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Permeability of ethanol solution through poly(lactic acid) film

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ABSTRACT: The permeation properties of ethanol solution through poly(lactic acid) (PLA) films were investigated. The total flux of ethanol solution through PLA films was strongly depended on the flux of water. In addition, the diffusion coefficient of water was 1000 times higher than that of ethanol, and decreased with increasing feed concentration. After the permeation measurement, crystallization ($X_{C\text{-}DSC}$ = 1–2%) was observed. However, the crystallinity was not dependent on the feed concentration. On the other hand, the mole ratio of ethanol and water molecules in the PLA film strongly depended on the feed concentration. Based on the results, we concluded that the interaction with ethanol molecules caused the decrease in diffusion coefficient of water in PLA film. Thus, the permeation mechanism of the ethanol solution to the PLA film was investigated in detail. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42031.

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INTRODUCTION

Recently, a wide variety of plastic materials derived from petroleum have been used as industrial products. Under these circumstances, poly(ethylene terephthalate) (PET) has become one of the most familiar plastic products in the field of plastic bottle packaging materials. The products that have been previously sold in glass bottles and cans are now being sold in PET bottles. In addition, the packaging for alcohol beverages such as wine and beer is shifting to the use of PET bottles because of the increasing demand for a packaging with improved impact resistance and weight reduction. However, petroleum-derived plastic materials, such as PET, have been an issue for global warming. The heavy consumption of fossil resources as raw materials and the future depletion of those resources have been considered as the major causes of global warming. Therefore, the demand for environmental-friendly plastic material with renewable resources, such as plant material, has been increasing.

Consequently, poly(lactic acid) (PLA), which has biodegradation properties and can be synthesized from plants such as corn, has attracted much attention. In addition, PLA has been studied as an alternative material for PET because of its high transparency, mechanical strength, and a melting point that can be easily molded as low as 150°C.[1,2] Moreover, PLA is expected in the application to plastic bottles, and considerable studies on important material properties such as gas barrier properties have been reported.[1,3] However, other important properties such as the permeability of an organic solvent (i.e., ethanol) have not been reported. As a measurement method to study the transmission behavior of the ethanol solution, the pervaporation (PV) method, which measures permeability, is only in the liquid-film-vapor system.[4] Considering that the feed solution and the film are in contact with each other in the PV method, the measurement can be carried at the same condition as that used in the application environment in plastic bottles. In addition, the measurement must be performed at the same condition because the concentration of ethanol in beverages such as alcoholic drinks is generally in the range of less than 50 wt %. Additionally, PLA has been reported to cause structural changes such as crystallization with the treatment of alcohol solvent.[5] Moreover, in the permeation through the polymer film, the feed solution can be dissolved and diffused only in the amorphous regions of the film. Therefore, the crystalline state of the film has great influence on the permeability of the solution.[4]

In this study, the permeation properties of ethanol solution through PLA films and the effect of ethanol solution on crystallization of PLA films were investigated.

EXPERIMENTAL

Preparation of Films

The PLA films were the same samples employed in our previous study.[3] The PLA polymer used in this study had a 4032D product (NatureWorks LLC, Minnetonka, USA). The isomer ratio was in the range of $L : D = 96.0 : 4.0 - 96.8 : 3.2$. PLA films were prepared by casting 2 wt % dichloromethane solution of each solvent onto a flat-bottomed Petri dish in a glass bell-type vessel and by drying under atmospheric pressure at room temperature. Each solvent was allowed to evaporate for 48 h. The

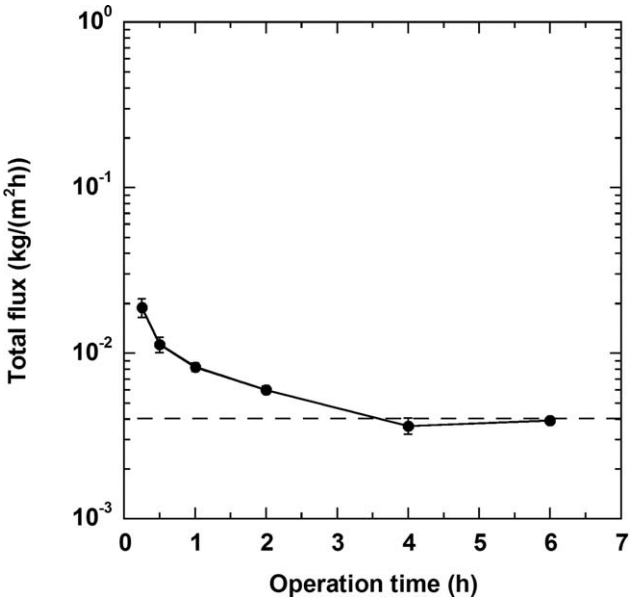

Figure 1. Relationship of total flux for ethanol solution through PLA film and operation time.

