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Preparation and properties of silica/poly(vinyl alcohol) organic–inorganic hybrid gas barrier films via sol–gel method with microwave irradiation

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ABSTRACT

Silica/poly(vinyl alcohol) (PVA) organic–inorganic hybrid gas barrier films were prepared by sol–gel method with microwave irradiation using tetraethoxysilane (TEOS), methyltriethoxysilane (MeTEOS) and poly(vinyl alcohol) on polypropylene (PP) substrates. Oxygen permeation through the films was measured by a variable-pressure method. Water vapor transmission rate of the films was also evaluated by dish method. Oxygen permeability coefficients of the hybrid layer was small and about one-sixth of those of poly(vinylidene chloride) (PVDC) and water vapor transmission rate of the hybrid layer was the same order of PVDC. Pencil hardnesses (50 g load) of the PP with the hybrid layers were more than HB. These values were considerably higher than that of PP (6B). These properties were thought to be due to well dispersion of inorganic segments (silica) and organic segments (PVA) at molecular level in the hybrid. From the results, it was found that the organic–inorganic hybrids could be applicable to gas barrier films.

Keywords: Organic–inorganic hybrid; Silica; Poly(vinyl alcohol); Gas barrier

1. Introduction

The gas barrier property of plastic films is an important factor for their application as packaging materials. Poly(vinylidene chloride) (PVDC) films and plastic films coated with PVDC have been utilized in packaging materials due to their high oxygen and water vapor barrier properties. Recently, the possibility of PVDC being an environmental pollutant due to high chlorine content has become a topic of concern for several individuals. From this viewpoint, PVDC should be replaced by other non-chlorine-containing materials. Inorganic compounds, such as glass and ceramics, are potential candidates for gas barrier materials instead of PVDC. The deposition of SiOx films on polymer films using vapor deposition has been used for gas barrier applications in food and pharmaceutical technologies [1]. Organic–inorganic hybrids [2,3] were also used for such applications. A large variety of organic–inorganic hybrids prepared by sol–gel method have been reported thus far [2–8]. Among these, the most common method of preparation is that utilizing the hydrogen bonding interactions between polar functional groups of organic polymers and silanol groups of silica gels. Examples include organic polymers such as poly(2-methyl-2-oxazoline), poly(*N*-vinylpyrrolidone) and polyethylene glycol homogeneously incorporated into silica gels at the molecular level [3, 5–8]. Such incorporation of inorganic elements at the molecular level in organic polymers has resulted in novel

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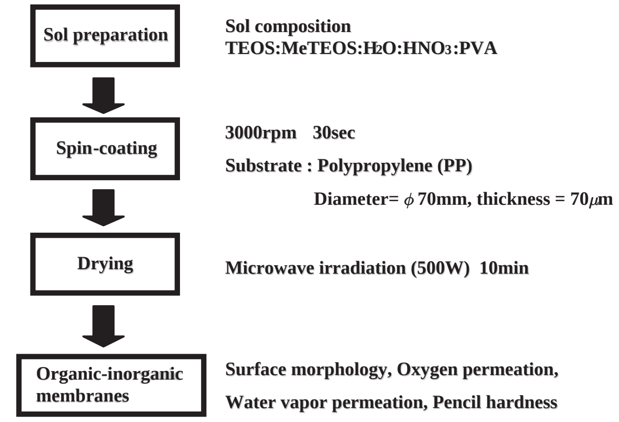

Fig. 1. Experimental procedure of silica/PVA organic–inorganic hybrid gas barrier films.

properties such as improved mechanical strength and thermal stability. Moreover, the incorporation of organic elements can likewise improve on the brittleness of inorganic materials. We have also succeeded in coating silica/poly(vinyl alcohol) (PVA) organic–inorganic hybrid gas barrier films on poly(ethylene terephthalate) by the sol–gel method [3]. The prepared films exhibited gas barrier ability; however, the long heating time of this technique restricted its practical applicability.

