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Instructions for use

Water and Oxygen Permeability of Silica Thin Films Containing Organic Polymers Coated on Poly (Ethylene Terephtalate) Substrate by the Sol–Gel Method

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ゾル–ゲル法による PET 基板上への有機高分子含有シリカ薄膜の作製と水蒸気及び酸素透過性

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Silica thin films containing organic polymers, such as poly(vinyl alcohol), poly(vinylpyrrolidone) or poly(vinyl acetate), were prepared on PET substrates by the sol–gel method. Poly(vinyl alcohol) was found to be most effective to suppress the water permeability of PET substrates coated with the organic–inorganic composite films among the three. Under the optimal condition, the water permeability coefficient was about 40% of that of PET substrates. The oxygen permeability coefficient was decreased with an increase in the poly(vinyl alcohol) content in the composites and was about 10% of that of PET substrates when a large amount of poly(vinyl alcohol) was included in the composites.
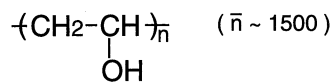[Received July 6, 1998; Accepted January 20, 1999]

1. Introduction

The sol–gel method has been known as a practical method to produce inorganic materials.[1] This method has several features as the low-temperature process, the easy preparation of high-purity materials and the variety of shapes of the products. These features have been applied to coating of oxide thin films on organic polymer substrates for surface modification.[2] Characteristics of polymer substrates like abrasion resistance, chemical durability to organic solvents, gas permeability, etc., are improved by coating of oxide thin films. However, it is difficult to form crack-free and good adhesive thin films on organic polymer substrates when only the inorganic component is coated on the substrates.[3]
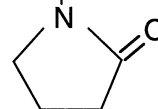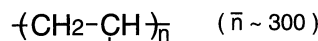
Organic–inorganic composite materials are also prepared by the sol–gel method.[2],[4] Such materials are expected to have novel characteristics which are difficult to obtain from each constituent. These materials are useful for the coating of thin films on organic polymer substrates. For example, ORMOCER coatings on polycarbonate and poly (ethylene terephtalate) (PET) have already been reported by Schmidt et al.[5]-[7] and organic–inorganic hybrid coatings on polycarbonate or PET for hard coatings have been also reported.[2],[8]-[10] We have recently found that crack-free thin films on polyimide and nylon-6 substrates can be obtained by using $Si(OC_2H_5)_4$ and $RSi(OC_2H_5)_3$ [R=methyl, vinyl, phenyl, polyvinyl] as starting materials and showed that the coatings on these organic polymers are effective to suppress the water permeability of the films.[3],[11]-[14] Very recently, polymer films without chlorine that can be used for gas barrier applications have been required, since burning of chlorine containing polymers causes the formation of dioxins. Coating of organic–inorganic hybrid thin films on polymer films is supposed to be one way to solve the problems.

When only tetramethoxysilane was used as a starting material, microcracks were observed in the films coated on PET substrates. Thus, in this study, silica thin films containing organic polymers such as poly(vinyl alcohol) (PVA),

poly(vinylpyrrolidone) (PVP), and poly(vinyl acetate) (PVAc) are coated on PET substrate by the sol–gel method to suppress gas permeability. The molecular structure of the polymers is shown in **Scheme 1**. Each polymer has an ability to form hydrogen bonds and can be expected to be incorporated in silica matrix homogeneously.[15],[16] Water and oxygen permeability coefficients of the coated films are evaluated, and the effects of the composition of coating solution and variety of organic polymers on the coefficients are discussed.

$$\text{+CH}_2\text{-CH+}_{\overline{n}} \quad (\overline{n} \sim 1500)$$
$$|$$
$$\text{OH}$$

PVA

$$\text{+CH}_2\text{-CH+}_{\overline{n}} \quad (\overline{n} \sim 300)$$

PVP

$$\text{+CH}_2\text{-CH+}_{\overline{n}} \quad (\overline{n} \sim 1500)$$
$$|$$
$$\text{OCCH}_3$$
$$\overset{||}{O}$$

PVAc

Scheme 1.