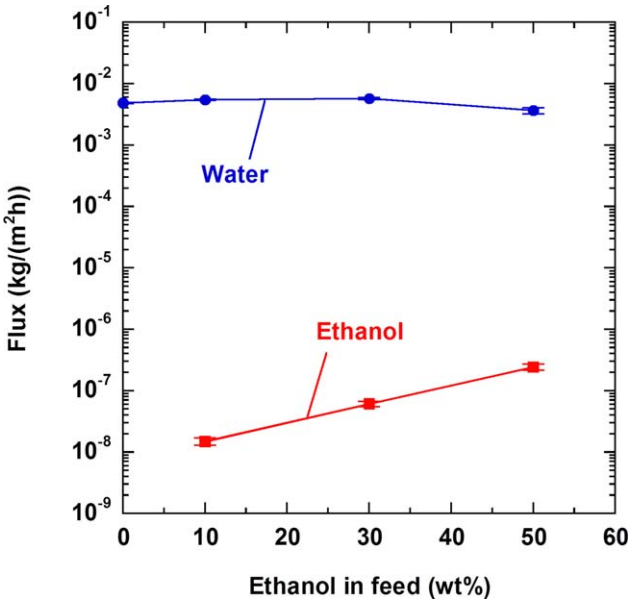

Figure 2. Water and ethanol flux for ethanol solution through PLA films at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dried PLA films were then thermally treated under a vacuum for 48 h at 70°C to eliminate the residual solvent and to obtain amorphous PLA films. Afterwards, the thermally treated PLA films were cooled at room temperature under atmospheric pressure. Proton nuclear magnetic resonance (^{1}H-NMR; JNM-ECA500, JEOL, Tokyo, Japan) analysis confirmed the removal of the residual solvent. The thickness of the films used in this study varied from 35 to 45 μm. The uncertainty of each film thickness was $\pm$ 1 μm.

Pervaporation

The pervaporation experiment was conducted according to the method in literature.[4] The ethanol solution (10, 30, 50 wt % ethanol solution) was used as the feed in all experiments. The feed stream was continuously flowing over the film surface at the constant temperature of 25 $\pm$ 1°C. The top of the feed solution was stirred at 200 rpm to reduce the concentration polarization layer. The effective area of the used round film was 18.1 cm^2. After reaching the steady state conditions, the permeated vapor was collected using liquid nitrogen under vacuum of under 10 mmHg for 4 h. The composition of the feed mixtures and the permeated mixtures was determined using a gas chromatograph (GC-18A, Shimadzu, Kyoto, Japan). TC-1701?GL Sciences, Tokyo, Japan?was used as a column and hydrogen flame ionization detector (FID) was used as the detector. The flux [kg/(m^2 h)] and α_P were determined from the following equations:

$$\text{Flux} = \frac{Q}{A \times t} \tag{1}$$

$$\alpha_P = \frac{P_{\text{Water}}/P_{\text{Ethanol}}}{F_{\text{Water}}/F_{\text{Ethanol}}} \tag{2}$$

where Q is the weight of the permeate (kg), A is the film area (m^2), t is the operating time (h). P_{Water}, $P_{Ethanol}$ are the weight fraction of water and ethanol in permeate, F_{Water}, $F_{Ethanol}$ are the weight fraction of water and ethanol in the feed.

Swelling and Sorption

The degree of swelling by ethanol solution (10, 30, 50 wt % ethanol solution) was measured at 25 $\pm$ 1°C. The films were stored in each solution for more than 24 hours until sorption equilibrium was attained. The film surface was wiped off and the weight was immediately measured. The film was then evacuated for 24 h in vacuum, and the weight of the dry film was measured. The degree of swelling was calculated using the following equation:

Table I. PV Data of PLA Films for Ethanol Solution at 25°C

Ethanol concentration in feed (wt %)	Total flux [kg/(m^2 h)]	Water flux [kg/(m^2 h)]	Ethanol flux [kg/(m^2 h)]	α_P (Water/Ethanol)
0	$4.87 \pm 0.12 \times 10^{-3}$	$4.87 \pm 0.12 \times 10^{-3}$	N/A	N/A
10	$5.50 \pm 0.34 \times 10^{-3}$	$5.50 \pm 0.34 \times 10^{-3}$	$0.15 \pm 0.02 \times 10^{-7}$	44,700 $\pm$ 9000
30	$5.68 \pm 0.23 \times 10^{-3}$	$5.68 \pm 0.23 \times 10^{-3}$	$0.61 \pm 0.06 \times 10^{-7}$	39,100 $\pm$ 5530
50	$3.64 \pm 0.40 \times 10^{-3}$	$3.64 \pm 0.40 \times 10^{-3}$	$2.42 \pm 0.28 \times 10^{-7}$	21,400 $\pm$ 7350

Table II. Degree of Swelling and Sorption Behavior of PLA Films for Ethanol Solution at 25°C

Ethanol concentration in feed (wt %)	Degree of swelling (wt %)	Ethanol concentration in film (wt %)	α_S (Water/Ethanol)	α_D (Water/Ethanol)	D_{water} (cm^2/s)	$D_{Ethanol}$ (cm^2/s)
0	0.28 ± 0.07	N/A	N/A	N/A	$6.20 \pm 0.15 \times 10^{-8}$	N/A
10	0.92 ± 0.10	11.6 ± 0.6	0.86 ± 0.04	48,700 ± 2500	$6.05 \pm 0.04 \times 10^{-8}$	$1.25 \pm 0.07 \times 10^{-12}$
30	2.55 ± 0.40	20.3 ± 4.3	1.74 ± 0.46	24,900 ± 610	$2.55 \pm 0.13 \times 10^{-8}$	$1.05 \pm 0.21 \times 10^{-12}$
50	4.01 ± 0.36	21.8 ± 1.0	3.60 ± 0.21	3700 ± 20	$0.72 \pm 0.01 \times 10^{-8}$	$1.98 \pm 0.09 \times 10^{-12}$

