Structure and Permeation Characteristics of an Aqueous Ethanol Solution of Organic−Inorganic Hybrid Membranes Composed of Poly(vinyl alcohol) and Tetraethoxysilane

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ABSTRACT: To inhibit the swelling of PVA membranes in aqueous alcohol solutions, which leads to lowered water permselectivity during separation, organic−inorganic hybrid membranes composed of poly(vinyl alcohol) (PVA) and tetraethoxysilane (TEOS) were prepared. When an aqueous solution of 85 wt % ethanol was permeated through the PVA/TEOS hybrid membranes during pervaporation, the separation factor for water permselectivity increased, but the permeation rate decreased, with increasing TEOS content. We concluded that the decreased permeation rate was caused by decreasing the degree of swelling of the membrane. Therefore, this decrease in the degree of swelling and the increase in membrane density were due to the formation of hydrogen bonds between the silanol groups resulting from the hydrolysis of TEOS and the hydroxyl group of PVA. When the PVA and PVA/TEOS hybrid membranes were annealed, the separation factor of these membranes increased with increasing annealing temperature and time. The fact that annealing at higher temperatures promoted the dehydration−condensation reaction between PVA and TEOS in PVA/TEOS membranes was related to the enhanced permselectivity of the PVA/TEOS membranes.

Introduction

Membrane separation techniques with easy operation and high energy savings are greatly appreciated in a variety of applications in the medical, food, industrial, energy, and environment fields. The chemical and physical structures of polymer membranes are engineered to improve membrane performance by several methods.

Alcohol is a clean energy source that can be produced by the fermentation of biomass. However, it needs to be highly concentrated. In general, aqueous alcohol solutions are concentrated by distillation, but an azeotrope (96.5 wt % ethanol) prevents further separated by distillation. Pervaporation, a membrane separation technique, can be used for separation of these azeotropes: pervaporation is a promising membrane technique for the separation of organic liquid mixtures such as azeotropic mixtures[1,2] or close-boiling point mixtures.[3,4]

Composite materials consisting of organic and inorganic materials have been recognized in various fields[5,6] as functional materials that have the merits of both the lightness, pliability, and molding of organic materials, plus the heat-resistance and strength of inorganic materials. As represented by fiber-reinforced plastics, however, these composite materials consist of a dispersed phase from the organic and inorganic compounds, on the order of micrometer size. Consequently, physical properties of these composite materials are due to the additivity rule of each component. Therefore, special or specific physical properties cannot be expected. Recently, the size of the dispersed phase at a nanometer or molecular size order has been controlled, and hybrid materials in which the organic and inorganic components are ideally homogeneous are being studied in a variety of fields. This organic−inorganic hybridization is dependent on the sol−gel method, in which the starting materials are in solution and syntheses at a low temperature are possible.[7−14] Using this sol−gel method, it is possible to homogeneously hybridize the organic and inorganic components.

Thus, in this study, we prepared novel organic−inorganic hybrid membranes via hybridization between organic and inorganic materials using the sol−gel reaction. In particular, it is well-known that poly(vinyl alcohol) (PVA) membranes are highly water permselective for aqueous ethanol solutions during PV. However, the swelling of the PVA membrane in an aqueous ethanol solution results in both an increase in solubility and diffusivity of ethanol, and consequently lowers the water permselectivity.[15] The control of membrane swelling has been attempted by cross-linking, surface modification, and annealing methods. However, it was difficult to effectively control the swelling of the membrane.

In this paper, to control swelling of PVA membranes, mixtures of PVA as an organic component and tetraethoxysilane (TEOS) as an inorganic component were applied to the sol−gel reaction, and PVA/TEOS hybrid membranes were prepared. The relationship between the structure of the PVA/TEOS hybrid membranes and their permeation and separation characteristics for an aqueous ethanol solution during pervaporation is discussed in detail.

Experimental Section

Materials. Poly(vinyl alcohol) (PVA), which was supplied by Nippon Synthetic Chemical Industry Co., Ltd., at an average degree of polymerization of 1650 and a degree of saponification of 99.7 mol %, was employed as the organic component. Tetraethoxysilane (TEOS), purchased from Shin-Etsu Chemical Co., Ltd., was used as the inorganic component. All other solvents and reagents were purchased from Wako

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Pure Chemical Industries, Ltd., and were of analytical grade and used without further purification.

Preparation of PVA Membranes. PVA powder was dissolved in DMSO at 80 °C to make a 5 wt % casting solution. After removal of the insoluble impurities using a glass filter, it was stirred for 1 h at 25 °C. The PVA membrane was prepared by pouring the casting solution onto stainless steel plates and then allowing the solvent to evaporate completely at 80 °C for 24 h.

Preparation of PVA/TEOS Hybrid Membranes. After the prescribed amount of TEOS per a weight of PVA was mixed with the PVA dissolved in DMSO at 25 °C to a concentration of 5 wt %, 1 M HCl was added to the PVA/TEOS mixture as an acid catalyst for the sol−gel reaction. The PVA/TEOS hybrid membranes were prepared by pouring the casting solutions onto stainless steel plates, and then allowing the solvent to evaporate completely at 80 °C for 24 h.

