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EFFECT OF SURFACE RESINTERING ON THE SURFACE MORPHOLOGY AND VAPOR PERMEATION PROPERTIES OF SKIVED POLY(TETRAFLUOROETHYLENE) MEMBRANES

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ABSTRACT

Surface sintering of skived poly(tetrafluoroethylene) membrane was carried out to improve the water permselectivity of the membrane. The surface morphologies of the modified and unmodified membranes were studied by scanning electron and atomic force microscopy. The results indicate that the surface sintering process can make the surface denser and smoother, resulting in higher water permselectivity but lower permeation rate. In addition, the va-

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por permeation performances were strongly related to the surface resintering temperature.

Key Words: Skived poly(tetrafluoroethylene); Surface resintering; SEM; AFM; Surface roughness; Pervaporation

INTRODUCTION

Pervaporation (1) and vapor permeation (2–4) have been studied extensively during past decades because of their economic advantages and abilities to separate azeotropic, heat sensitive, and isomeric mixtures (5–9). Numerous polymers that have good water permselectivity, such as poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA), have been used to fabricate pervaporation membranes (10–11). However, the applications of these membranes were sometimes limited due to their lack of chemical or thermal stability. Poly(tetrafluroethylene) (PTFE) is known for its chemical and thermal stability and high hydrophobicity (12). The high chemical and thermal stability of PTFE makes it a very attractive polymer for fabricating pervaporation membranes. However, this hydrophobicity may mean that its water permselectivity might not be high enough for practical application. Although hydrophilic polymer membranes are usually preferred for the water selective pervaporation (or vapor permeation) process, hydrophobic polymer membranes have been reported to have high water permselectivity (13). One of our major aims in the present work was to determine if PTFE membranes could have suitable water permselectivity and permeation rate for pervaporation (or vapor permeation) processes.

Porous PTFE membranes can be used as ethanol-selective membranes for lipophilic pervaporation processes (14). The porous PTFE membranes are usually prepared by the stretching method. The pore sizes of the membranes prepared by the stretching method are 0.1–3 μm. Because ethanol has higher vapor pressure and higher affinity for PTFE than water does, the stretched PTFE membranes can still have selectivity with pore sizes much larger than the molecular sizes of ethanol and water. However, when being applied to the water-selective (dehydration) pervaporation process, the pore size is too large to accommodate water permselectivity. Therefore, in the present work, the skived PTFE (s-PTFE) membrane was used. The s-PTFE membranes were fabricated by slicing a PTFE rod, made from powder consolidation by sintering under high pressures, into thin films. Compared to the stretched PTFE membranes, the s-PTFE membranes are much more dense with low water permselectivity. Further modification is required to improve the selectivity. Sintering polymeric membranes above the glass transition temperature could make the membranes denser so that the selectivity could be improved. In the present work, the sintering process was used to improve the

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water permselectivity. Although sintering can improve the selectivity, the permeation rate declines because the membrane is denser. In the normal sintering process, the whole membrane is subject to high temperature; hence, sintering occurs throughout the membrane. If sintering only occurs near the surface but not throughout the membrane, the permeation rate decline would be improved. Therefore, in the present work, the surface sintering process was used instead of the bulk sintering process. The surface sintering was carried out by contacting the membrane surface with a heat source for a short time. Because only the membrane surface contacts the heat source, only the region near surface was subject to high temperature. Although the heat transfer across the membrane could raise the temperature in the bulk region, the temperature should still be much lower inside the membrane than that in the surface region. Therefore, sintering is more complete near the surface region than in the bulk region. Because the PTFE powders had been sintered once to make the PTFE rod for skiving, we call the subsequent subjection of the membrane to surface heating "surface resintering."

In this work, a series of surface resintered s-PTFE membranes were prepared. The effect of heat treatments on the surface morphology was studied by scanning electron microscopy (SEM), atomic force microscopy (AFM), and contact angle measurements. In addition, vapor permeation of the water/ethanol solution was performed to investigate the water permselectivity and permeation rate of the surface resintered s-PTFE membranes. The effects of heat treatment and feed composition on the vapor permeation performance of the prepared membranes were also investigated.

EXPERIMENTAL

Materials

The PTFE molding powders (Teflon 7A) with an average molecular weight (M_n) of approximately 8×10^6–10×10^6 were provided by DuPont (Wilmington, DE). S-PTFE membranes with a thickness of approximately 100 μm were purchased from Sam Yang Co Ltd, Taiwan. The surface resintering process was performed by contacting the membrane surface with a heat source for about 2 minutes. The temperature of the heat source, denoted by resintering temperature, was adjusted from 260°C to 360°C.

