

Pervaporation Characteristics and Structure of Poly(vinyl alcohol)/Poly(ethylene glycol)/Tetraethoxysilane Hybrid Membranes

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ABSTRACT: Poly(vinyl alcohol) (PVA) blended with poly(ethylene glycol) (PEG) was crosslinked with tetraethoxysilane (TEOS) to prepare organic-inorganic PVA/PEG/TEOS hybrid membranes. The membranes were then used for the dehydration of ethanol by pervaporation (PV). The physicochemical structure of the hybrid membranes was studied with Fourier transform infrared spectra (FT-IR), wide-angle X-ray diffraction WXR, and scanning electron microscopy (SEM). PVA and PEG were crosslinked with TEOS, and the crosslinking density increased with increases in the TEOS content, annealing temperature, and time. The water permselectivity of the hybrid membranes increased with increasing annealing temperature or time; however, the permeation fluxes decreased at the same time. SEM pictures showed that phase separation

took place in the hybrid membranes when the TEOS content was greater than 15 wt %. The water permselectivity increased with the addition of TEOS and reached the maximum at 10 wt % TEOS. The water permselectivity decreased, whereas the permeation flux increased, with an increase in the feed water content or feed temperature. The hybrid membrane that was annealed at 130°C for 12 h exhibited high permselectivity with a separation factor of 300 and a permeation flux of 0.046 kg m⁻² h⁻¹ in PV of 15 wt % water in ethanol. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3640–3648, 2007

Key words: pervaporation; poly(vinyl alcohol); tetraethoxysilane; hybrid membranes

INTRODUCTION

Ethanol, a clean and renewable energy resource that can be produced through fermentation from renewable biomass, has drawn much attention from the government and researchers.^{1,2} However, it needs to be highly concentrated. Ethanol is concentrated by distillation from aqueous solutions usually; it forms an azeotrope with 96.5 wt % ethanol in an aqueous solution, which prevents it from being further concentrated.³ As a novel membrane technology that offers easy operation, effectiveness, and high energy savings, pervaporation (PV) has applications in the separation and purification of liquid mixtures, particularly for the dehydration of organic compounds and the separation of azeotropic or close-boiling-

point mixtures.^{4–6} At present, the dehydration of ethanol by PV is being actively studied.^{7,8}

Poly(vinyl alcohol) (PVA), one of the most studied hydrophilic materials, is used in the dehydration of organic solutions because of its strong hydrophilicity, excellent stability, and good film-formation properties.^{9–11} However, PVA easily swells in aqueous solutions, and this usually results in a decrease in the water permselectivity of PVA membranes.¹² Therefore, a lot of research has focused on how to control the swelling of PVA membranes and to improve their water permselectivity and permeation flux. For example, in the PV separation of water-ethanol mixtures through crosslinked and surface-modified PVA membranes,¹³ these membranes have exhibited water permselectivity enhanced by a factor of nearly 2 compared with that of the only crosslinked membrane, and the total flux is at least unchanged. Many efforts have been concentrated on improving PVA membrane performance via blending.^{14,15} Of these, hybridization between organic polymers and inorganic substances is one of the most widely used techniques. The hybridization of PVA membranes can not only restrict their swelling but also provide the inherent advantages of the organic and inorganic components. A lot of PVA-based hybrid membranes were have been reported. PVA/SiO₂ organic-inorganic hybrid membranes containing sulfonic

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acid groups have been prepared with the sol-gel process under acidic conditions.¹⁶ Crosslinked PVA/poly(acrylic acid)/silica hybrid membranes have been prepared for use as proton-exchange membranes for direct methanol fuel cells.¹⁷ However, they are seldom used for PV separation. One example is a PVA/tetraethoxysilane (TEOS) hybrid membrane prepared via hydrolysis and condensation reactions and used for the PV dehydration of organic solutions.^{3,18,19}

Most researchers have obtained higher permselectivity by sacrificing permeation flux. The reported PVA-based hybrid membranes have been mostly symmetrical, such as PVA/TEOS hybrid membranes.³ Although this kind of membrane provides high permselectivity, it has the disadvantage of low permeation flux ($5 \text{ g m}^{-2} \text{ h}^{-1}$) because of the high thickness of 20–40 μm . Therefore, we have attempted to improve both the permeation flux and permselectivity of the PVA membranes used for dehydration of ethanol solutions. Membranes were prepared through spin coating to form a separating layer on cellulose acetate (CA) microfiltration supports; the thickness of the separating layer was about 2 μm . To increase the permeation flux and water permselectivity, poly(ethylene glycol) (PEG) and TEOS were incorporated, respectively.

EXPERIMENTAL

Materials, chemicals, and instruments

PVA, with a polymerization degree of 1750 ± 50 , was purchased from Chinese Chemical, Ltd. (Shanghai, China). PEG, with a polymerization degree of 6000, was purchased from Shanghai Chemical, Ltd. (Shanghai, China). TEOS was purchased from Shanghai Chemical. All other solvents and reagents, obtained from Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China), were analytical-grade and were not further purified before use. A CA microfiltration membrane, with a pore size of 0.45 μm and a thickness of about 20 μm , was purchased from Shanghai Xinya Purification Instruments, Ltd. (Shanghai, China). A spin coater (model KW-4A) was purchased from the Microelectronic Research Institute at the Chinese Academy of Science (Beijing, China). A Pervap 2201 PV setup was purchased from Sulzer Chemical, Ltd. (Neunkirchen, Germany).

PVA/PEG/TEOS hybrid membrane preparation

Measured amounts of PVA and PEG were dissolved in 88 mL of double-distilled water at 90°C for 3 h to form a homogeneous solution. The solution was mixed with a measured amount of TEOS and 2 mL of 36 wt % hydrochloric acid and then was stirred at 30°C for 10 h to produce a sol-gel reaction. The total mass fraction of PVA, PEG, and TEOS was 10 wt %.