$$\text{Degree of swelling}(\%) = \frac{W_S W_D}{W_D} \times 100 \quad (3)$$

where W_S (g) is the weight of the swollen film and W_D (g) is the weight of the dry films. The swollen film was blotted to remove excess ethanol solution. W_S measurement was repeated until a constant weight was obtained. The composition of water and ethanol that was sorbed in the film at equilibrium was analyzed. The surface of an equilibrated film was wiped off and sorbate evaporated by heating 100°C in vacuum for more than 2 h. The sorbed solution was collected with a cold trap cooled by liquid nitrogen, and the composition determined using a gas chromatograph.[6] The water/ethanol solubility selectivity α_S was calculated using the following equation:

$$\alpha_S = \frac{M_{\text{Water}}/M_{\text{Ethanol}}}{F_{\text{Water}}/F_{\text{Ethanol}}} \quad (4)$$

where M_{Water} and M_{Ethanol} are the weight fractions of water and ethanol in the film, and F_{Water} and F_{Ethanol} are the weights of water and ethanol in the solution.

In this study, we calculated the average apparent diffusion coefficient that can be calculated from the swelling sorption measurement and PV measurement.[7] Diffusion according to the first law of Fick represented by the following equation:

$$J = -D(C)\frac{dC}{dX} \quad (5)$$

where J is the flux, D is diffusion coefficient, and C is concentration per unit area of the swollen film. From Fick's equation, the average apparent diffusion coefficient was calculated using the following equation:

$$J = \frac{\bar{D}C_1}{l} = \frac{\bar{D}kS}{l} \quad (6)$$

where $\bar{D}$ is apparent diffusion coefficient, C_1 is the concentration of feed solution, and k was determined from the following equation:

$$\frac{1}{k} = \frac{S}{d_S} + \frac{100}{d_m} \quad (7)$$

where d_S and d_m represent the density of each of the film and solvent. When the solution is multi-component, the the flux of water and ethanol are represented by the following equations:

$$J_{\text{Ethanol}} = \frac{\bar{D}_{\text{Ethanol}} C_{\text{Ethanol}}}{l} = \frac{\bar{D}_{\text{Ethanol}} k S_{\text{Ethanol}}}{l} \quad (8)$$

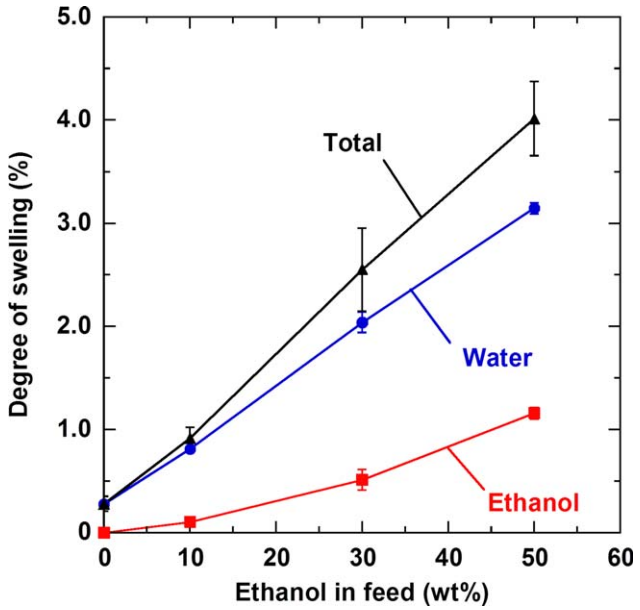

Figure 3. Degree of swelling for ethanol solution through PLA films at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

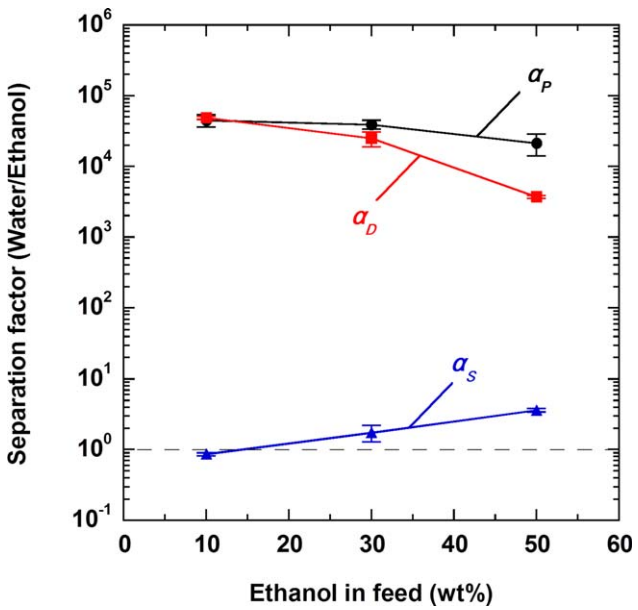

Figure 4. Water/ethanol separation factor for ethanol solution through PLA films at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

