packed in the pouches made of undamaged SiO_x deposited nylon 6 and various commercial films. There were remarkable differences in the reflectance and the psychometric lightness among these packaging materials. These changes were observed to be more significant in the

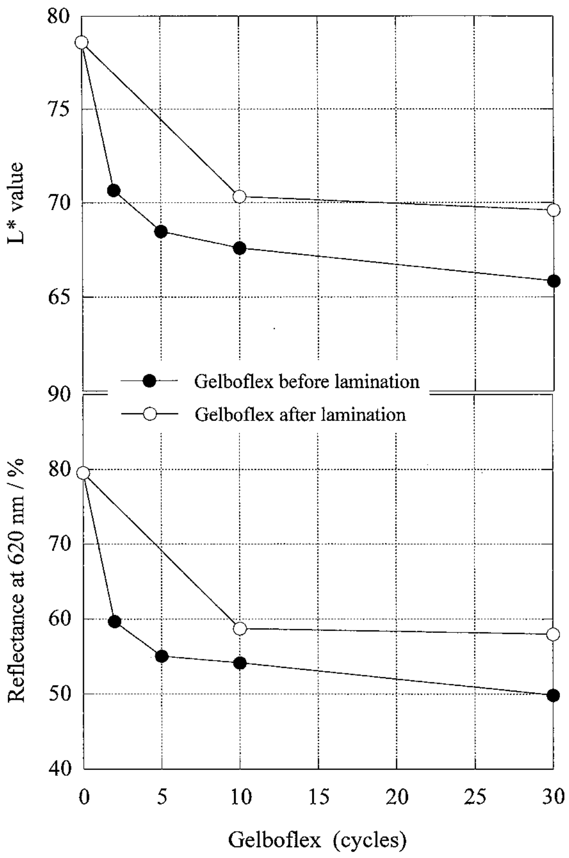

Figure 8 Changes in the reflectance at 620 nm and the psychometric lightness L^* for the SiO_x deposited nylon 6 films with Gelboflex cycles carried out before and after lamination.

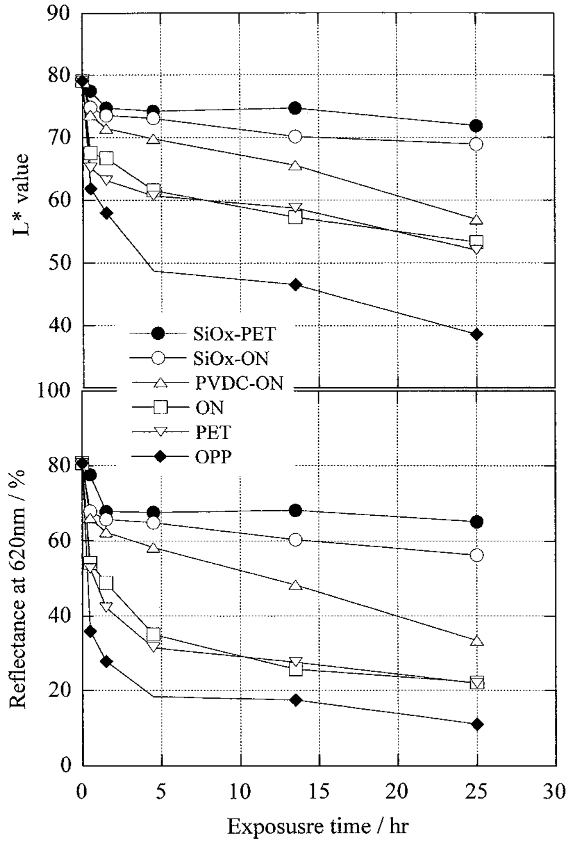

Figure 9 Changes in the reflectance at 620 nm and the psychometric lightness L^* for SiO_x deposited nylon 6 and various commercial films.

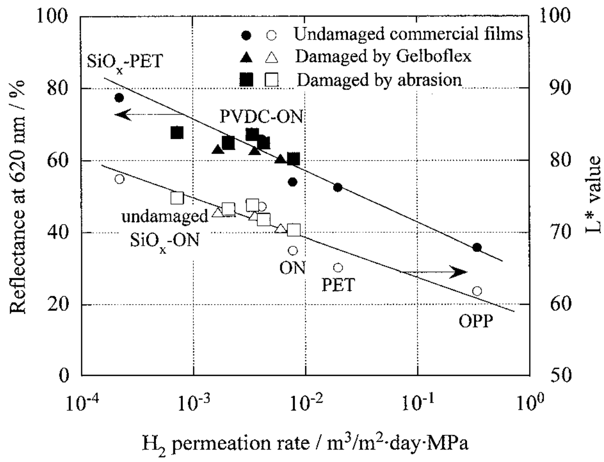

Figure 10 Reflectance and the psychometric lightness L^* of the copper plates kept in H_2S for 30 min as functions of H_2 permeation rate of the films.

order of,

$$SiO_x\text{-PET} < SiO_x\text{-ON} < \text{PVDC-ON} < \text{ON} < \text{PET} < \text{OPP}$$

It should be noted that this is exactly the same tendency to that for the H_2 permeation rates listed in Table I. It may be interesting to plot the reflectance and the psychometric lightness L^* of the damaged SiO_x deposited nylon 6 films and those of various commercial films utilized as functions of H_2 permeation rate. Such plots are shown in Fig. 10. Both the reflectance and the psychometric lightness decreased proportionally to the logarithm of H_2 permeation rates. These plots indicate that when the H_2 permeation rate is low, the corrosion rate shows a strong dependence on the H_2 permeation rate.

4. Conclusions

We examined the damage imposed on the SiO_x deposited nylon 6 films accompanying abrasion with a cotton cloth and the Gelboflex tests. Change in the gas barrier property with the progress of the damage was evaluated by the corrosion rate of the copper plates kept in the pouches made of the damaged films and exposed to H_2S.

Abrasion with a cotton cloth gave a lot of stripes on the SiO_x layer alined to the abrasion direction. Further some micro cracks were formed on the SiO_x layer and the corrosion rate of the copper approached that of the copper plate kept in the pouch made of the uncoated nylon 6 film.

Flexing by the Gelboflex tester gave twisting and crushing deformations on the SiO_x deposited nylon 6 films. Damage of SiO_x layer by such deformations progressed gradually with the number of Gelboflex cycles. This tendency was clearly shown by the change in the corrosion rate of the copper plates which increased gradually with the number of the Gelboflex cycles. Even 30 cycles of the Gelboflex test did not make any pinholes in the films.

Comparisons of the corrosion rate of the copper plates kept in the pouches made of various commercial films and those obtained for the damaged SiO_x deposited nylon 6 films showed a clear relationship between H_2 permeation rate and the corrosion rate of the copper plates by H_2S.

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