Permeation Measurements. The pervaporation was carried out using the apparatus described in previous studies[16−25] under the following conditions: permeation temperature, 40 °C; pressure of the permeate side, 1×10^{-2} Torr. The effective membrane area was 13.8 cm^2. An aqueous solution of 85 wt % ethanol was used as the feed solution. The permeate was collected in a U-tube at liquid nitrogen temperature. The permeation rates of aqueous alcohol solutions during pervaporation were determined from the weight of the permeate collected in the cold U-tube, the permeation time, and the effective membrane area. The compositions of the feed solution and permeate were determined by a gas chromatograph (Shimadzu GC-9A) equipped with a flame ionization detector (FID) and a capillary column (Shimadzu Co. Ltd.; Shimalite F) heated to 200 °C. The results from the permeation of aqueous alcohol solutions during pervaporation were reproducible, and the errors inherent in the permeation measurements were on the order of a few percent.

The separation factor, $\alpha_{\text{sep H}_2\text{O/EtOH}}$, during pervaporation was calculated from eq 1,

$$\alpha_{\text{sep H}_2\text{O/EtOH}} = (P_{\text{H}_2\text{O}}/P_{\text{EtOH}})/(F_{\text{H}_2\text{O}}/F_{\text{EtOH}}) \qquad (1)$$

where $F_{\text{H}_2\text{O}}$ and F_{EtOH}, $P_{\text{H}_2\text{O}}$, and P_{EtOH} are the weight fractions of water and ethanol in the feed solution and the permeate, respectively.

Membrane Density. The density of the membranes was measured by the flotation method[26] using a mixed solution of benzene and tetrachlorocarbon at 40 °C.

Degree of Swelling of Membranes. The PVA and PVA/TEOS hybrid membranes were dried completely under reduced pressure at 40 °C and weighed. These membranes were immersed into an aqueous solution of 85 wt % ethanol in a sealed vessel at 40 °C. After the weight of the membranes became constant, they were taken out of the vessel, wiped quickly with filter paper, and weighed. The degree of swelling (DS) of the membrane was determined by eq 2,

$$\text{DS} = W_{\text{s}}/W_{\text{d}} \qquad (2)$$

where W_{s} is the weight of the membrane swollen in an aqueous solution of 85 wt % ethanol and W_{d} is the weight of the dried membrane.

Contact Angle Measurements. The contact angles for methylene iodide on the surface of PVA and PVA/TEOS hybrid membranes were measured using a contact angle meter (Erma, model G-1) at 25 °C. The contact angles, θ, were determined by eq 3,

$$\theta = \cos^{-1}\{(\cos \theta_{\text{a}} + \cos \theta_{\text{r}})/2\} \qquad (3)$$

where θ_{a} and θ_{r} are the advancing contact angle and the receding contact angle, respectively.

Annealing of Membranes. The PVA and PVA/TEOS hybrid membranes were placed between filter papers and annealed under a nitrogen atmosphere and the following conditions: at 130 °C for 3, 8 and 24 h, and at 100, 130, and 160 °C for 8 h.

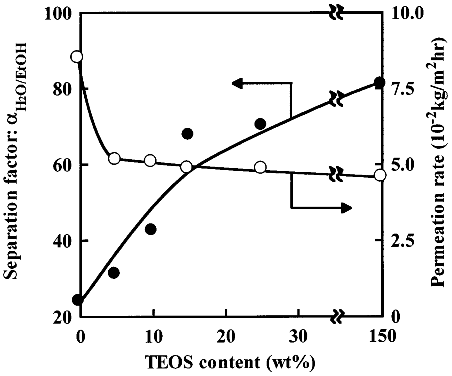


Figure 1. Effects of the TEOS content in PVA on the permeation rate (○) and the separation factor for the water permselectivity (●) of an aqueous solution of 85 wt % ethanol through the PVA/TEOS hybrid membranes by PV at 40 °C.

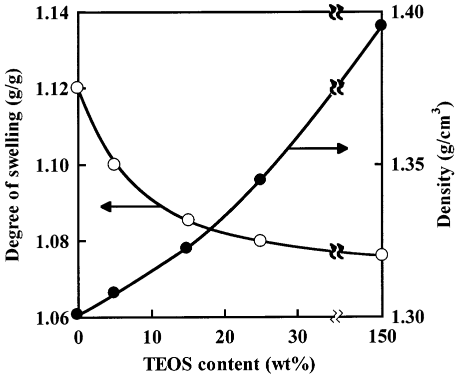


Figure 2. Effects of the TEOS content in PVA on the degree of swelling (○) of the PVA/TEOS hybrid membranes in aqueous solution of 85 wt % ethanol and their density (●) at 40 °C.

Measurement of Wide-Angle X-ray Diffraction (WAXD). The WAXD of the PVA/TEOS hybrid membranes was measured by an X-ray diffraction apparatus (Macscience Co., Ltd. Model MXP D10001A). Nickel-filtered Cu Kα radiation was used for the measurements, which were performed at 2θ between 5.00 and 40.00°. The X-ray generator was run at 40 kV and 30.0 mA.