The solution was allowed to stand for 36 h to liberate air bubbles and was then coated onto the CA microfiltration support through spin coating with a rotation speed of 1000 rpm for 15 s and then 5000 rpm for 10 s. The obtained film was evaporated in the atmosphere for 24 h, and then it was further dried in a vacuum at 80°C for another 24 h. The thickness of the film that formed on the porous matrix was about 2.0 μm . The hybrid membrane containing X wt % TEOS was simply termed PPT-X.

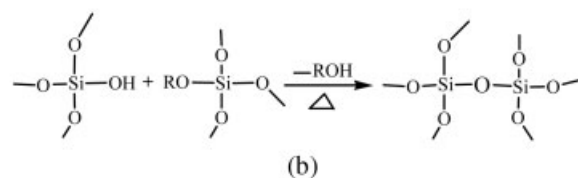
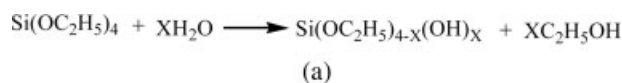
To analyze the effects of annealing on the physicochemical structure and permeation performances, the hybrid membrane was treated with annealing at 100 and 130°C for 12 h in a vacuum oven or with an annealing treating at 100°C for 3, 6, or 12 h.

Characterization of the hybrid membranes

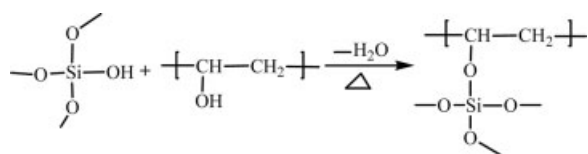
The chemical structure characteristics of the hybrid membranes were studied with a Fourier transform infrared apparatus (FTIR; FT-IR 740SX, Nicolet, Madison, WI) equipped with smart attenuated total reflectance. FTIR spectra were observed at 25°C in the range of 400–4000 cm^{-1} . All the membrane samples were dried in a vacuum at 80°C for 8 h before characterization. The effects of the addition of PEG and TEOS, the annealing temperature, and the annealing time on the crystallinity of PVA was studied with wide-angle X-ray diffraction (WAXD; CAD4-PDP11/44, Enraf-Nonious Co., Delft, Holland) in the range of 5–35° at room temperature. The surface and cross-sectional morphology of the membranes were viewed with scanning electron microscopy (SEM; model 1530, Leo, Oberkochen, Germany).

PV of the hybrid membranes

PV experiments were carried out on a Pervap 2201 (Sulzer Chemtech, Neunkirchen, Germany) with a feed flow rate of 30 L/h at 50, 60, or 70°C. The effective surface area of the membrane in contact with the feed was 70 cm^2 . The pressure on the permeate side was maintained at 20 mbar with a vacuum pump. The permeate was collected in CaCl_2 solution cold traps ($< -30^\circ\text{C}$). The concentrations of the feed and perme-



Scheme 1 (a) Hydrolysis and (b) condensation reactions for TEOS (R = $-\text{H}$ or $-\text{C}_2\text{H}_5$).



Scheme 2 Crosslinked reaction for PVA with TEOS.

ate were measured with an Abbe refractometer (accuracy = ± 0.0001 units, WAY-2S, Shanghai Cany Precision Instrument Co., Ltd., Shanghai, China).

The permeation properties of the hybrid membranes were characterized by the total permeation flux (J_p) and separation factor (α_{sep}) as follows:

$$J_p = W_p / (A - t) \quad (1)$$

$$\alpha_{sep} = \frac{P_{water} / P_{ethanol}}{F_{water} / F_{ethanol}} \quad (2)$$

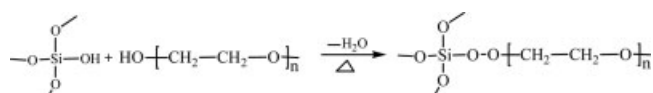
where W_p is the mass of the permeate; A is the effective surface area of the membrane; t is the time of PV; P_{water} and $P_{ethanol}$ are the concentrations of water and ethanol in the permeate, respectively; and F_{water} and $F_{ethanol}$ are the concentrations of water and ethanol in the feed, respectively.

RESULTS AND DISCUSSION

Fabrication of the hybrid membranes

The effects of both PEG and TEOS contents on the phase behavior of solutions were investigated. Phase separation occurred in the process of PVA blending with PEG in water when the mass ratio of PEG to PVA was greater than 1 : 4. A clear polymer solution was formed at a PVA/PEG mass ratio of 9 : 1. The obtained solution underwent a sol-gel reaction with TEOS in the presence of hydrochloric acid. Phase separation took place in the mixture when the TEOS content (in the polymers and TEOS) was more than 25 wt %. Therefore, we employed a 9 : 1 PVA/PEG mass ratio to prepare the hybrid membranes containing 0–25 wt % TEOS in this study.

The chemical structure and reaction routes for the hybrid membranes are displayed in Schemes 1–3. In preparing the hybrid membranes, TEOS was hydrolyzed in the presence of an acid catalyst, and this led to the formation of silanol groups. The resultant silanol groups formed siloxane bonds because of the dehydration or dealcoholysis reaction with other silanol or ethoxy groups during the drying of the



Scheme 3 Crosslinked reaction for PEG with TEOS.