Recently, microwave irradiation has attracted considerable attention as a heating method in the laboratory for the synthesis of organic [9], polymer [10], and inorganic materials [11]. Unlike the conventional heating method, microwave irradiation offers a clean, energy-effective, fast, and convenient heating process, which results in a higher yield and shorter reaction time. We already reported the preparation of silica/PVA organic–inorganic hybrid gas barrier layers on polypropylene (PP) films via the sol–gel method by microwave irradiation [12].

In the present paper, we wish to report the effect of PVA content on the oxygen barrier property, the water vapor barrier property and surface hardness of silica/PVA organic–inorganic hybrid gas barrier films via the sol–gel method by microwave irradiation.

2. Experimental

2.1. Preparation of silica/PVA organic–inorganic hybrid gas barrier films

Silica/PVA organic–inorganic hybrid gas barrier films were prepared using the sol–gel method. Fig. 1 illustrates the experimental procedure of silica/PVA organic–inorganic hybrid gas barrier films. The sols were composed of tetraethoxysilane (TEOS), methyltriethoxysilane (MeTEOS), H_2O and HNO_3. The compositions of the sols are shown in Table 1. Commercially available reagent grade chemicals were used. PVA was added to a mixture of H_2O and HNO_3. After the mixture was stirred for several hours at 343 K, a mixture of TEOS and MeTEOS was added at room temperature. Then the mixture was stirred overnight to obtain a homogeneous sol. PP films with a thickness of 70 μm were used as the supports. The support was spun at a rate of 3,000 rpm for 30 s, and 0.5 cm^3 of the sol was dropped on the support. Following the spin-coating procedure, films were exposed to microwave irradiation (2.45 GHz) at 500 W for 10 min for promotion of a solvent evaporation, hydrolysis and condensation.

2.2. Characterization of the films

Prepared silica/PVA organic–inorganic hybrid gas barrier films were transparent and the thicknesses of hybrid layers were measured by a contact-type film thickness meter (Hakattaro G, Seiko EM Co., Ltd).

Oxygen permeation through the films at 313 K was measured by a variable pressure method using a gas permeation measurement apparatus (K-315N-01, Tsukubarikaseiki Co., Ltd).

Water vapor transmission rate of the films was evaluated by dish method (JIS Z0208). A test dish with a diameter of 60 mm and a depth of 25 mm was made from aluminum. Granular calcium chloride products

Table 1
Sample name and compositions of the sols

	Compositions of the sols (molar ratio)				
Sample	TEOS	MeTEOS	H_2O	HNO_3	PVA
OP10	0.75	0.25	14.0	0.01	10 wt%
OP20	0.75	0.25	14.0	0.01	20 wt%
OP30	0.75	0.25	28.0	0.01	30 wt%
OP40	0.75	0.25	37.3	0.01	40 wt%
OP50	0.75	0.25	46.7	0.01	50 wt%

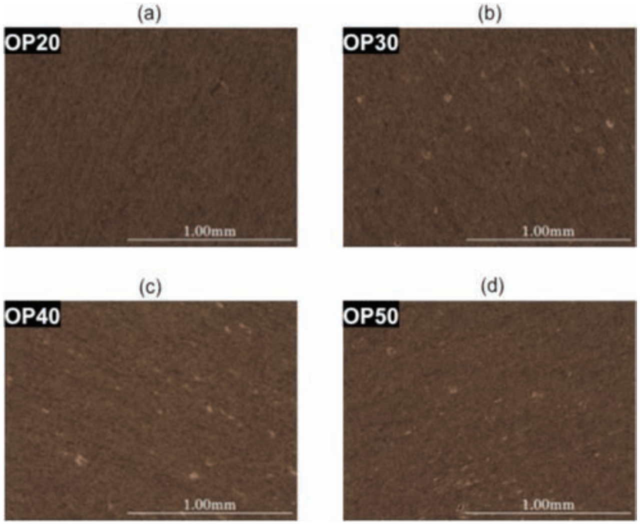

Fig. 2. Optical micrographs of the surface morphologies for the films. (a) OP20; (b) OP30; (c) OP40 and (d) OP50.

were used to maintain the RH (relative humidity) inside the dish about zero. The film was cut into circle shapes and used to cover the test dish. The test dish with the film was kept in a constant temperature/humidity chamber (AE-215, Advantec Toyo Kaisha, Ltd.) at 313 K, 90%RH and the weight of the dish was measured every 24 h. The water vapor transmission rate was calculated from the weight change, W and elapsed time, t and permeation area, A using the following equation:

$$\mathrm{WVTR} = W \times 240(A \times t), \quad (1)$$

where WVTR is water vapor transmission rate.