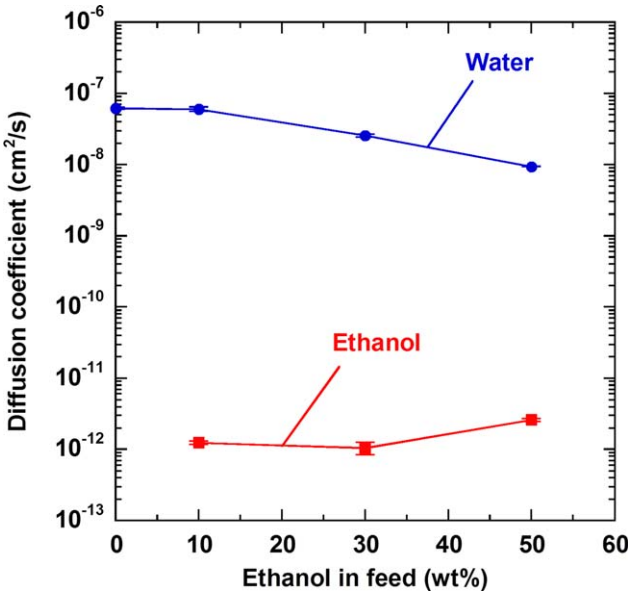

Figure 5. Diffusion coefficient of water and ethanol for ethanol solution through PLA films at 25°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$J_{\text{Water}} = \frac{\bar{D}_{\text{Water}} C_{\text{Water}}}{l} = \frac{\bar{D}_{\text{Water}} k S_{\text{Water}}}{l} \tag{9}$$

In addition, α_D was calculated by substituting into the eq. (10) with the value of the average apparent diffusion coefficient of water and ethanol.

$$\alpha_D = \frac{\bar{D}_{\text{Water}}}{\bar{D}_{\text{Ethanol}}} \tag{10}$$

Characterization Analysis

All characterization data were determined in the film state for at least three samples to confirm the reproducibility of the experimental results.

The thermal analysis data were measured using a Diamond DSC differential scanning calorimeter (DSC) (Perkin-Elmer, Shelton, USA). Sample-pan-kit alum (Perkin-Elmer, Shelton, USA) was aluminum. As these data are used for discussing crystalline structure and crystallinity, the first heating scan data (i.e., before annealing) represent the optimum condition relative to the second heating scan data. Heat scan was performed from 20°C to 200°C at a heating rate of 10°C/min in a nitrogen atmosphere. The glass transition temperature (T_g) was determined as the middle point of endothermic transition. The crystallization temperature (T_c) and melting temperature (T_m) were determined as the maximum value of each peak. Crystallinity (X_{C-DSC}) was estimated using equation (11):

$$X_{\text{C-DSC}} = \frac{\Delta H_m + \Delta H_c}{\Delta H_m^0} \times 100 \tag{11}$$

where ΔH_m and ΔH_c are the enthalpies of melting and crystallization of a polymer (J/g), respectively, and $\Delta H^0{}_m$ is the enthalpy of the PLA (L-donor 100%) crystal with infinite crystal thickness and a value of 93 J/g.[8]

Wide-angle X-ray diffraction (WAXD) measurement was performed using a Rint 1200 X-ray diffractometer (Rigaku, Tokyo, Japan) using a Cu-Kα radiation source at 40 kV and 20 mA in a dispersion angle of 3.00° to 30.00° and a scanning speed of 2°/min at 23 ± 1°C. The d-spacing was calculated according to Bragg's conditions (12), which presented the mean distance between polymer chains.

$$\lambda = 2d \sin\theta \tag{12}$$

where λ is the wavelength of the X-ray and has a value of 1.54 Å, and d is distance of the lattice spacing (Å). In addition, the value of θ was the diffraction angle at the maximum intensity of the peak that was determined from the Gauss function.

Orthoscope observation was performed using an Olympus BX-51 Polarization microscope (POM) (Olympus Inc., Tokyo Japan) at cross Nicol condition. Polarization images were observed under an additive color at 530 nm with a sensitive color plate.

Scanning electron microscope (SEM) was performed using a High-Resolution Field Scanning Emission Electron microscopy (S5200, JEOL, Tokyo Japan).

RESULTS AND DISCUSSION

Pervaporation

The result of the operation time-dependence of the flux of ethanol solution through PLA film is shown in Figure 1. The 50 wt % ethanol solution was used as a feed solution. The flux was reduced up to 4 h and reached a steady condition after. Therefore, PV measurements were carried for an operation time of 4 h.

The flux of ethanol solution, ethanol, and water, as well as the separation factor α_P for PLA film are summarized in Table I. In addition, relationship between the flux for PLA film and feed concentration is shown in Figure 2. With increasing feed concentration, the flux of water was almost constant in the range of 4.87–5.68 × 10^{-3} kg/(m^2h) up to 30 wt %. However, the value decreased to 3.64 × 10^{-3} kg/(m^2h) at 50 wt %. Whereas the flux of ethanol increased by 0.15 × 10^{-7} kg/(m^2h) to 2.42 × 10^{-7} kg/(m^2h). From this result, it became clear that the total flux of ethanol solution through PLA films was mainly depended on the flux of water. In addition, the water vapor transmission rate (WVTR) of PLA has been reported, and it is known that WVTR through PLA depends on molecular weight, crystallinity, and stereocomplexation.[9–11] Its value of amorphous PLA was about 2.1–2.4 × 10^2 g/(m^2day) at 25°C, and converted value to the flux was 8.75–10.0 × 10^{-3} kg/(m^2h). Therefore, it became clear that the flux of water and water vapor through PLA film were almost the same.