Differential Scanning Calorimetry Characterization

Differential scanning calorimetry (DSC) analysis was performed on a Perkin-Elmer DSC-7 differential scanning calorimeter in flowing nitrogen (60 cm^3/min) at a heating rate of 20°C/min.

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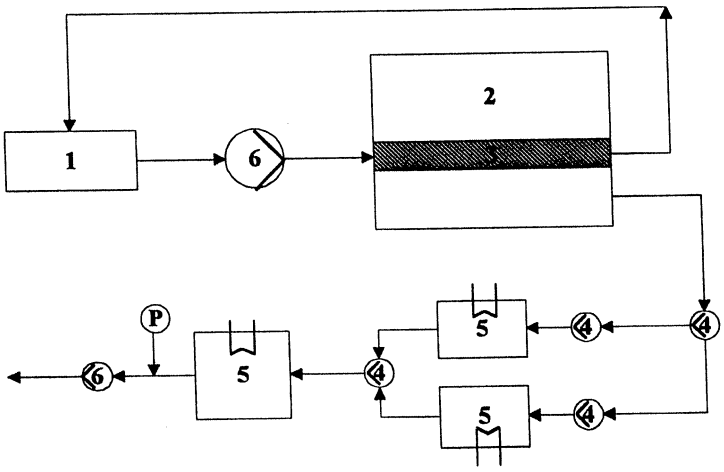
Vapor Permeation Measurement

A traditional vapor permeation process (15) was used. The vapor permeation experiment was carried out with the same apparatus as with pervaporation, except that for the vapor permeation experiment, the feed solution was not in contact with the membrane. The setup is depicted in Fig. 1. The feed solution was va-



1:	Feed.	2:	Permeation cell.
3:	Membrane.	4:	Teflon cock.
5:	Cooled trap.	6:	Circulation pump.
7:	Vacuum gauge.		

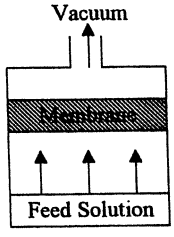


Figure 1. Vapor permeation apparatus.

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porized first and then permeated through the membrane. The effective area was 10.2 cm^2. The permeation rate was determined by measuring the weight of the permeate. The compositions of the feed solution and the permeate were measured by gas chromatography (G.C. China Chromatography 8700 T).

The separation factor is defined as

$$\alpha_{A/B} = \frac{Y_A/Y_B}{X_A/X_B}$$

where X_A and X_B are the weight fractions of water and alcohol in the feed vapor (A being the species with higher permeation values), and Y_A and Y_B are the weight fractions of water and alcohol in the permeate.

Contact Angle Measurements

The contact angle of water was measured with a CA-D type face-contact angle meter (Kyowa Interface Science Co Ltd). The dimensions of the droplets were measured 10 seconds after placing the droplets on the knob. The droplets must be small enough so that their shapes are approximately spherical. The contact angle was then calculated by the following equation:

$$\text{Contact angle} = 2\tan^{-1}(h/r)$$

where h is the height of the spherical segment and r is the radius of the spherical segment.

SEM and AFM Analysis

The membrane surface structures were examined through an Hitachi (Model S570) scanning electron microscope and an atomic force microscope (Digital Instrument, DI 5000).

Roughness

AFM analysis gives the following parameters for the samples: average plane roughness (R_a), square mean-plane roughness (R_{ms}), and 10-point mean-plane roughness (R_z). The specific plane of AFM is shown schematically in Fig. 2. The area of the specific plane is represented by Q. The height of the plane is represented by $Z = f(x,y)$. The mean height of the specific plane is represented by Z_0.

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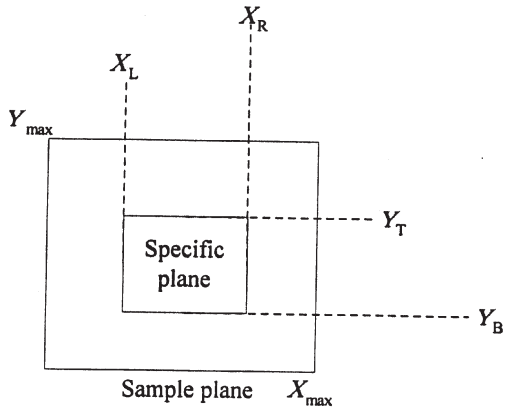

Figure 2. Specific plane of atomic force microscopy.