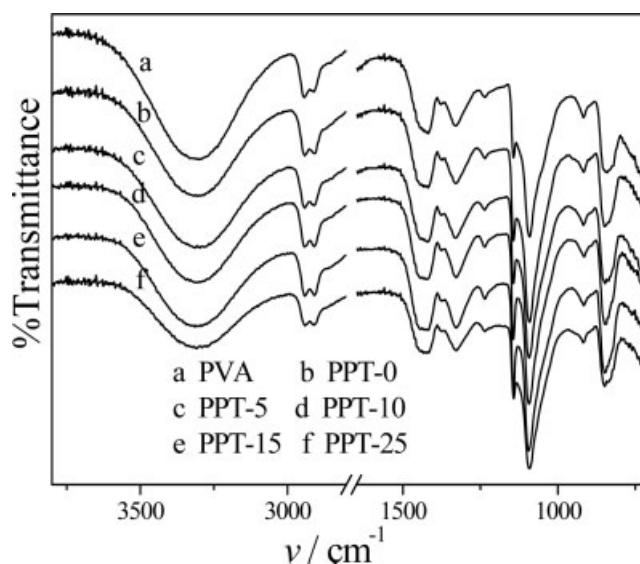


Figure 1 FTIR spectra of PVA and PPT-X membranes (where X is 0, 5, 10, 15, or 25).

membranes. These reactions led to cohesive bodies between siloxane in the membranes.^{3,20} Because these bodies of siloxane were dispersed in the membrane, the silanol groups of siloxane and the dissociative hydroxyl groups of PVA and PEG formed hydrogen and covalent bonds, which are the cross-link spots in the hybrid membranes.

Chemical structure of the hybrid membranes

The chemical structures of PVA and the hybrid membranes were investigated with FTIR, as indicated in Figure 1. The reflectance intensity of the —OH band at 3400 cm^{-1} decreased with the addi-

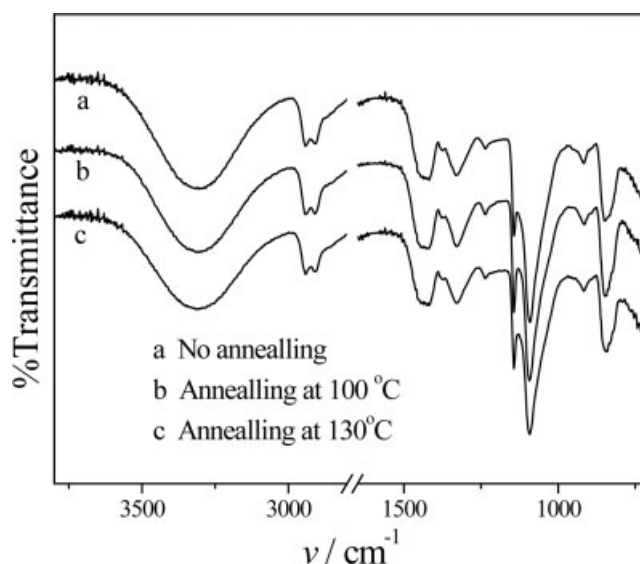


Figure 2 FTIR spectra of hybrid membrane PPT-10 without annealing and with annealing at 100 and 130°C for 12 h.

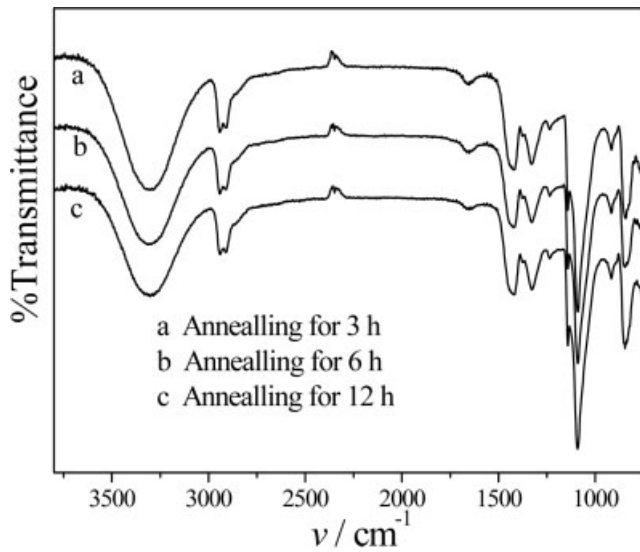


Figure 3 FTIR spectra of hybrid membrane PPT-10 with annealing at 100°C for 3, 6, and 12 h.

tion of PEG and TEOS because the PVA content decreased with the addition of PEG to the hybrid membranes. The hydroxyl group —OH in the membrane decreased with the addition of PEG because there was less —OH moiety in PEG than in PVA. On the other hand, the silanol groups in siloxane crosslinking with —OH in PVA and PEG also resulted in the decrease of —OH. At the same time, the intensity of the peak around 1100 cm^{-1} increased. This indicates that —OH of silanol underwent a reaction with —OH in the organic component to form covalent bond Si—O—C, which overlapped the original C—O bond.

Figures 2 and 3 show the effects of the annealing temperature and time on the FTIR spectra of PPT-10,

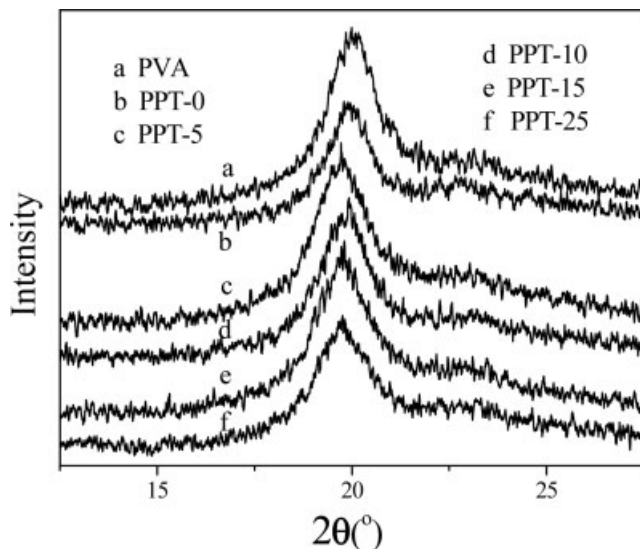


Figure 4 WAXD graph of PVA and PPT-X (where X is 0, 5, 10, 15, or 25) membranes without annealing.