Table II and Figure 3 show the result of swelling and sorption. The sorption amount of ethanol and water to PLA film increased with increasing feed concentration. When the concentration of ethanol was increased from 10 wt % to 50 wt % and the degree of swelling of water for PLA film was increased by about four times (from 0.81% to 3.15%), the degree of swelling of ethanol significantly increased by 11 times (from 0.11% to 1.16%). Ethanol

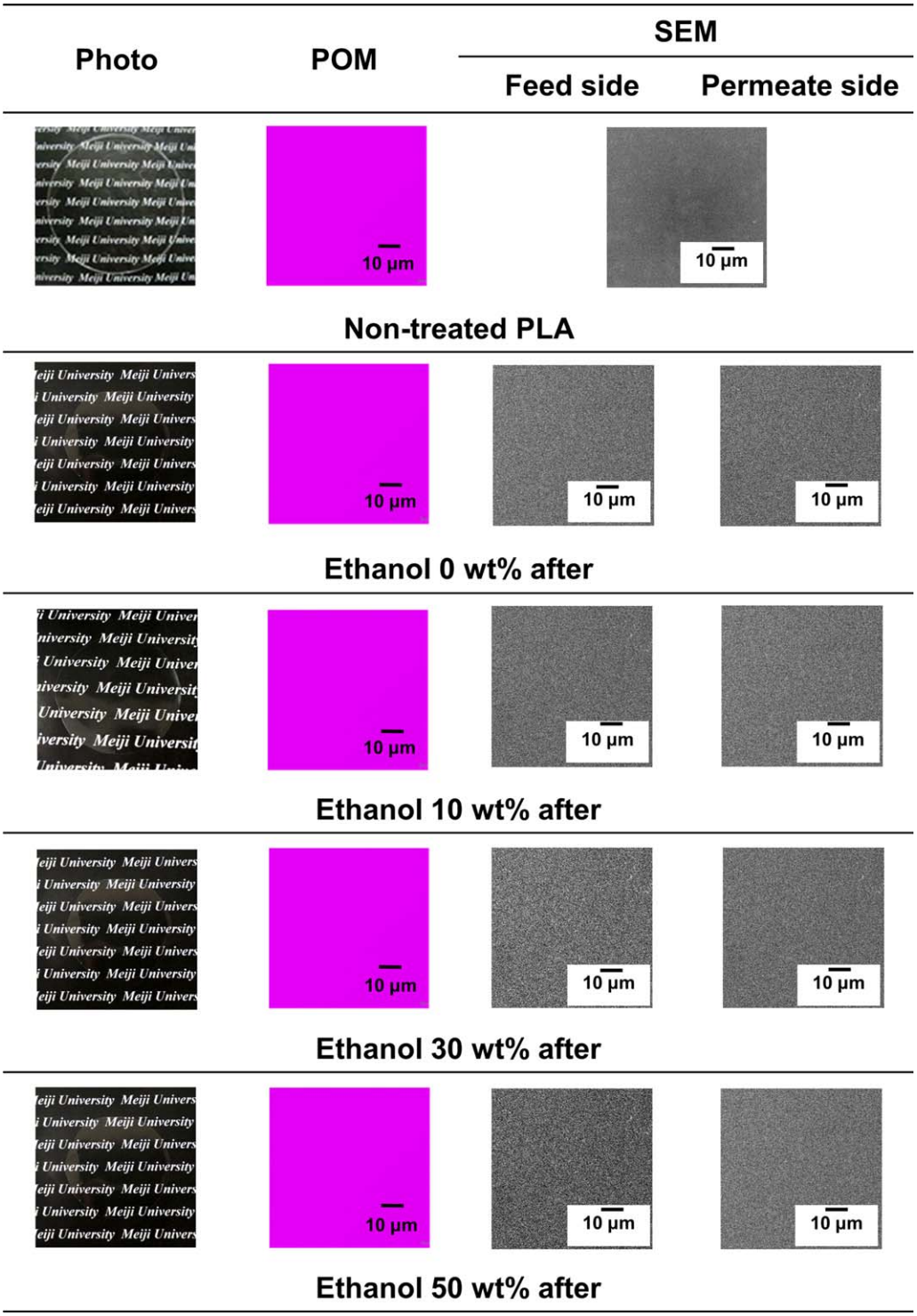

Figure 6. Photograph, POM, and SEM images of PLA films before and after PV measurement. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that was easily sorbed into the PLA film contributed to the swelling the film; therefore, we suggested that water was sorbed easier. However, by comparing the composition ratio of the film with that of the feed solution, the concentration of ethanol in the film was 11 wt % when the feed concentration was 10 wt %, and almost 20 wt % when the feed concentration was 50 wt %. In addition, the permeation mechanism of ethanol and water was different in each feed concentration because the sorption and diffusion mechanisms were different. Therefore, detailed investigation was carried out by analyzing the selectivity of each component.