The definitions of Z_0, R_a, and R_{ms} are as follows (16):

$$Z_0 = \frac{1}{Q}\int_{Y_T}^{Y_B}\int_{X_L}^{X_R} f(x, y)dxdy$$

$$R_a = \frac{1}{Q}\int_{Y_T}^{Y_B}\int_{X_L}^{X_R} \left| f(x, y) - Z_0 \right| dxdy$$

$$R_{ms} = \left[\frac{1}{Q}\int_{Y_T}^{Y_B}\int_{X_L}^{X_R} \{f(x, y) - Z_0\}^2\, dxdy\right]^{1/2}$$

RESULTS AND DISCUSSION

Effect of Surface Resintering Temperature on the Surface Morphology of the S-PTFE Membrane

SEM was used to investigate the effect of surface resintering temperature on the membrane morphologies. Vapor permeation performances of membranes are strongly related to their structure. Therefore, examining the change of membrane morphology before and after heat treatment was helpful for understanding the effect of surface resintering on separation performance. An SEM micrograph of the membrane cross-sectional structure is shown in Fig. 3. The s-PTFE membrane is quite dense, which is different from the stretched PTFE membrane. The surface morphology of the untreated s-PTFE membrane surface (A) and the resintered membranes (B, C, D) are shown in Fig. 4. The membrane becomes denser with increasing surface resintering temperature.

Figure 3. Scanning electron micrographs of the cross-sectional structure of the s-PTFE membrane.

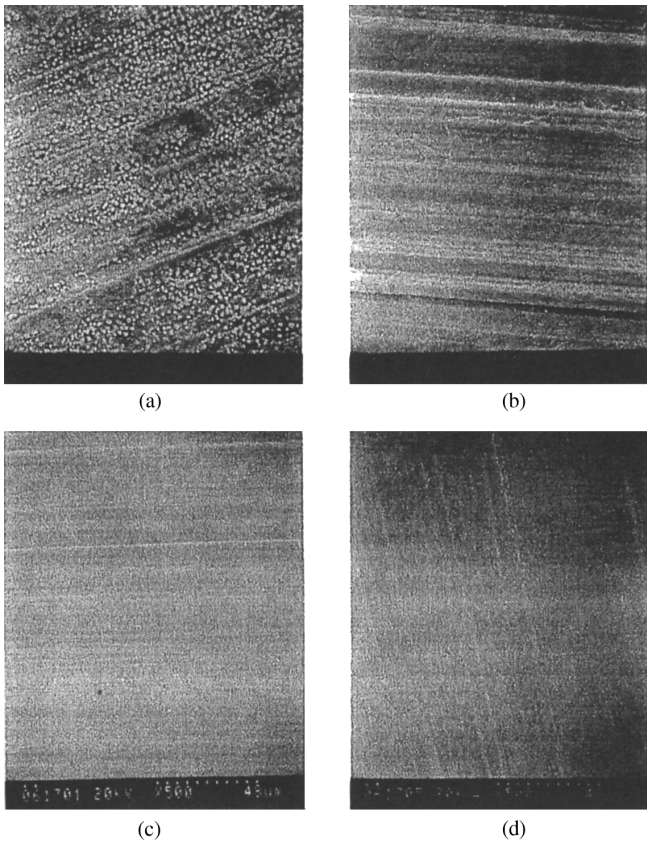

Figure 4. Scanning electron micrographs of the s-PTFE membrane surface: (a) unmodified; (b) 260°C resintered; (c) 300°C resintered; (d) 360°C resintered.

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Table 1. Surface Roughness of the Resintered s-PTFE Membrane Surface by AFM

Surface Resintering Temperature (°C)	R_a (nm)	R_{ms} (nm)	R_z (nm)	H_d (nm)
260	325.5	402.3	2.3	949.5
300	159.9	193.6	1.3	741.7
360	135.8	167.7	1.1	586.4

R_a = average plane roughness; R_{ms} = square mean roughness; R_z = 10-point mean-plane roughness; H_d = Hist depth