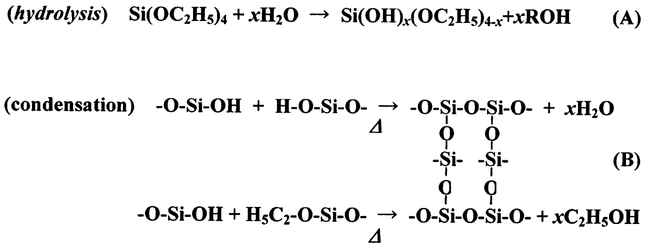
Transmission Electron Micrographs (TEM). The PVA and PVA/TEOS hybrid membranes were embedded in epoxy resin and sliced into thin films (thickness ≈50 nm) with a microtome (Leica; Reichert Ultracut E). The structure of these membranes was observed by a transmission electron microscope (TEM) (JEOL JEM-1210) at an accelerating voltage of 80 kV.

Results and Discussions

Effect of the TEOS Content on Permeability. Figure 1 shows the effects of the TEOS content in the PVA/TEOS hybrid membranes on the permeation rate and separation factor for the water permselectivity of an aqueous solution of 85 wt % ethanol during pervaporation at 40 °C. As can be seen in Figure 1, with increasing TEOS content, the separation factor for water permselectivity increased, but the permeation rate became constant after a decrease at low TEOS content.

To clarify the effects of TEOS on the permeation and separation characteristics of PVA/TEOS hybrid membranes, the degree of swelling of the membrane in an aqueous solution of 85 wt % ethanol and the membrane density were examined. Figure 2 shows that the degree of swelling of the PVA/TEOS hybrid membranes de-

Scheme 1. Hydrolysis and Condensation Reaction for TEOS

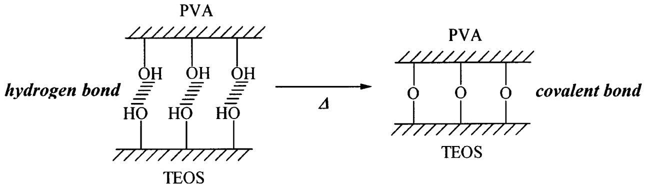


$$\mathrm{Si(OC_2H_5)_4} + x\mathrm{H_2O} \rightarrow \mathrm{Si(OH)}_x(\mathrm{OC_2H_5})_{4-x} + x\mathrm{ROH} \quad \text{(A)}$$

$$\text{-O-Si-OH} + \text{H-O-Si-O-} \xrightarrow[\Delta]{} \text{-O-Si-O-Si-O-} + x\mathrm{H_2O} \quad \text{(B)}$$

$$\text{-O-Si-OH} + \mathrm{H_5C_2}\text{-O-Si-O-} \xrightarrow[\Delta]{} \text{-O-Si-O-Si-O-} + x\mathrm{C_2H_5OH}$$

Scheme 2. Tentative Illustration for the Interaction between PVA and TEOS



creased remarkably, whereas the membrane density increased with increasing TEOS content. The results from Figure 2 suggest that the decrease in permeation rate upon increasing TEOS content can be attributed to both a remarkable decrease in the degree of swelling of the membrane, and a significant increase in the membrane density. In particular, the change in the structure of the PVA/TEOS hybrid membranes with an increase in TEOS content caused a decrease in both solubility and diffusivity of the permeants. Consequently, the permeation rate decreased with increasing TEOS content. On the other hand, the increase in the total separation factor for water permselectivity was due to an increase in the sorption and diffusion selectivity, based on the change in the PVA/TEOS hybrid membrane structure with an increase in the TEOS content.

To investigate the improvements in the separation factor and increase in membrane density in detail, the reaction mechanism of the PVA/TEOS hybrid membrane was discussed.

Formation of PVA/TEOS Hybrid Membranes. Scheme 1 shows the process of the polycondensation reaction of TEOS.[27] In the first step of the process of preparing PVA/TEOS hybrid membranes, TEOS was hydrolyzed in the presence of an acid catalyst (A), and silanol groups were formed. These resulting silanol groups yielded siloxane bonds due to the dehydration or dealcohlysis reaction (B) with other silanol groups or ethoxy groups during the membrane drying. These reactions led to cohesive bodies between siloxane in the membrane. Since these bodies of siloxane were dispersed in the membrane, the silanol groups in the siloxane and the hydroxyl groups in the PVA-formed hydrogen and covalent bonds, which are the cross-linking points, as illustrated in Scheme 2. The increase in membrane density and the decrease in the degree of swelling of the membrane with increasing TEOS content in Figure 2 could be attributed to the formation of these hydrogen and covalent bonds.

It is well-known that PVA is a crystalline polymer. Its crystallinity is due to strong hydrogen bonds between the hydroxyl groups and increases with increasing annealing temperature. However, it is known that the crystallinity is governed by the annealing temperature. We have previously reported that the fine structure of PVA membranes could be controlled by annealing under various conditions and that their water permselectivity for an aqueous ethanol solution during pervaporation could be controlled by the annealing conditions. On the other hand, it has been reported that the polycondensation reaction of TEOS is strongly dependent on the annealing temperature and time, and the structure of the resulting product was strongly influenced by them.[28] Therefore, when the PVA/TEOS hybrid membranes were annealed, an improvement of the permeation and separation characteristics by controlling the fine structure in the PVA/TEOS membranes was expected. Thus, the effects of the annealing temperature and time on the permeation and separation characteristics were examined by annealing the PVA/TEOS hybrid membranes under various conditions.