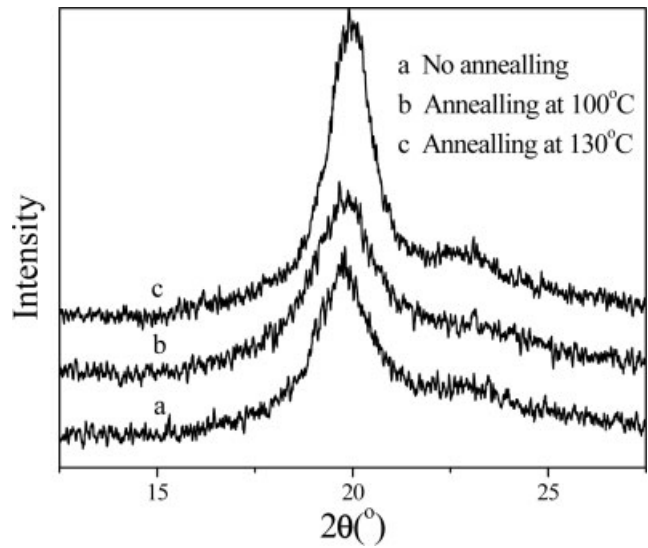


Figure 5 WAXD graph of hybrid membrane PPT-10 without annealing and with annealing at 100 and 130°C for 12 h.

respectively. The reflectance intensity of the —OH band at 3400 cm^{-1} decreased with increasing annealing temperature or time. This led to a decrease in the intensity of the peak of Si—O—C. It suggests that the crosslinking degree increases with increasing annealing temperature or time.

Physical structure of the hybrid membranes

The crystalline diffraction of the hybrid membranes was studied with WAXD, and their spectra are displayed in Figure 4. The typical peak of PVA appeared at $2\theta \approx 20^\circ$,¹⁹ and the intensity of the peak decreased with the addition of PEG. This indicates that the dispersed PEG molecules in the membranes

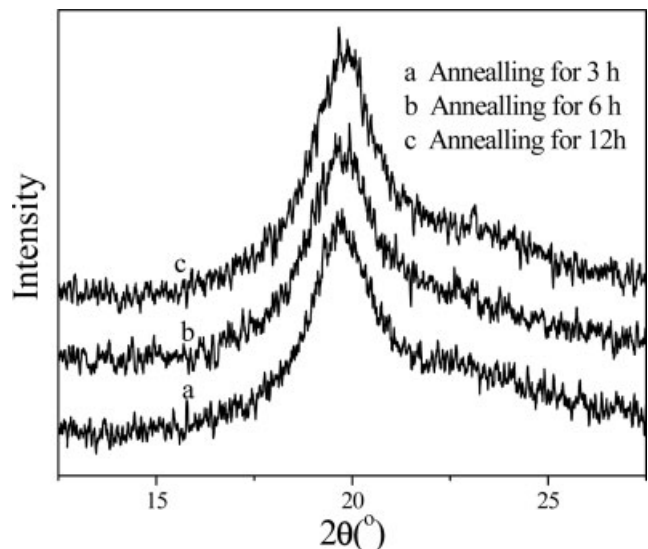


Figure 6 WAXD graph of hybrid membrane PPT-10 with annealing at 100°C for 3, 6, and 12 h.