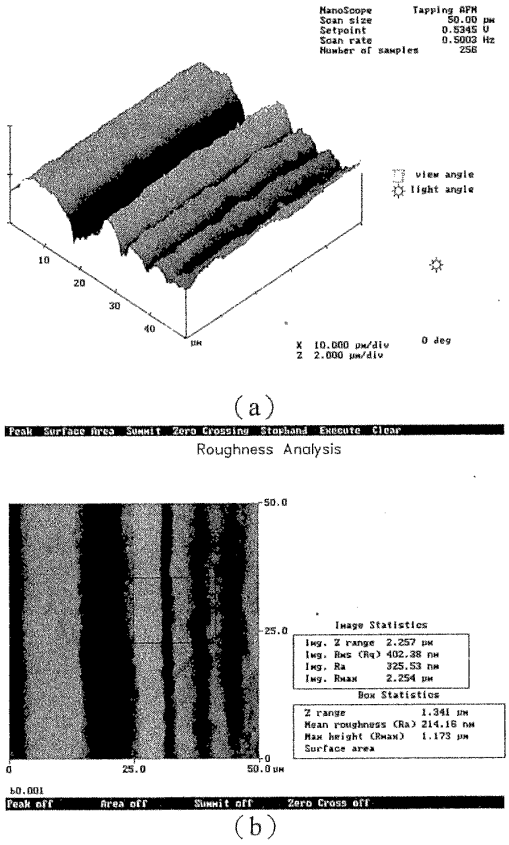

Figure 5. Atomic force microscopy images of the s-PTFE membrane surface (260°C resintered): (a) 3-dimensional image; (b) 2-dimensional image.

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To further evaluate the effect of heat treatment on the surface structure of the s-PTFE membranes, we used AFM to examine the membrane surface structure. The values of surface roughness and the AFM photographs are shown in Table 1 and Figs. 5–7, respectively. The membrane surface structure varies with the surface resintering temperature. The results indicate that the surface roughness decreases when the surface resintering temperature increases.

According to the SEM and AFM analyses, when the surface resintering temperature increased, the membrane surface became denser and smoother (roughness decreased). Therefore, we expected the vapor permeation performance to be influenced by the resintering temperature.

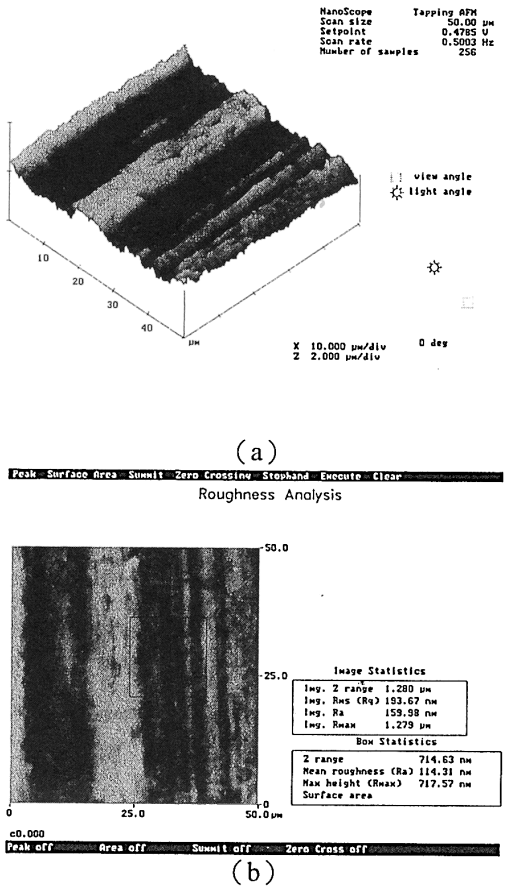

Figure 6. Atomic force microscopy images of the s-PTFE membrane surface (300°C resintered): (a) 3-dimensional image; (b) 2-dimensional image.

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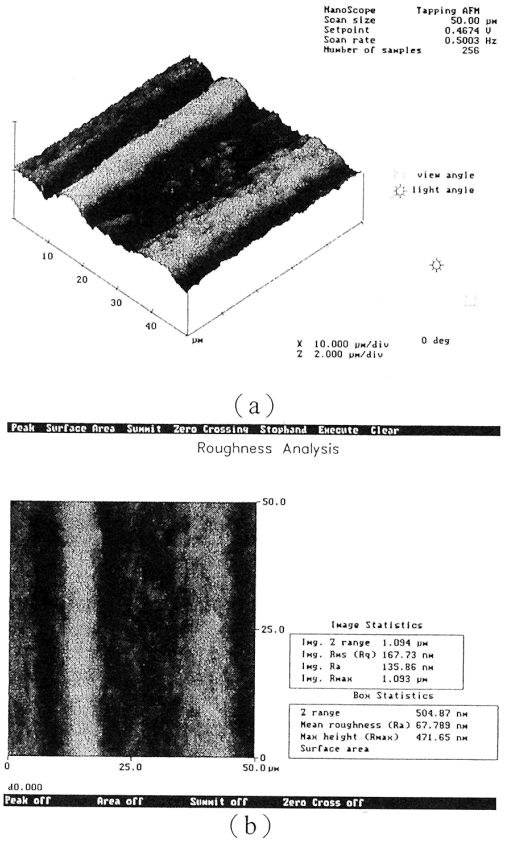

Figure 7. AFM images of the s-PTFE membrane surface (360°C resintered): (a) 3-dimensional image; (b) 2-dimensional image.