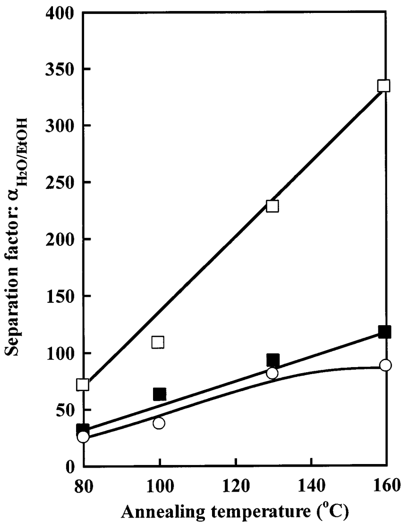


Figure 3. Effects of the annealing temperature on the separation factor for the water permselectivity of an aqueous solution of 85 wt % ethanol through the PVA membranes (○) and PVA/TEOS hybrid membranes with 5 wt % TEOS (■) and 25 wt % TEOS (□). The annealing time was 8 h.

Permselectivity of Annealed PVA/TEOS Hybrid Membranes. The effects of the annealing temperature on the separation factor of PVA and PVA/TEOS hybrid membranes with a TEOS composition of 5 and 25 wt % are shown in Figure 3. In this case, the annealing time of the PVA and PVA/TEOS hybrid membranes was fixed for 8 h and the annealing temperatures were 80, 90, 130, and 160 °C. As can be seen in this figure, the PVA/TEOS hybrid membranes had better separation characteristics than the PVA membranes over the entire range of annealing temperatures. The separation factor for PVA and PVA/TEOS hybrid membranes also increased with increasing annealing temperature, and this tendency increased with an increase in the TEOS content. Figure 4 shows the permeation rate and membrane density for PVA and PVA/TEOS membranes as a function of the annealing temperature. The permeation rate of every membrane decreased with increasing annealing temperature; however, the decrease of the PVA/TEOS hybrid membrane with higher TEOS contents was smaller. On the other hand, the density of the PVA and PVA/TEOS hybrid membranes increased with increasing annealing temperature. The density of PVA/TEOS hybrid membranes with higher TEOS content was higher, but the density of the PVA membrane decreased significantly at 130 °C and over. The PVA/TEOS hybrid membrane with a higher TEOS content

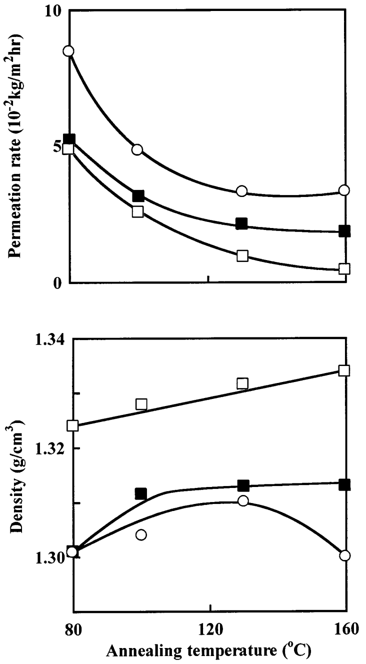


Figure 4. Effects of the annealing temperature on the permeation rate for an aqueous solution of 85 wt % ethanol through the PVA membranes (○), and PVA/TEOS hybrid membranes with 5 wt % TEOS (■) and 25 wt % TEOS (□) and their density. The annealing time was 8 h.

was also more sensitive to annealing temperature. The increase in PVA membrane density was probably due to the increase in crystallinity of the PVA membrane because of the hydrogen bonds. The increase in the density of the PVA/TEOS hybrid membrane can be attributed to an increase in the hydrogen bonds between the silanol groups in the silane particle, the hydroxyl groups in the PVA, and the covalent bonds between them, as shown in Scheme 2. The decrease in the density of the PVA membrane annealed at 130 °C effects on the decomposition of the PVA molecule. The increase in the separation factor for water permselectivity in Figure 3 and the decrease in the permeation rate in Figure 4 with increasing annealing temperature and TEOS content were significantly influenced by the membrane density.

Figure 5 shows the effects of the annealing time on the separation factor of annealed PVA and PVA/TEOS hybrid membranes with TEOS contents of 5 and 25 wt % TEOS. In Figure 5, the annealing temperature of the PVA and PVA/TEOS hybrid membranes was fixed at 130 °C, and the annealing time was changed. As can be seen in Figure 5, the separation factor of all membranes increased with increasing annealing time. In particular, the separation factor of the PVA/TEOS hybrid membrane with a TEOS content of 25 wt % increased remarkably with increasing annealing time. This PVA/TEOS hybrid membrane also had a very high separation factor for water permselectivity. This fact suggests that varying the annealing time was more effective for improving separation characteristics of the PVA/TEOS hybrid membrane than varying the annealing temperature.