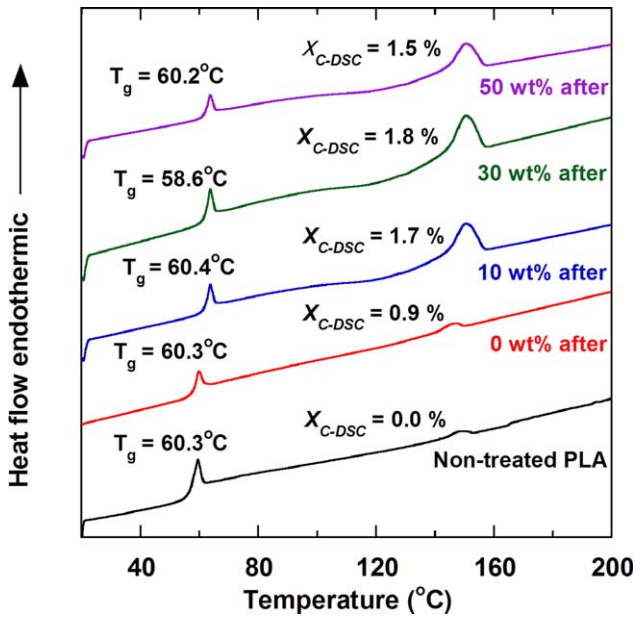

Figure 7. DSC thermograms of PLA films before and after PV measurement. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The relationship between separation factor α_P for PLA film and feed concentration is shown in Figure 4. In α_P, water/ethanol selectivity was constant in the error range of 39,100–44,700 up to 30 wt %. When the feed concentration increased up to 50 wt %, α_P decreased to less than 21,400. Furthermore, the selectivity was 1 or more in all feed concentrations. This result indicates that the PLA film had water permselective property.

Table II summarizes α_S and α_D which were calculated from the results of swelling sorption measurement and PV measurement. In addition, the relationship between α_S and α_D for PLA film and feed concentration is shown in Figure 4. When the feed concentration increased, α_S also increased. The solubility parameter was one of the digitizing methods for analyzing the interaction between polymer materials and organic solvents. The solubility parameters of PLA, ethanol, and water were 21.2, 26.6, and 47.9 $MPa^{1/2}$, respectively.[5] In general, considering that the interaction is strong as indicated by the values of the solubility parameter of the solvent and polymer film, PLA had a stronger interaction with ethanol than water. When the ethanol concentration was increased and a strong interaction with PLA exists, α_S increased as the film swelled. On the other hand, α_D was 1 or more in all feed concentrations. This result indicates

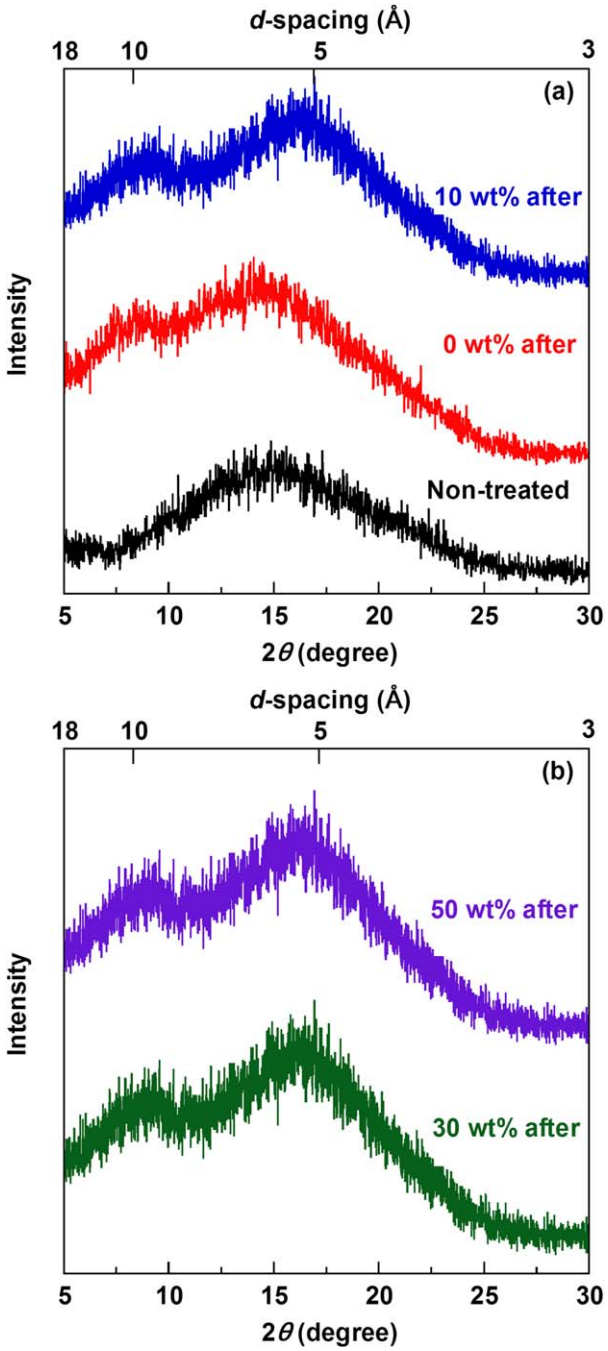

Figure 8. WAXD patterns of PLA films (a) before, 0, 10 wt % after PV measurement and (b) 30, 50 wt % after PV measurement. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Thermal Properties of PLA Films Before and After PV Measurement