The pencil hardness test (load: 50 g) according to JIS K-5400 was conducted to determine the surface hardness of the films.

3. Results and discussion

3.1. Surface morphologies and thickness of the films

Optical micrographs of the surface morphologies for the films are shown in Fig. 2. OP20, OP30 and OP40 had no cracks and exhibited a smooth surface (Fig. 2a–c). Although OP50 also had no cracks, the surface was not a smooth (Fig. 2d). The difference between OP50 and others was caused by hydrophilicity of the sol. As PVA content increases, hydrophilicity and viscosity of the sol also increases. Thus the sol coating on hydrophobic PP substrates becomes difficult.

The hybrid layer thickness of OP10, OP20, OP30, OP40, OP50 were 3.1, 3.6, 3.6, 4.3, 4.9, respectively. The thickness of the hybrid layer almost increased as PVA content increased. This increase of the thickness is thought to be due to rise of the viscosity of the sol.

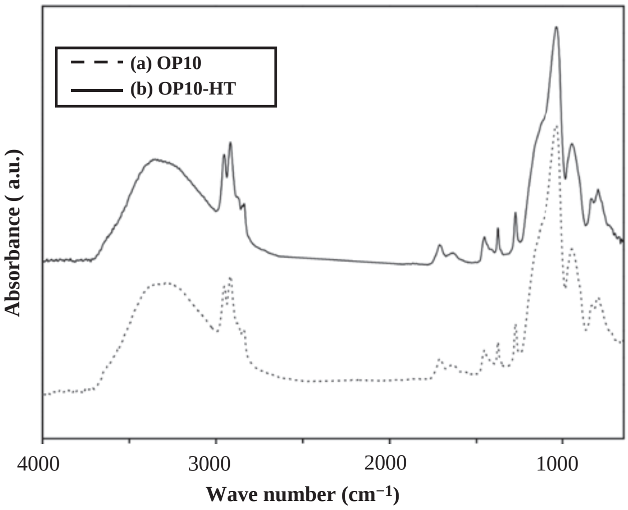

Fig. 3. IR spectra of (a) OP10 and (b) OP10-HT.

3.2. Structure of the films

The structures of the silica/PVA organic–inorganic gas barrier films were determined using a Fourier-transform infrared spectrometer (FTIR) (FT/IR-4100, JASCO Co.). The IR spectra of OP10 and OP10-HT are presented in Fig. 3. OP10-HT was heated at 373 K for 12 h in air at heating and cooling rates of 0.5 K/min instead of microwave irradiation (conventional heating procedure). Both the films show a typical band at $\sim$960 cm^{-1} associated with the stretching mode of Si–OH along with the characteristic bands related to the Si–O–Si bond ($\sim$1,200, 1,050, 800 cm^{-1}), which confirm the presence of the Si–O–Si network in the films [13,14]. The adsorption band near 2,900 cm^{-1} is assigned to the C–H stretching vibration of PVA. The strong and broad band at $\sim$3,700–3,000 cm^{-1} is assigned to the hydroxyl groups of Si–OH and PVA [14]. Other characteristic bands originating from PVA and CH_3–Si were also observed. No difference was observed in the spectra of OP10 (microwave irradiation) and OP10-HT (conventional heating). This result indicates that microwave irradiation is more efficient in shortening the reaction time than the conventional heating technique.