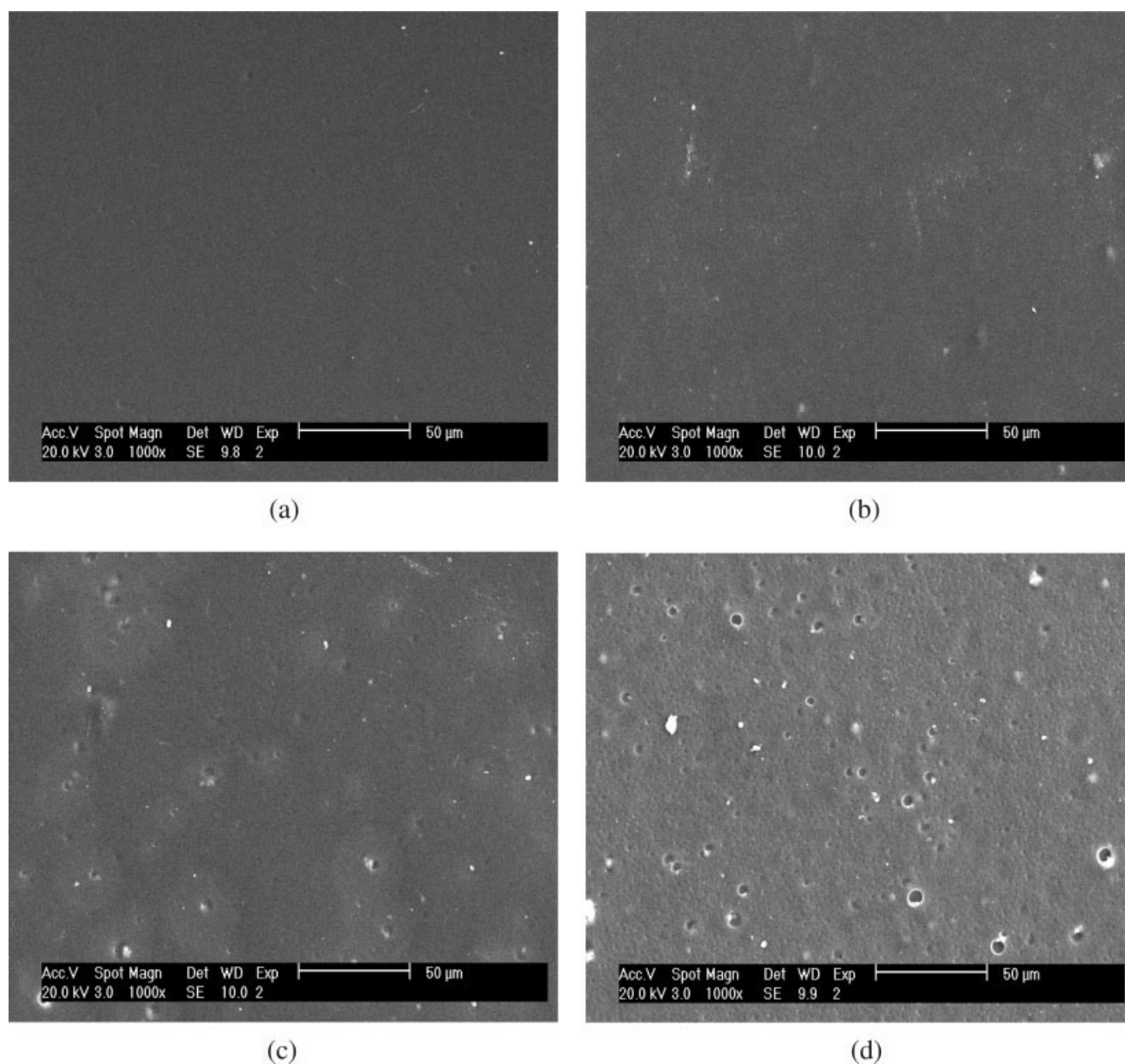


Figure 7 SEM surface images of the separating layers of the hybrid membranes: (a) PPT-0, (b) PPT-10, (c) PPT-15, and (d) PPT-25.

prevented a crystalline region from being formed, and the crystallinity of the PVA-based membrane decreased. A small amount of added TEOS resulted in an increase in the crystallinity of PPT-5. This may have happened because the crosslinking first taking place between PEG and TEOS resulted in PEG getting together. Figure 4 shows that the intensity of the peak decreased with increasing TEOS content, and this agreed with the PVA/TEOS hybrid membranes.¹⁸ This was due to the fact that the dispersed siloxane in the membranes increased with increasing TEOS content, and this prevented crystalline region from being formed. TEOS self-crosslinking occurred with further increasing TEOS content, and the formed inorganic particles dispersed in the mem-

brane; then, the crystal structure was destroyed, and this led to the crystallinity of the hybrid membranes decreasing markedly. Figures 5 and 6 show that the crystallinity of PPT-10 increased with the annealing temperature and time, respectively, because of the dehydration or dealcoholysis reaction between PVA and TEOS. Correspondingly, the water permselectivity increased, and the permeation flux decreased.

The surface microstructure of the hybrid membranes was studied with SEM, as displayed in Figure 7. Figure 7(a) reflects a homogeneous phase in PPT-0. Figure 7(b) shows that the inorganic components and some of the organic components underwent a reaction to form a homogeneous phase in the hybrid membrane containing 10 wt % TEOS. The inorganic

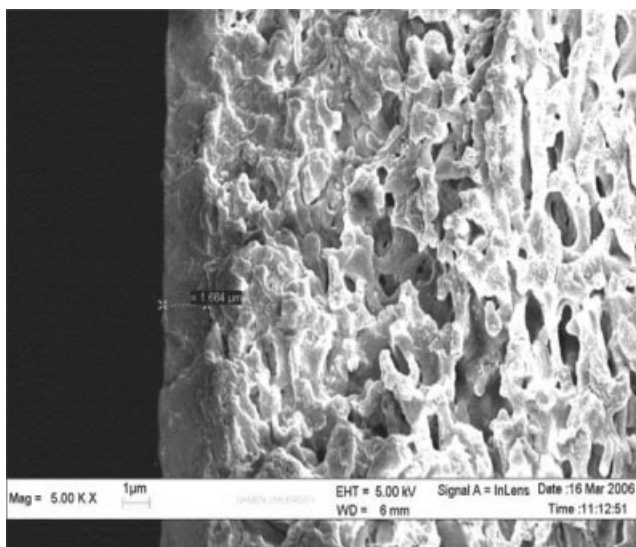


Figure 8 SEM cross-sectional image of PPT-10.

and organic phases can be distinguished clearly at 15 wt % TEOS, as indicated in Figure 7(c). This suggests incomplete crosslinking between the inorganic and organic components. Serious phase separation occurred with the further addition of TEOS, such as the hybrid membranes containing 25 wt % TEOS, as reflected in Figure 7(d); this was due to the self-congregation of TEOS from the inorganic phase.

An SEM picture of the cross-sectional view of PPT-10 is shown in Figure 8, which reflects the hybrid separating layer and the porous CA support layer. Part of the membrane casting solution went into the pores of the support to form a semiseparating layer. The thickness of the separating layer was about 2 μm , the semiseparating layer was about 4 μm thick, and the support layer was about 16 μm thick.

PV separation of an ethanol–water mixture

Effect of PEG

The PVA membrane prepared in our laboratory had a separation factor of 23.51 and a permeation flux of $0.289 \text{ kg m}^{-2} \text{ h}^{-1}$ in the PV separation of 15 wt % water in ethanol at 50°C . Under the same operating conditions, the PVA/PEG blending membrane (PVA/PEG mass ratio = 9 : 1) had a separation factor of 17.45 and a permeation flux of $0.508 \text{ kg m}^{-2} \text{ h}^{-1}$. This suggests that the blend of PVA and PEG could increase the membrane permeation flux with sacrificing the separation factor. The reason is that the $-\text{OH}$ moieties decreased with the incorporation of PEG, so the hydrophilicity of the membranes decreased; subsequently, the separation factor decreased. These results agree with the FTIR characterization. The crystallinity of PVA decreased with

the addition of PEG, and this resulted in an increase in the free volume. This favored the permeation of permeant molecules through the membranes and resulted in an increase in the permeation flux, which was proved by WAXD.