Figure 6 shows the effects of annealing time on the permeation rate of annealed PVA and PVA/TEOS hybrid membranes, and on the membrane density. The permeation rate decreased with increasing annealing time, and the PVA/TEOS hybrid membrane density

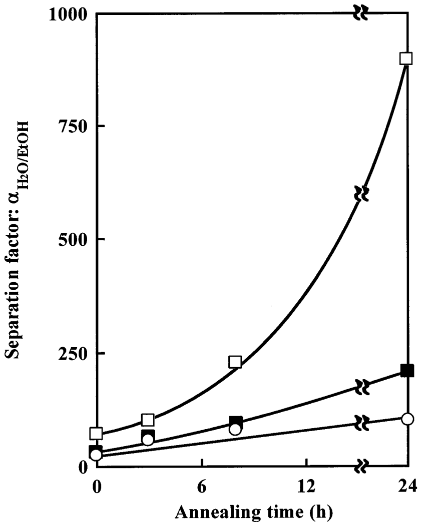


Figure 5. Effects of the annealing time on the separation factor for the water permselectivity of an aqueous solution of 85 wt % ethanol through the PVA membranes (○) and PVA/TEOS hybrid membranes with 5 wt % TEOS (■) and 25 wt % TEOS (□). The annealing temperature was 130 °C.

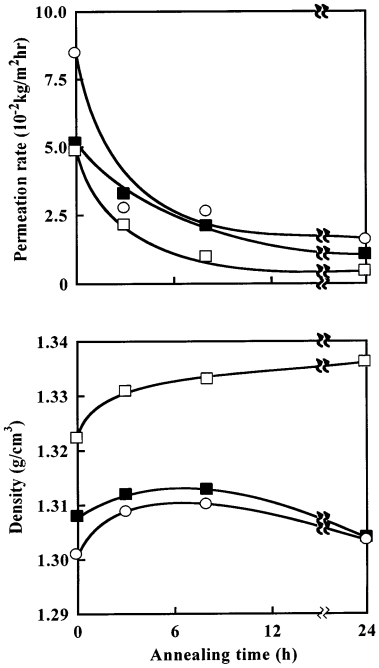


Figure 6. Effects of the annealing time on the permeation rate for an aqueous solution of 85 wt % ethanol through the PVA membranes (○) and PVA/TEOS hybrid membranes with 5 wt % TEOS (■) and 25 wt % TEOS (□) and their density. The annealing temperature was 130 °C.

with a higher TEOS content had a lower permeation rate. The density of the PVA and PVA/TEOS hybrid membranes with TEOS content of 5 wt % peaked at an annealing time of 8 h, but the density of the PVA/TEOS hybrid membrane with a TEOS content of 25 wt % increased with increasing annealing time. These results suggest that the partitioning characteristics were improved, but the permeability was slightly decreased, because the structure of the PVA/TEOS hybrid membrane with a higher TEOS content became denser with increasing annealing temperature. These results support that increasing the annealing temperature or time yields PVA/TEOS hybrid membranes with a denser structure.

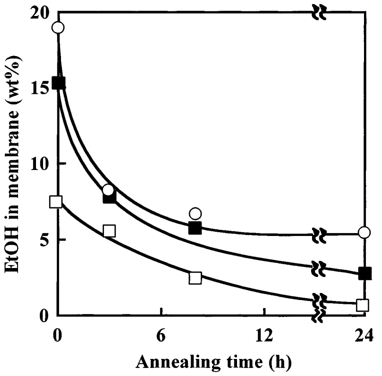


Figure 7. Effects of the annealing time on the ethanol concentration in the PVA membrane (○) and PVA/TEOS hybrid membranes with 5 wt % TEOS (■) and 25 wt % TEOS (□) for an aqueous solution of 85 wt % ethanol. The annealing temperature was 130 °C.

Table 1. Separation Factor, Sorption Selectivity, and Diffusion Selectivity of Unannealed PVA and PVA/TEOS Hybrid Membranes

TEOS (wt%)	$\alpha_{\mathrm{sep\ H_2O/EtOH}}$	$\alpha_{\mathrm{sorp\ H_2O/EtOH}}$	$\alpha_{\mathrm{diff\ H_2O/EtOH}}$
0	26.3	24.3	1.08
2	32.8	31.6	1.03
5	72.3	69.8	1.03

Chemical Structure of PVA/TEOS Hybrid Membrane. In general, the permselectivity of polymer membranes is dependent on their chemical and physical structures, which influence the solubility of permeants in the membrane and the diffusivity of permeants through the membrane. Therefore, we investigated the chemical and physical structures of the PVA/TEOS hybrid membranes to elucidate their permeation and separation characteristics.

Figure 7 shows the effect of the annealing time on the ethanol concentration in the PVA and PVA/TEOS hybrid membranes for an aqueous solution of 85 wt % ethanol. In this figure, it is clear that with increasing annealing time, the ethanol concentration in these membranes decreased significantly. Furthermore, the ethanol concentration in the PVA/TEOS hybrid membrane was lower than in the PVA membrane. In other words, the increase in annealing time and TEOS content led to the preferential incorporation of water into the PVA/TEOS hybrid membrane from an aqueous ethanol solution. This discussion is supported by the sorption selectivity, $\alpha_{\mathrm{sorp\ H_2O/EtOH}}$, in Table 1, determined from Figures 1 and 7 using eq 4,

$$\alpha_{\mathrm{sorp\ H_2O/EtOH}} = (M_{\mathrm{H_2O}}/M_{\mathrm{EtOH}})/(F_{\mathrm{H_2O}}/F_{\mathrm{EtOH}}) \quad (4)$$

where $M_{\mathrm{H_2O}}$ and M_{EtOH} and $F_{\mathrm{H_2O}}$ and F_{EtOH} are weight fractions of water and ethanol in the membrane and the feed solution, respectively.