2. Experimental procedure

Tetramethoxysilane (TMOS) was used as a starting alkoxide. H_2O containing 0.06 mass% HNO_3 was added to TMOS, and the solution was stirred for 1 h at room temperature for hydrolysis of TMOS. The molar ratio of H_2O to TMOS was kept to be 2. Then, proper amounts of aqueous solution of poly(vinyl alcohol) ([$-CH_2-CH-OH$]$_n$, $n\sim$1500, PVA), polyvinylpyrrolidone ([$-CH_2-CH-NCH_2$ CH_2CH_2CO]$_n$, $n\sim$ 350, PVP), or methanolic solution of poly(vinyl acetate) ([$-CH_2-CH-OCOCH_3$]$_n$, $n\sim$1500, PVAc) were poured into the hydrolyzed TMOS. After being stirred for 1 h at room temperature in a closed container, the solution obtained was used for coating.

PET substrates with a thickness of 25 μm were used for coating. The coating was carried out on the substrates in a dipping–withdrawing manner (withdrawing speed : 0.5 mm/s) in a dry box with relative humidity less than 30%. The coating films obtained were dried at 50°C for 1 d and kept desiccator before measurement of water and oxygen permeability coefficients.

The cross section of the coating films was observed using a scanning electron microscope for the evaluation of the thickness of the coating films.

Water and oxygen permeability measurements for these coated PET substrates were performed with a hand-made permeation apparatus reported elsewhere.[3),11)-14)] The permeation apparatus was evacuated at 10^{-1} Pa for several hours, and then water vapor (6.10×10^2 Pa, saturated vapor pressure of water at 0°C) or oxygen (4.00×10^4 Pa) was introduced to the upstream side. The permeated pressure on the downstream side was monitored with an MKS-Baratron transducer (MKS-220B).

For multilayer membranes, the permeability coefficient of each layer has the following relationship (1).[14)]

$$d/P = d_1/P_1 + d_2/P_2 + \cdots + d_n/P_n \qquad (1)$$

where P and d are the permeability coefficient and thickness of the whole system, and P_n and d_n are the permeability coefficient and thickness of each layer. By using this equation, the permeability coefficient of coating films on PET substrates was calculated.

3. Results and discussion

When only TMOS was used as a starting material, microcracks were observed in the thin films coated on PET substrates because of lack of flexibility of the coating films. The addition of proper amounts of PVA, PVP and PVAc to the sol solution yielded crack-free coating films, and the thickness of the coating films was about 1 μm. Table 1 shows the state of the coating films using PVA on PET substrate. In this table, x represents the molar ratio of PVA (monomer unit) to the total moles of (TMOS+PVA). Open circles and crosses indicate that coating films are homogeneous and cracked, respectively. When PVA is used as the starting material, homogeneous and crack-free films are obtained in the composition range from $x=0.2$ to

Table 1. State of the PET Substrates Coated with Thin Films in the TMOS–PVA System. Compositons are Represented as x=PVA/(TMOS+PVA) (mol/mol)

X	0	0.1	0.2	0.3	0.4	· · ·	1.0
TMOS - PVA	×	×	○	○	○	· · ·	○

○ ; homogeneous   × ; cracked

Fig. 1. SEM photograph of the cross section of the thin film formed from TMOS–PVA sol on PET substrate.

Fig. 2. Composition dependence of water permeability coefficient of PET substrates coated with thin films in the TMOS–PVA system.

1.0. Figure 1 shows an SEM photograph of the cross section of thin film formed from TMOS–PVA sol on PET substrate. The upper side is the coating film and the lower side is the PET substrate. This photograph shows that a uniform coating with very smooth surface is obtained. In the films, PVA can form hydrogen bonds with Si–OH produced by hydrolysis of TMOS. The formation of Si–O–Si network by condensation polymerization of Si–OH is partly hindered by PVA, and coating films must be given good flexibility as a result, which prevents cracks in the films. As the ratio of PVA was increased, however, the thin films showed less water durability, which arose from dissolving of PVA in water.