Effects of the TEOS content

Figure 9 shows PV performances of the hybrid membranes containing different TEOS contents without annealing in the separation of 15 wt % water in ethanol at 50°C . The water permselectivity increased first and then decreased with increasing TEOS content, but the change in the permeation flux was complex. The water permselectivity reached a maximum value when the TEOS content was 10 wt %. Crosslinking points increased between TEOS and PVA or PEG with increasing TEOS content when it was less than 10 wt %, and this resulted in an increase in the membrane density and water permselectivity and a decrease in the permeation flux. This agreed with the FTIR observations. However, the water permselectivity decreased slightly when the TEOS content was more than 10 wt %. This suggests that the sol-gel reaction between TEOS and PVA or PEG could not complete in this case; a particulate that formed through TEOS self-crosslinking can be seen in Figure 7 and resulted in an increase in the membranes' hydrophobicity.

In general, the crosslinking density increased with increasing TEOS content, and this resulted in an increase in the density of the membranes and a decrease in the permeation flux through the hybrid membranes. However, the permeation flux of PPT-10

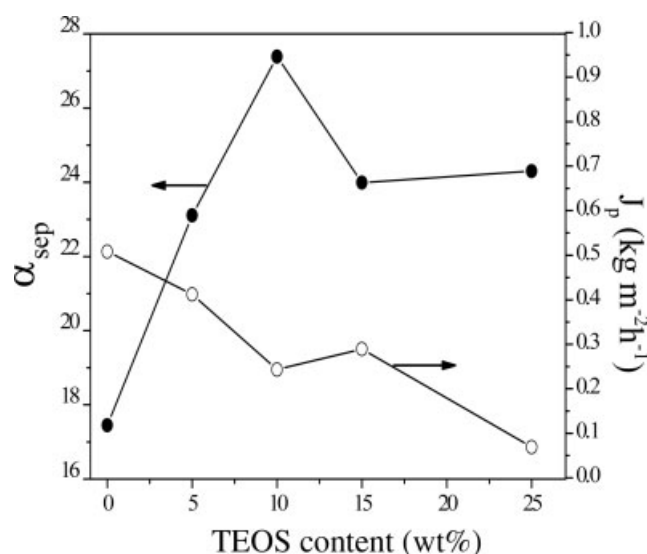


Figure 9 PV performance of PVA/PEG/TEOS hybrid membranes containing different TEOS contents in the separation of 15 wt % water in an ethanol solution at 50°C (α_{sep} = water permselectivity; J_p = permeation flux).

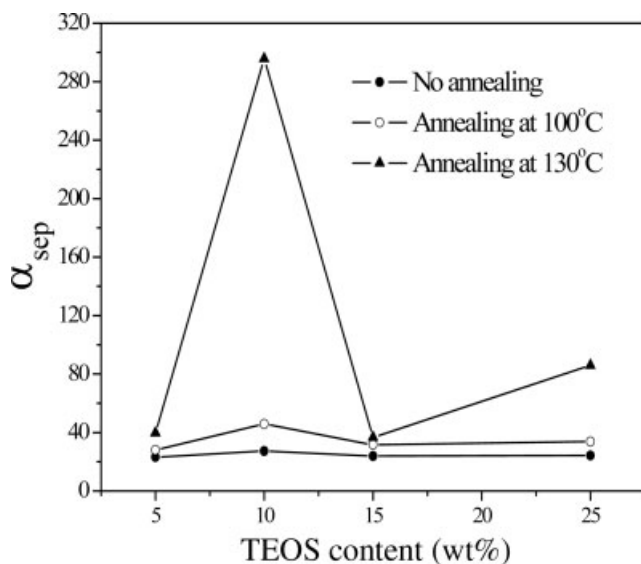


Figure 10 Water permselectivity (α_{sep}) of PVA/PEG/TEOS hybrid membranes without annealing and with annealing at 100 and 130°C for 12 h in PV of 15 wt % water in an ethanol solution at 50°C.

was less than that of PPT-15. It may be that the crosslinking point was dispersed homogeneously in PPT-10, and an ideal compact separating layer formed. Therefore, PPT-10 had the highest separation factor and less permeation flux.

Effects of the annealing temperature and time

Figures 10 and 11 show the PV performances of the hybrid membranes without annealing and with annealing at 100 and 130°C for 12 h in PV of 15 wt %

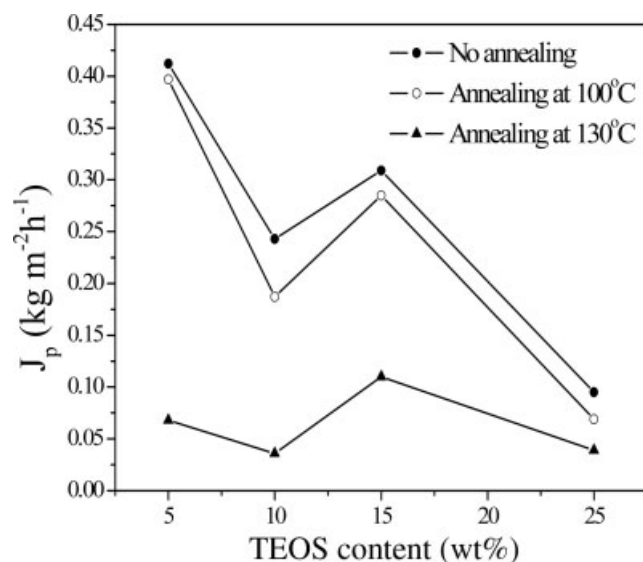


Figure 11 Permeation flux (J_p) of PVA/PEG/TEOS hybrid membranes without annealing and with annealing at 100 and 130°C for 12 h in PV of 15 wt % water in an ethanol solution at 50°C.