As can be seen in Table 1, both separation factor and sorption selectivity of the unannealed PVA and PVA/TEOS hybrid membranes increased with increasing TEOS content. On the other hand, the diffusion selectivity was calculated from these separation factor and sorption selectivity using eq 5.

$$\alpha_{\mathrm{diff\ H_2O/EtOH}} = \alpha_{\mathrm{sep\ H_2O/EtOH}}/\alpha_{\mathrm{sorp\ H_2O/EtOH}} \quad (5)$$

The diffusion selectivity of unannealed PVA and PVA/TEOS hybrid membranes was very low, regardless of the TEOS content.

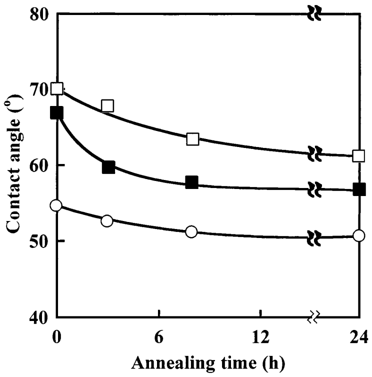


Figure 8. Effects of the annealing time on the contact angles for methylene iodide on the surface of the PVA membranes (○) and PVA/TEOS hybrid membranes with 5 wt % TEOS (■) and 25 wt % TEOS (□). The annealing temperature was 130 °C.

Table 2. WAXD Data of the PVA and PVA/TEOS Hybrid Membranes with 25 wt % TEOS

membrane	2θ	d(Å)
PVA crystalline unannealed	19.86	4.467
TEOS:25 wt % anneal at 130 °C for 24 h crystalline	19.76	4.489

Since the selectivity for permeants incorporated in the membranes is significantly influenced by the chemical properties of the membrane surface, the contact angles on the surface of the PVA/TEOS hybrid membrane were measured.

Figure 8 shows the contact angles for methylene iodide on the surfaces of PVA and PVA/TEOS hybrid membranes as a function of annealing time. In this figure, since methylene iodide was used for the measurement of the contact angle of the membrane surface, a higher contact angle implies a more hydrophilic membrane surface. As can be seen in Figure 8, with increasing TEOS content, the contact angle increased. This result suggests that the surface of the membrane became more hydrophilic and supports the contention that the PVA/TEOS hybrid membranes with a higher TEOS content could preferentially incorporate water from an aqueous ethanol solution, as shown in Figure 7. On the other hand, with increasing annealing time, the contact angles for methylene iodide decreased in all membranes, and the membrane surface became more hydrophobic. This result is in contrast with the fact that water could be selectively absorbed into the PVA/TEOS hybrid membrane with an increase in the annealing time, as shown in Figure 7.

The theoretically absorbed compositions in the PVA membranes with different crystallinities for an aqueous solution of 85 wt % ethanol has been analyzed by the Flory–Huggins equation.[29–31] Their analysis suggested that the change in the crystallinity of the membrane, as the PVA membrane was annealed at various temperatures, was affected not only by the internal part of the membrane but also by the surface of the membrane.[32] In this report, with decreasing crystallinity of the PVA membrane, the theoretical ethanol concentration in the PVA membrane decreased, and the surface of the PVA membrane became more hydrophilic. This result can explain the disagreement between the fact that water could be selectively absorbed into the PVA/

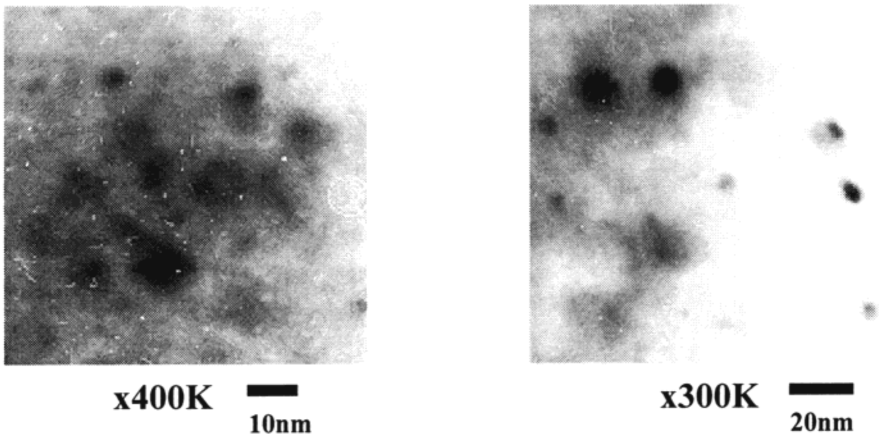


Figure 9. Transmission electron micrographs of a PVA/TEOS membrane with 150 wt % TEOS.