	T_g (°C)	Tc (°C)	T_m (°C)	ΔHc (J/g)	ΔH_m (J/g)	X_C (%)	Reference
Non-treated PLA	60.3 ± 2.1	N/A	N/A	N/A	N/A	0.0	[3]
Ethanol 0 wt % after	60.3 ± 0.5	115.7 ± 0.3	148.9 ± 0.3	−7.7 ± 0.4	8.5 ± 0.2	0.9 ± 0.2	
Ethanol 10 wt % after	60.4 ± 2.4	116.2 ± 0.5	149.2 ± 0.1	−5.9 ± 0.6	7.5 ± 0.5	1.7 ± 0.1	This study
Ethanol 30 wt % after	58.6 ± 1.4	115.8 ± 0.5	148.3 ± 0.4	−6.0 ± 0.4	7.7 ± 0.2	1.8 ± 0.1	
Ethanol 50 wt % after	60.2 ± 0.4	115.5 ± 0.4	147.8 ± 0.1	−3.3 ± 0.4	4.7 ± 0.1	1.5 ± 0.1	

that the water molecule with a smaller molecular size (0.311 nm) was easily diffused than the ethanol molecule with a larger molecular size (0.460 nm).[12] α_D decreased gradually up to 30 wt % and significantly decreased at 50 wt %. Furthermore, given that the value and the trend of α_P was similar to α_D than α_S, α_P relied heavily on diffusion selectivity. Accordingly, the diffusion coefficient, which is a dominant factor when determining the diffusion selectivity, was investigated in detail.

The diffusion coefficients of water and ethanol calculated from the results of the swelling sorption measurement and the PV measurement are summarized in Table II. Relationship between diffusion coefficient of ethanol and water for PLA film and feed concentration is shown in Figure 5. The diffusion coefficient of water had a value of about 1000 times higher than that of ethanol. When the feed concentration was increased, the diffusion coefficient of ethanol was almost constant in the error range, whereas the diffusion coefficient of water decreased. In ethanol solution, the water molecules that formed a hydrogen bond with water molecules were connected with ethanol molecules via hydrogen bonding to form hydrates.[13,14] In addition, it has been reported that PLA can cause structural changes such as crystallization by treatment with an alcohol solvent.[5] The interaction of ethanol molecules and water molecules or the interaction between ethanol molecules and PLA could be considered as the cause of the decrease in diffusion coefficient of water during the increased feed concentration. Clearly, the interaction of PLA and ethanol was observed by analyzing the film structure after permeation. Accordingly, the effect of ethanol solution on the crystal structure of the PLA was investigated.

Films Characterization

The appearances in the photo of PLA films before and after PV measurements are shown in Figure 6. PLA film was clouded when they have crystalline structures.[5] However, after PV measurement, the PLA films were not clouded.

Furthermore, DSC curves of PLA films before and after PV measurement are shown in Figure 7, and Table III presents the analysis result. The endothermic peak that indicates the glass transition was observed from PLA film before and after PV measurement in the vicinity of 50–60°C. The T_g values of PLA films before and after PV measurement were 58.6–61.2°C, which was within the range of literature value 55–69°C.[1,15–20] In addition, the peak of Tc was not observed in clear. Furthermore, the X_{C-DSC} before PV measurement was 0.0% and increased to 1–2% after PV measurement. This result indicated that fine crystallization of PLA was occurred after permeation of ethanol solution, but PLA was almost amorphous state.

The WAXD patterns of PLA films before and after PV measurement are shown in Figure 8. Before PV measurement, sharp peak was not observed in the PLA film, and halo was observed near the *d*-spacing at 5.5 Å. After PV measurement, a halo was observed near the *d*-spacing at 10.5 Å. However, sharp peak because of crystal structure was not observed.

Figure 6 shows the POM and SEM images of the PLA films before and after PV measurements. In POM observation, the crystalline arrangement of the molecules was not observed in the PLA film before and after the PV measurement. Meanwhile, in the SEM observation, the surface was smooth before the permeation; however, irregularities were observed on the surface of the feed side and the permeate side after permeation. Evidently, the results of SEM observation and DSC measurement show that crystallization occurred not only on the film's surface but also in the bulk of the film.

In addition to the measurement of characterization, the interaction between water and ethanol molecules in the film was analyzed.

Causes of the Decrease in Diffusion Coefficient of Water

The relationship between the ratio of ethanol and water molecules in the feed solution and in the PLA film is shown in Figure 9. When the feed concentration was at 10 wt %, the ratio of ethanol molecule in the film was higher than that of the feed solution because of the solubility to the PLA film. However, when the feed concentration was over 30 wt %, the ratio of ethanol molecule number in the film was lower than that in the feed solution. Therefore, the polymer chain gaps were presumed to increase because of the dissolution of ethanol into the film, and water molecules were easily dissolved into the film. In addition, the water and ethanol molecules formed a hydrate. When the concentration of the feed solution was 10 wt %, the ratio of the number of water and ethanol molecules was about 20: 1 in the water/ethanol hydrate. However, when the concentration of the feed solution was 50 wt %, the ratio was about 8: 1 in water/ethanol hydrate. These results reveal that the hydration of water and ethanol molecules decreased the diffusivity of water molecules.

The relationship between the concentration of the feed solution and the ratio of the volume of ethanol solution that occupied the free volume of the PLA (occupied volume ratio) is shown in Figure 10. The occupied volume ratio was calculated using the following equation:

$$\text{Occupied volume ratio (vol \%)} = \frac{\text{Volume of ethanol solution sorbed in membranes}}{\text{Free volume of PLA}} \times 100 \quad (13)$$

The numerator is obtained by converting the degree of swelling to volume, and denominator is fractional free volume (*FFV*) of the PLA (*FFV* = 0.192) which was calculated from the group contribution method of van Krevelen.[21] When the feed concentration was 10 wt %, the water/ethanol hydrate occupied about 6.2 vol % of the free volume. When the feed concentration was 50 wt %, the value became about 30 vol %. Therefore, we inferred that the water/ethanol hydrate inhibited diffusion of each other in the free volume, and the diffusion coefficient of the hydrate decreased with increasing the concentration of the feed solution.