water in ethanol at 50°C. The water permselectivity increased and the permeation flux decreased with increasing annealing temperature. The hybrid membranes with annealing exhibited a larger permselectivity variation with the TEOS content than the membranes without annealing. This suggests that the effect of annealing on the membrane crosslinking is obvious. The higher the annealing temperature was, the higher the crosslinking degree was in the membrane, as reflected in the FTIR spectra. These points all agree with the idea that the higher the annealing temperature was, the denser the membrane was, and this led to a lower permeation flux and a higher permselectivity. Annealing had a great impact on the membrane with 10 wt % TEOS. A sharp increase in the water permselectivity was observed, especially with annealing at 130°C, whereas the permeation flux was low. The water permselectivity increased with crosslinking, but too much led to a low permeation flux. Therefore, the membrane had both high permeation flux and water permselectivity via annealing at 100°C.

Figures 12 and 13 show PV characteristics of the hybrid membrane with annealing at 100°C for 3, 6, and 12 h in PV of 15 wt % water in ethanol at 50°C. The water permselectivity increased and the permeation flux decreased with increasing annealing time. The reason is that the crosslinking degree increased with increasing annealing time, and this was proved by FTIR. This was also confirmed by the WAXD observations. However, the membrane crystallinity did not change remarkably, as depicted in Figure 6. This indicated that the annealing time did not have much impact on the membrane crystallinity. Similarly to the effect of the annealing temperature, the

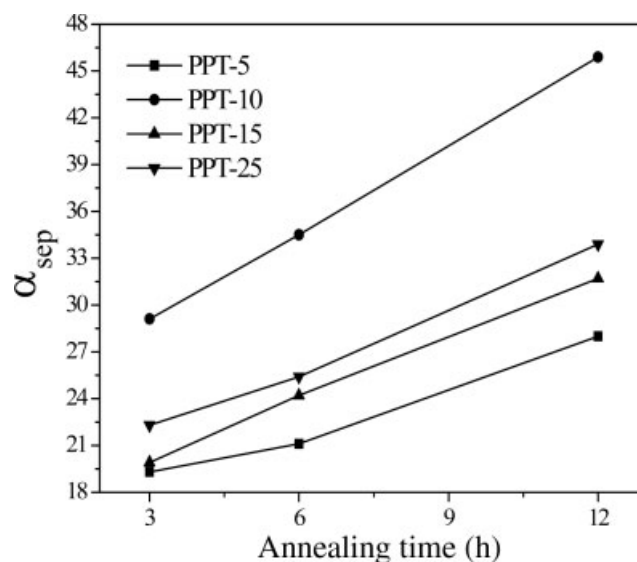


Figure 12 Water permselectivity (α_{sep}) of PVA/PEG/TEOS hybrid membranes with annealing at 100°C for 3, 6, and 12 h in PV of 15 wt % water in an ethanol solution at 50°C.

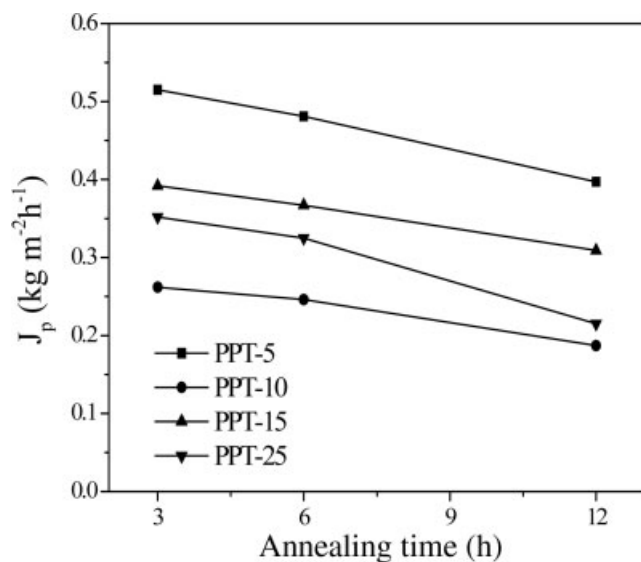


Figure 13 Permeation flux (J_p) of PVA/PEG/TEOS hybrid membranes with annealing at 100°C for 3, 6, and 12 h in PV of 15 wt % water in an ethanol solution at 50°C.

membrane possessed the optimum separation properties at 10 wt % TEOS.

Effects of the operating conditions

Membrane performance in PV separation is influenced not only by the membrane and the characteristics of the permeants but also by the process operating parameters, such as the pressure of the permeate side, feed concentration, and temperature. The influence of the feed concentration and temperature

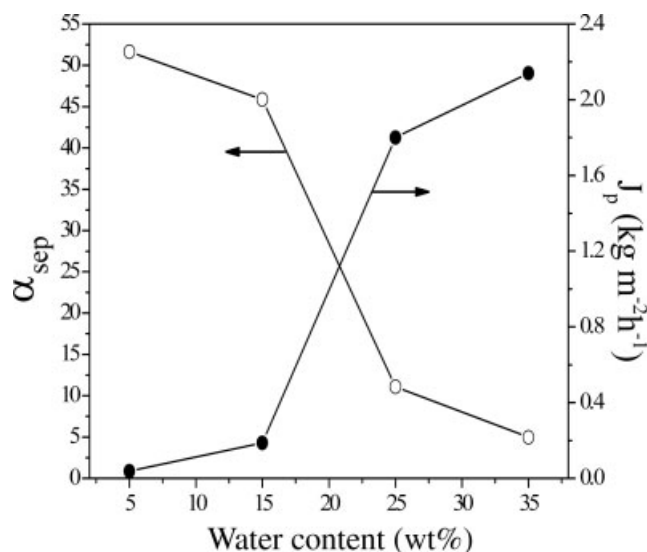


Figure 14 Effects of the feed water content on the PV performance of PPT-10 at 50°C (α_{sep} = water permeability; J_p = permeation flux).

on the membrane performance is discussed in this section.