3.3. Oxygen permeation through the films

Fig. 4 shows the oxygen permeances of silica/PVA organic–inorganic hybrid gas barrier films. The oxygen permeances of OP10, OP20, OP30, OP40, OP50 were

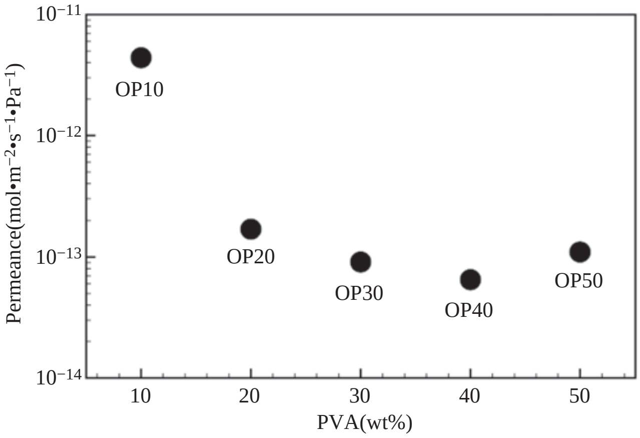

Fig. 4. Oxygen permeances of the films.

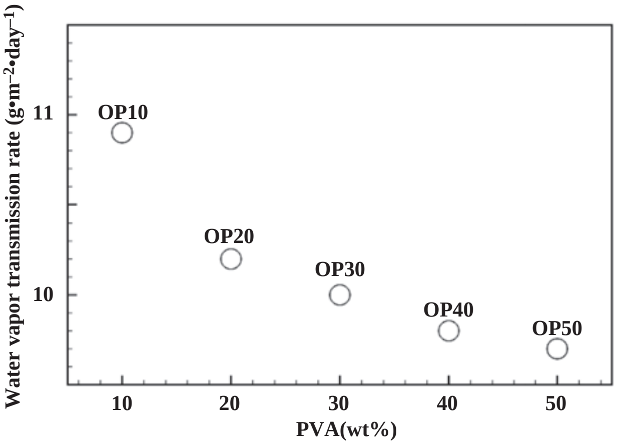

Fig. 5. Water vapor transmission rates of the films.

4.4×10^{-12}, 1.7×10^{-13}, 9.1×10^{-14}, 6.5×10^{-14}, 1.1×10^{-13} mol m^{-2} s^{-1} Pa^{-1}, respectively, while that of the PP film was 1.7×10^{-11} mol m^{-2} s^{-1} Pa^{-1}. The oxygen permeances of the films decreased until OP40 (40 wt% PVA) as PVA content increased due to the increase of the film thickness. Oxygen permeance increase of OP50 is due to defects in the hybrid layer caused by high hydrophilicity and viscosity of the sol as mentioned in Section 3.1. The permeance of OP40 was about 1/260 of that of PP film. This value indicates that the silica/PVA organic–inorganic hybrid layer is effective in suppressing the oxygen permeation. The high gas barrier property can be explained by the formation of a dense structure during coating procedure.

3.4. Water vapor transmission rates of the films

Water vapor transmission rates of silica/PVA organic–inorganic hybrid gas barrier films are shown in Fig. 5. The water vapor transmission rates of OP10, OP20, OP30, OP40, OP50 were 10.9, 10.2, 10.0, 9.8, 9.7 g m^{-2} d^{-1}, respectively. The water vapor transmission rates of the films decreased as PVA content increased. The main reason of this decrease of water vapor transmission rates is thought to be due to the increase of the film thickness on PP substrate as shown in Section 3.1. Higher PVA content caused higher viscosity of the sol. Thus the thickness of the hybrid layer becomes large as increased PVA content.

3.5. Pencil hardness of the films

Table 2 shows pencil hardness of silica/PVA organic–inorganic hybrid gas barrier films and PP film. The pencil hardness of the films was more than HB and increased as PVA content increased, while that of PP film was 6B. In pencil hardness test, the hardest is a 6H, followed by 5H, 4H, 3H, 2H, and H. F is the middle of the hardness scale; then comes HB, B, 2B, 3B, 4B, 5B, and 6B, which is the softest. The pencil hardness of the hybrid films are much higher than that of PP film, and is due to the inorganic matrix being main component of the hybrid layer.