Figure 2 shows the composition dependence of the water permeability coefficient of the PET substrates coated with thin films in the TMOS–PVA system. The coefficient of the PET substrates coated with thin films in the tetraethoxysilane–vinyltriethoxysilane (TEOS–VTES) system is also plotted with solid triangle for comparison (TEOS/VTES=

80/20). The coefficient of PET substrates without coating films is shown as a dotted line.

In the TEOS–VTES system, the coefficient is nearly equal to that of non-coated PET substrates. We have already shown that when thin films in the TEOS–VTES system were coated on nylon-6 substrates, water permeability was suppressed greatly by the coating.[9] The differences in the effect of thin films in the TEOS–VTES system coated on these two substrates on the water permeability coefficient is assumed to be due to the difference of interaction between substrates and films. Nylon-6 substrates have amide groups in the structure which are good proton acceptors, and this causes much interaction between silanol groups in the films and the substrates. In this case, the thin films strongly adhere to the nylon-6 substrates. It is supposed that this strong adhesion led to the formation of siloxane network on nylon-6 substrates, and the water permeability was suppressed by the network. In contrast to nylon-6, the coating films on PET substrates can be peeled off easily by a peel adhesion tape test. Small polarity of polymer network of PET makes it difficult to form enough siloxane network on the substrates to suppress the water permeability and to obtain good adhesive thin films.

In the TMOS–PVA system, when a small amount of PVA was contained in the thin films, the water permeability of coated PET is suppressed by 40% of that of non-coated PET. This indicates that the addition of a small amount of PVA improved the adhesion of thin films to PET to some extent and also the formation of siloxane network on PET substrates. Easier formation of siloxane network on PET substrates is thought to contribute to decrease the water permeability coefficient. As the ratio of PVA was increased, thin films showed less water durability and more absorption of water. This would cause the increase of the water permeability in the films with large amounts of PVA.

Silica thin films containing other organic polymers such as PVP, PVAc, were coated on PET substrates and water permeability coefficients of the coating films were evaluated. These polymers are also expected to play a similar role to PVA. Figure 3 shows the composition dependence of water permeability coefficient of the coating films. The coefficient of the coating films in this figure was calculated by Eq. (1).[14] Open circles, solid triangles, solid squares indicate the TMOS–PVA, TMOS–PVP and TMOS–PVAc systems, respectively. In all the systems, the coefficient is decreased when a small amount of organic polymer is added. This shows that the addition of organic polymers, which can form hydrogen bonds with silica component and have some interaction with PET substrates, yields a good film formation ability and results in decreasing the coefficient. The coefficient is raised with further increase of the ratio of organic polymer to TMOS, because the added polymer partly inhibits the formation of siloxane network. PVAc and PVP are expected to inhibit the formation of siloxane network more strongly than PVA, since the substituent of PVP and PVAc is more bulky than that of PVA as shown in Scheme 1. This causes the larger coefficients in the TMOS–PVP and TMOS–PVAc systems to be larger than in the TMOS–PVA system.