Figure 14 shows the PV performance of PPT-10 (with annealing at 100°C for 12 h) versus the feed water content in the mass fraction range of 5–35 wt %. The separation factor decreased with an increase in the water content, but the change in the permeation flux was reverse. This may be the effect of the plasticization and interaction between the permeant molecules in the membrane.^{12,13} Amorphous areas in PVA-based membranes tend to swell and result in more flexible molecule chains in aqueous mixtures. The interaction between water and PVA chains is strong, resulting in an increase in the sorption of water in membranes. Therefore, the mobility of the PVA chains in the membranes increased, and the activation energy for permeation decreased. Thus, with increasing water content, the permeation activation energy decreased, and this led to an increase in the permeation flux. On the other hand, the sorption of the permeant molecules and the plasticization action resulted in an increase in the degree of swelling and the free volume of the membranes. Both resulted in an increase in ethanol diffusion through the membranes and a decrease in the water permselectivity.

Figures 15 and 16 show the effects of the feed temperature on the PV performance of the hybrid membranes in PV of 15% water in ethanol. The water permselectivity decreased and the permeation flux increased with increasing feed temperature. The curves at different feed temperatures have similar shapes. The membrane had a maximum water permselectivity at 10 wt % TEOS and a minimum permeation flux at 25 wt % TEOS. The mobility of the poly-

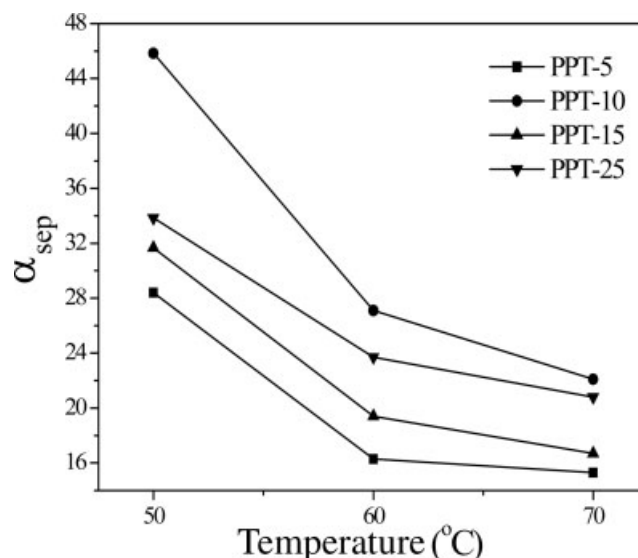


Figure 15 Effects of the feed temperature on the water permselectivity (α_{sep}) of PVA/PEG/TEOS hybrid membranes in PV of 15 wt % water in an ethanol solution.

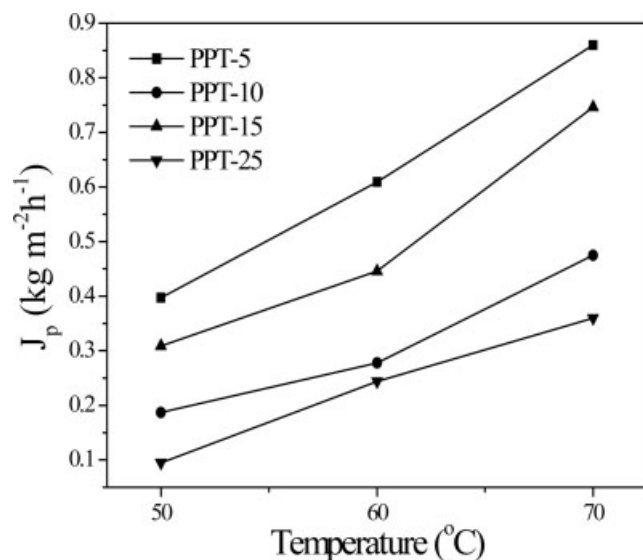


Figure 16 Effects of the feed temperature on the permeation flux (J_p) of PVA/PEG/TEOS hybrid membranes in PV of 15 wt % water in an ethanol solution.

meric chains and the motion energy of the permeant molecules increased with increasing feed temperature, and this led to an increase in the free volume of the membranes. Therefore, the diffusion coefficient of the permeant molecules increased because of the combined effects, and this resulted in the increase in the permeation flux. However, an increase in the free volume of the membranes resulted in the diffusion rate of ethanol increasing faster than that of water, and this led to a decrease in the water permselectivity.

CONCLUSIONS

Organic PEG and inorganic TEOS were used to modify a PVA membrane to improve its permeation properties. The modified hybrid membrane was tested by the PV separation of ethanol–water mixtures. The effects of the addition of PEG, the TEOS content, the annealing temperature and time, the feed temperature and concentration on membrane permeation were studied. The water permselectivity of the membrane decreased and the permeation flux increased with the addition of PEG, and the water permselectivity increased with the addition of TEOS.

Increasing the annealing temperature or time made the water permselectivity increase and the permeation flux decrease. The membrane possessed a high PV performance under the conditions of 10 wt % TEOS, an annealing temperature of 100°C, and an annealing time of 12 h. The water permselectivity decreased and the permeation flux increased with increasing feed temperature or feed water content. The FTIR studies indicated that TEOS underwent a reaction with PEG and PVA and formed Si—O—C bonds. WAXD studies indicated that compromise crystallinity was formed in the membrane with 10 wt % TEOS. SEM pictures suggested that the inorganic particulate size was less than 100 nm, and the thickness of the separating layer was about 2 μm .

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