Table 2
Pencil hardness of the hybrid films and PP film

Sample	PP	OP10	OP20	OP30	OP40	OP50
Pencil hardness	6B	HB	2H	2H	3H	4H

3.6. Oxygen permeability coefficients of the films

For multi-layer membranes, the permeability coefficient of the whole system, P and the permeability coefficient of each layer, P_n have the following equation:

$$L/P = L_1/P_1 + L_2/P_2 + \ldots + L_n/P_n, \tag{2}$$

where L and L_n are the thickness of the whole system and of each layer. By using this equation, the oxygen permeability coefficient of silica/PVA organic–inorganic hybrid gas barrier layer on PP film was calculated.

Fig. 6 shows the oxygen permeability coefficient of OP40, PVDC and PVA. The oxygen permeability coefficient of OP40 calculated from the permeance and thickness was 2.8×10^{-19} mol m m^{-2} s^{-1} Pa^{-1}. This value was about one-sixth of those of PVDC (1.7×10^{-18} mol m m^{-2} s^{-1} Pa^{-1} at 298 K) [15] and the same order of that of PVA (1.7×10^{-19} mol m m^{-2} s^{-1} Pa^{-1} at 293 K) [15]. These PVDC and PVA data is from the

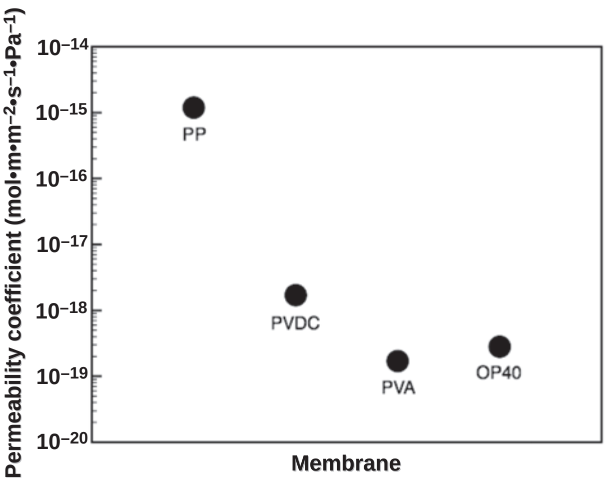

Fig. 6. Oxygen permeability coefficient of PP, PVDC, PVA and OP40.

literature. Therefore, the hybrid layer could be applicable for oxygen barrier.

3.7. Water vapor transmission rates (thickness 25 μm) of the films

Water vapor transmission rates (thickness 25 μm) of the silica/PVA organic–inorganic hybrid gas barrier layers were also calculated by using Eq. (2) and thickness is normalized as 25 μm. The calculated water vapor transmission rates (thickness 25 μm) are shown in Fig. 7 with reported values of PP and PVDC [16]. The water vapor transmission rate of OP40 was 5.3 g m^{-2} d^{-1}. This value is the same order of PVDC (1 g m^{-2} d^{-1}) [16]. The reported water vapor transmission rate of PVA was 306 g m^{-2} d^{-1} (thickness 100 μm) [17]. This value is considerably higher than that of OP40. This high value is due to swelling of PVA caused by hydroxyl groups in the molecular structure. Water molecules can adsorb in PVA molecular chain network and permeate easily.

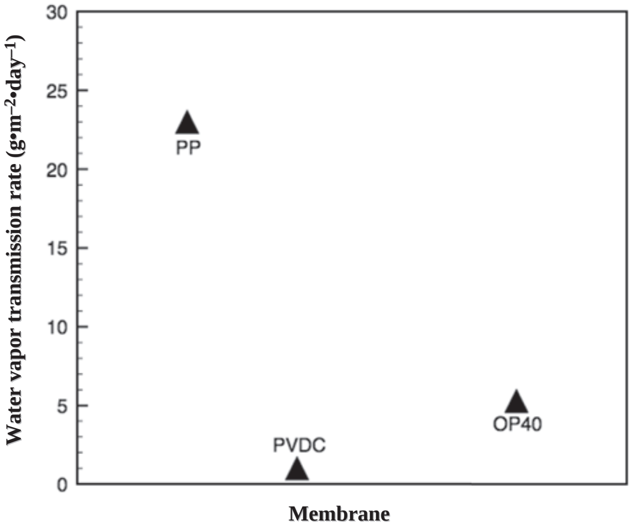

Fig. 7. Water vapor transmission rates (thickness 25 μm) of PP, PVDC and OP40.