TEOS hybrid membrane and the fact that the contact angles for methylene iodide decreased with increasing annealing time. Therefore, the ethanol concentration in the PVA membranes using the Flory−Huggins equation was affected not only by the affinity between PVA and the permeants but also by the molecular size of the permeants. Thus, the sorption selectivity during the solution process into the PVA membrane of an aqueous ethanol solution is more significantly dependent on the affinity between the PVA and the permeants, and consequently, the water molecule with a smaller molecular size can be preferentially incorporated into the PVA membrane. In the PVA/TEOS hybrid membrane, the size-selectivity of the membrane structure occurred not only inside the membrane but also on the surface of the membrane. As a result, it is presumed that the water molecule, with a smaller molecular size, could be selectively incorporated into the PVA/TEOS hybrid membrane, although the surface of the membrane became hydrophobic.

Physical Structure of PVA/TEOS Hybrid Membrane. The WAXD measurements were mainly performed for the crystalline diffraction in PVA. Table 2 summarizes the refraction angle of the crystalline peak, 2θ, and the spacing, d (020), of the unannealed PVA membrane and the annealed PVA/TEOS hybrid membrane containing TEOS 25 wt %, which was annealed at 130 °C for 24 h. The annealed PVA/TEOS hybrid membrane had a large d spacing value at the crystalline peak. This suggests that the noncrystalline region in PVA became more dense by introducing TEOS and by annealing to enhance the polycondensation reaction in the membrane. This change in the noncrystalline region of PVA affected the PVA molecule chains, and changed the rougher crystalline region. This idea is supported by the measurements of the membrane density.

The WAXD measurements concluded that the noncrystalline region, where the partitioning of an aqueous ethanol solution occurred, became denser by introducing the TEOS and by annealing to encourage the polycondensation reaction.

The TEM observation of the PVA/TEOS hybrid membranes shows how TEOS molecules were introduced into the PVA membrane matrix. This contrast between PVA and TEOS could not be observed in the PVA/TEOS hybrid membranes prepared under the conditions in this study. Thus, it was presumed that the PVA and the cohesion bodies of the TEOS were randomly dispersed at the molecular level. On the other hand, in the PVA/TEOS membrane containing excess TEOS (150 wt %), the cohesive structure of TEOS was observed in the membrane as shown in Figure 9. These TEOS bodies were spheres of less than 10 nm. This result suggests that the polycondensation reaction between the cohesion bodies of TEOS progressed independently and that the silica sol particles were formed in the presence of excess TEOS.

Performance of PVA/TEOS Hybrid Membranes. In Table 3, the permeation and separation characteristics for an aqueous ethanol solution through water permselective polymer membranes during pervaporation are summarized. The separation factors for the annealed PVA/TEOS hybrid membranes are relatively higher than those for other polymer membranes. However, the permeation rates of the annealed PVA/TEOS hybrid membranes are smaller. These results suggest that the annealing of PVA/TEOS hybrid membranes introduces to denser membranes, and the addition of TEOS to the PVA membrane is very effective. In future, it is necessary to improve the permeation rate further. If more suitable conditions of the hybrid membrane preparation from PVA and TEOS are investigated, and an ultrathin membrane is prepared from the PVA/TEOS hybrid, an appearance of the PVA/TEOS hybrid membranes with both high permeation rate and high separation factor will be expected. This study suggests a possibility of appearance of novel organic−inorganic hybrid membranes.

Structure and Permeation Characteristics of PVA/TEOS Hybrid Membranes. On the basis of the above results, the change in the structure of the PVA/TEOS hybrid membranes with respect to their permeation and separation characteristics for an aqueous ethanol solution during pervaporation is illustrated in Figure 10. The addition of TEOS into the PVA membrane led to a dense membrane structure due to the polycondensation reaction of TEOS; the motion of the PVA molecular chains in the noncrystalline region of the PVA membrane matrix was restrained by the polycondensation reaction. Furthermore, both the sorption selectivity and the diffusion selectivity were enhanced. These selectivities increased with increasing TEOS content, and consequently, the partitioning for an aqueous ethanol solution was improved.

The annealing of the PVA/TEOS hybrid membranes yielded hydrogen bonds between the hydroxyl groups

Table 3. Permeation and Separation Characteristics for an Aqueous Ethanol Solution through Some Polymer Membranes during Pervaporation

membrane	feed (wt %)	temp (°C)	permeation rate $(\mathrm{kg/cm^2 \cdot h})$	separation factor $(\alpha_{\mathrm{sep\ H_2O/EtOH}})$	ref
cellophane	75.6	60	6.0	5	35
cellulose acetate	95.6	60	0.2	5.9	36
poly(tetrafluoroethylene)-*g*-poly(vinylpyrrolidone)	95.6	25	2.2	2.9	37
Nafion-H^+-$(CH_2)_2NH^+$	95.6	70	5.0	2.5	38
polyacrylonirile−poly(vinylpyrrolidone) blend	95.6	20	2.2	3.2	39
poly(maleimide-*co*-acrylonitrile)	95	15	0.036	44.8	40
poly(acrylic acid-*co*-acrylonitrile)	81.5	15	0.013	876	41
polystyrene	95.6	40	0.005	101	42
polyvinylchloride	95.6	40	0.003	63	43
alginic acid	95.6	40	0.048	8.8	33
chitosan	95.6	40	0.065	17	34
chitosan acetate salt	95.6	40	0.074	20	44
glutaraldehyde cross-linked chitosan	95.6	40	0.033	390	44
PVA/TEOS hybrid[a]	85	40	0.005	329	this study
PVA/TEOS hybrid[b]	85	40	0.004	893	this study

[a] TEOS content 25 wt %, annealed at 160 °C, 8 h. [b] TEOS content 25 wt %, annealed at 130 °C, 24 h.