Figure 4 shows the composition dependence of oxygen permeability coefficient of the coated PET substrates. Open circles, solid triangles, solid squares indicate the TMOS–PVA, TMOS–PVP, TMOS–PVAc systems, respectively. The coefficient of PET substrates without coating films is shown as a dotted line. In the TMOS–PVA system, the coefficient is decreased with an increase of PVA content and is about 10% of that of PET substrates when a large amount of PVA was included in the composite films. In the case of polymer/(TMOS+polymer)=0.6, the coefficient
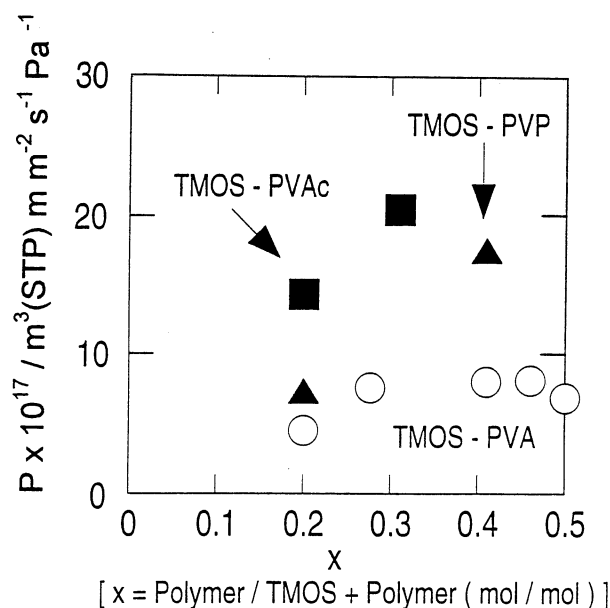

Fig. 3.   Composition dependence of water permeability coefficient of coating films.
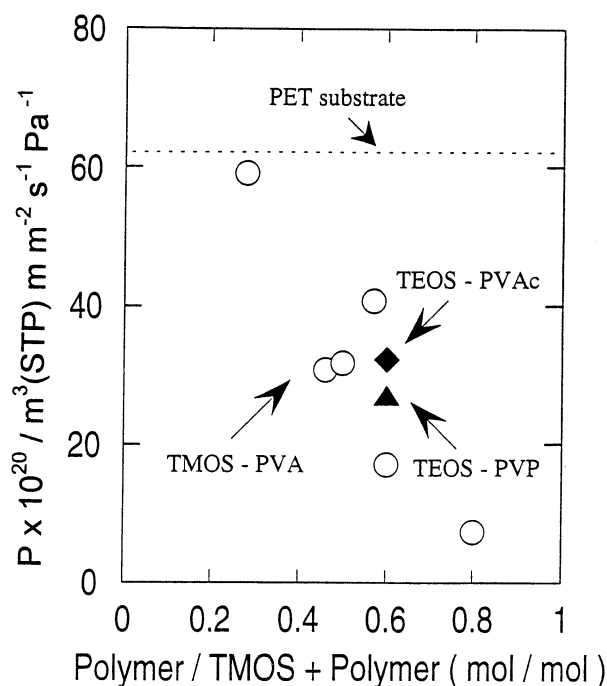

Fig. 4.   Composition dependence of oxygen permeability coefficient of coated PET substrates. ○ : TMOS–PVA system, ▲ : TMOS–PVP system, ◆ : TMOS–PVAc system.

of the TEOS–PVA system is almost the same as or slightly smaller than that of the TEOS–PVP or TEOS–PVAc systems. The permeability coefficient of PVA is known to be much smaller than that of PET,[17] and this causes the decrease of the coefficient with an increase of PVA content. The water permeability coefficients of the PET substrates coated with films containing a small amount of PVA are most effectively suppressed, as shown in Fig. 2, while the oxygen permeability coefficients of the PET substrates coated with films containing a small amount of PVA are only slightly suppressed, and the coefficient is decreased with

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further increase of PVA content in the composite, as shown in Fig. 4. This shows that siloxane network has a strong affinity for oxygen, and oxygen can easily permeate through the coating films with a small amount of PVA.

4. Conclusion

Silica thin films containing organic polymers, such as PVA, PVP or PVAc, were prepared on PET substrates by the sol-gel method. PVA was found to be the most effective agent to suppress the water permeability of PET substrates coated with the organic-inorganic composite films. The water permeability coefficients were decreased when a small amount of PVA was added, and were increased with further increase of PVA content. Addition of a small amount of PVA caused the formation of siloxane network on PET substrates, and this contributed to decrease the water permeability coefficient. The oxygen permeability coefficient was decreased with an increase in the PVA content in the composites and was about 10% of that of PET substrates when a large amount of PVA was contained in the composites.

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