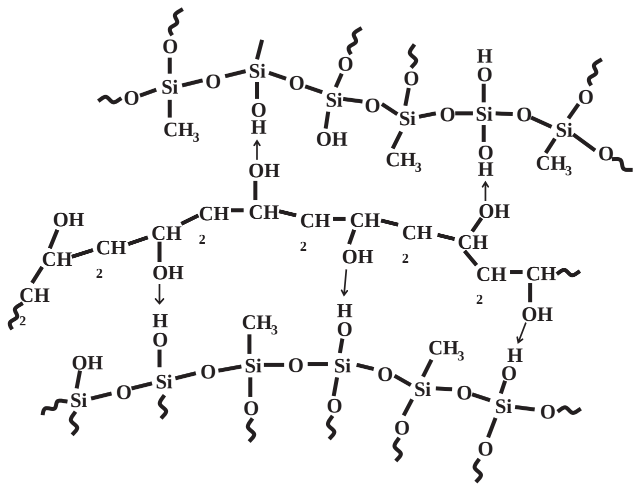

Fig. 8. Schematic representation of the structure of silica/PVA organic–inorganic hybrid gas barrier films.

These results indicated that the prepared silica/PVA organic–inorganic hybrid gas barrier films had high oxygen and water vapor barrier property. This property is a novel property of the organic–inorganic hybrid gas barrier film due to dispersion of inorganic segments (silica) and organic segments (PVA) at the molecular level and the effect of MeTEOS. The gelation process of acid-catalyzed silica gels begins the hydrolysis and followed the condensation reaction [18]. As these reactions make progress, new siloxane bonds (Si–O–Si) are formed, creating additional crosslinking and surface area in the gel network. But, when PVA is added in this type of silica gel, these molecules can hydrogen bond to silanol group (Si–OH) or react with Si–OH. These hydrogen bonds and the bridging bonds by reaction could prevent swelling of PVA. Thus the organic–inorganic hybrids indicated high water vapor barrier property in comparison with PVA. MeTEOS, with acid catalysts, was hydrolyzed and condensed with the simultaneously hydrolyzing as was the case with TEOS. The influence of MeTEOS, however, resulted in hybrids with slight hydrophobicity due to the C–H bonds of methyl groups, thus enabling films flexibility and water vapor barrier. Fig. 8 indicates a possible schematic structure of the silica/PVA organic–inorganic hybrid gas barrier films. As shown, silica and PVA were dispersed at a molecular level due to strong hydrogen bonding between hydroxyl groups in PVA and Si–OH in silica.

4. Conclusions

Silica/PVA organic–inorganic hybrid gas barrier layers on PP film were successfully prepared by the sol–gel method with microwave irradiation. Oxygen permeances and water vapor transmission rates of the hybrid films were evaluated as the function of PVA content. The oxygen permeability coefficient and the water vapor transmission rates (thickness 25 μm) were calculated from oxygen permeances and water vapor transmission rates of the hybrid films and thickness of the films. The calculated values indicated that the hybrid layers had a high barrier property. It was also investigated that the effect of microwave irradiation on the preparation of silica/PVA organic–inorganic hybrid gas barrier membranes. The results indicated that microwave irradiation was effective for synthesizing the hybrid films in a short time and the hybrid films could be applicable to oxygen barrier films.

Symbols

WVTR	water vapor transmission rate, g m^{-2} d^{-1}
W	weight change, mg
t	elapsed time, h
A	permeation area, cm^2
L	thickness of the whole system, m
L_n	thickness of each layer, m
P	permeability coefficient of the whole system, mol m m^{-2} s^{-1} Pa^{-1}
P_n	permeability coefficient of each layer, mol m m^{-2} s^{-1} Pa^{-1}

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