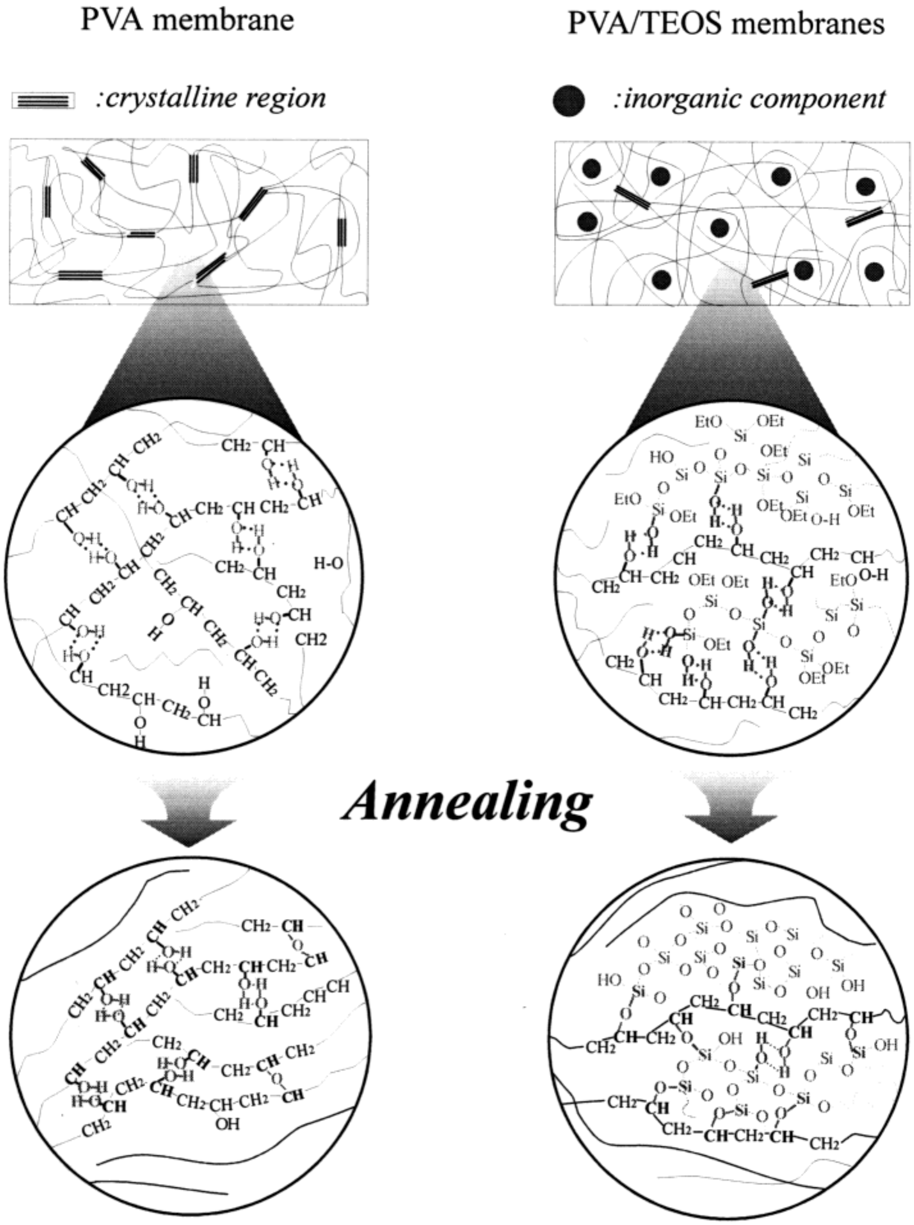


Figure 10. Structure of unannealed and annealed PVA and PVA/TEOS hybrid membranes.

in the PVA, and the silanol groups in the condensate of TEOS formed covalent bonds between them. Consequently, denser PVA/TEOS hybrid membranes were constructed. As a result, the membrane swelling decreased remarkably, and highly water permselective membranes were obtained.

Conclusions

Organic−inorganic hybrid pervaporation membranes were prepared from PVA and TEOS using the sol−gel reaction. The addition of TEOS into the PVA membrane decreased the swelling of the membrane and improved the water permselectivity of the PVA/TEOS hybrid membrane. These results were obtained based on the hydrogen bonds as a cross-linking point in the PVA/TEOS hybrid. The PVA/TEOS hybrid membranes were also annealed under various conditions. The water permselectivity in the PVA/TEOS hybrid membrane increased significantly with annealing temperature and time. These improvements in the partitioning characteristics could be attributed to the fact that the TEOS reaction was present in the noncrystalline region of the PVA membrane, and thus a denser noncrystalline region was formed.

From the above results, it is clear that a novel organic−inorganic hybrid membrane, which had decreased membrane swelling and high permselectivity, could be prepared from PVA and TEOS using the sol−gel method.

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