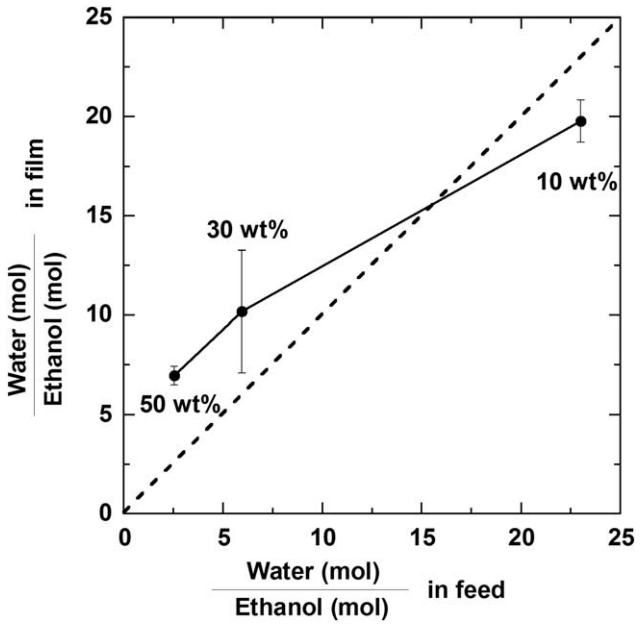

Figure 9. Relationship between the molecular amount in feed solution and that in PLA films.

In the measurement of the characterization, small changes in X_{C-DSC} = 1–2% were only observed in the crystallinity. However, the crystallinity was not dependent on the ethanol concentration. On the other hand, the mole ratio of ethanol molecules and water molecules in the film and the ratio of water/ethanol hydrate occupying the free volume in the film strongly depended on the concentration of the feed solution. Based on the results, we conclude that the decrease in the diffusion coefficient of water molecule was caused by the interaction with ethanol molecule.

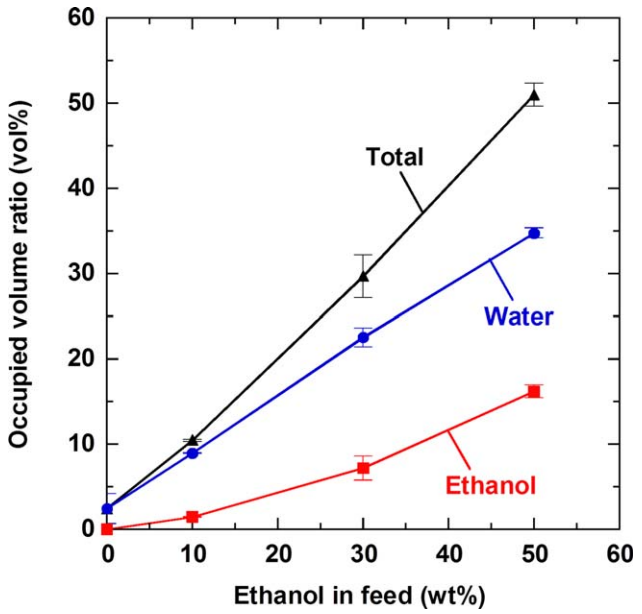

Figure 10. Relationship between the feed concentration of ethanol and occupied volume ratio of ethanol solution in PLA films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In summary, it is considered that the flux of the water will decrease with increasing ethanol concentration in the feed. On the other hand, the water with a small molecular size became easily dissolved into the film because the ethanol molecules swelled the film when the concentration of the feed solution was 30 wt % or less. Therefore, when the diffusion coefficient of water decreased, the flux of water did not change. However, when the concentration of feed solution was 50 wt %, the hydration of water and ethanol molecules decreased the diffusivity of water molecules. As a result, the flux of water decreased. Thus, it became clear that the permeation mechanism of the ethanol solution to the PLA film was different depending on feed concentration.

CONCLUSIONS

The permeation properties of ethanol solution through PLA films and the effect of ethanol solution on crystallization of PLA films were investigated. The total flux of ethanol solution through PLA films was mainly depended on the flux of water, and the total flux was almost constant up to feed concentration at 30 wt %, and decreased at 50 wt %. Evidently, the diffusion coefficient of water had a value that was 1000 times higher than ethanol. From this result, it became clear that the flux relied heavily on the diffusion coefficient. Furthermore, the diffusion coefficient of water decreased with increasing feed concentration. After PV measurement, the crystallization of PLA films was observed (X_{C-DSC} = 1–2%), and the crystallinity was not dependent on the feed concentration. On the other hand, the mole ratio of ethanol and water molecules, and the ratio of water/ethanol hydrate occupying the free volume in PLA film strongly depended on the feed concentration. Based on the results, we concluded that the decrease in the diffusion coefficient of the water molecule was caused by the interaction with the ethanol molecule. Evidently, this study revealed that the permeation mechanism of the ethanol solution to the PLA film was different depending on the feed concentration. In this study, so that we analyzed the permeation properties of the ethanol solution to the PLA film in detail, it will be a foothold in material design of PLA (i.e., Improvement of barrier properties to ethanol solution) aimed at application to alcoholic beverage plastic bottles.

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