Effect of Surface Resintering Temperature on the Water Vapor Permeation Performance

The water vapor permeation rates through the s-PTFE membranes were measured and the results are shown in Table 2. The vapor permeation rate decreased with increasing surface resintering temperature. The decrease in permeation rate can be explained by the fact that the membrane surface becomes denser and smoother when the surface resintering temperature increases. The contact angle experiment was also performed to estimate the surface variation of the resintered s-PTFE membranes. The results (Table 3) show that the contact angle of the unmodified s-PTFE membrane is 114 (deg), which is higher than those of the

Table 2. Water Vapor Permeation Rates Through the s-PTFE Membrane

Surface Resintering Temperature (°C)	Permeation Rate ($g/m^2 \cdot h$)
unmodified	770
260	629
300	584
360	339

resintered s-PTFE membranes. This observation confirms that the surface roughness decreases and the membrane denseness increases as the surface resintering temperature increases.

According to the experimental results, the membrane surface property correlates with the water permeation rate. In theory, the bulk structure can also have influence on the permeation results. However, we believe that the surface structure is more important than the bulk structure for explaining the effect of sintering temperature on the water permeation rate. Because the sintering process was performed by contacting the membrane surface with a heat source for a short time, only the region near the surface was subject to high temperature. Although the heat transfer across the membrane could raise the temperature in the bulk region, the temperature in the bulk region should still be much lower than that in the surface region. Therefore, sintering is more complete near the surface than in the bulk region, and the structure near the surface should be denser than that in the bulk region. Hence, the membrane permeation property is basically determined by the surface structure (the densest region). Besides SEM and AFM, DSC was also used to characterize the membrane property. The DSC curves are shown in Fig. 8. The temperature of the crystal fusion (the peak temperature) increased as the surface resintering temperature increased, and the area under the peaks increased with increasing resintering temperature. The area represents the heat required to fuse the

Table 3. Effect of Surface Resintering Temperature on Water Contact Angle

Surface Resintering Temperature (°C)	Water Contact Angle (deg)
unmodified	114
260	112
300	111
360	105

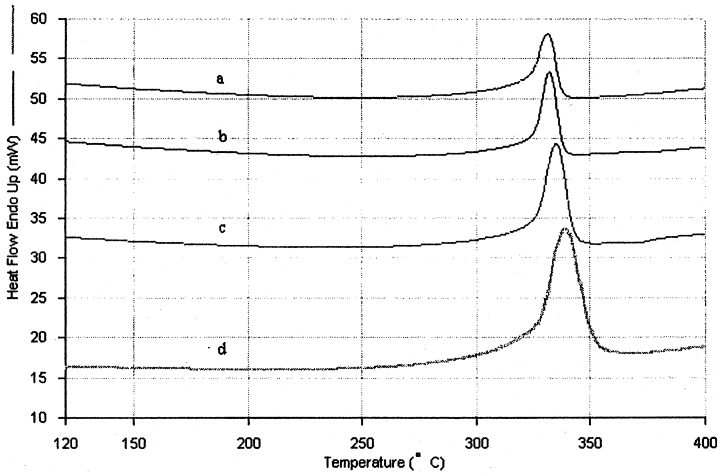

Figure 8. Differential scanning calorimetry curves of the s-PTFE membrane: (a) unmodified; (b) 260°C resintered; (c) 300°C resintered; (d) 360°C resintered.

crystals in the membrane, and the results are listed in Table 4. The results presented in Fig. 8 and Table 4 can be interpreted as the degree that crystallization increases with increasing sintering temperature. The increase in the degree of crystallization would usually result in decreased permeation rate. Therefore, the decrease in water permeation shown in Table 2 could be partly due to the increase in the degree of crystallization.

Effect of Feed Composition on the Vapor Permeation Performance

The results indicate that raising the surface resintering temperature makes the membrane surface denser and smoother. The denser surface structure results

Table 4. Effect of Surface Resintering Temperature on the Heat Required to Fuse the Crystals

Surface Resintering Temperature (°C)	Heat Required to Fuse the Crystals (J/g)
unmodified	19.8
260	25.9
300	27.4
360	31.8

in a decrease in the water permeation rate. Usually, the denser structure allows for higher water permselectivity. Vapor permeation experiments in which aqueous ethanol solution (10 wt% of ethanol) was used through the s-PTFE membranes were performed. The permeation rate and the water selectivity of the untreated s-PTFE (without sintering) were 800g/m^2·h and 1.4, respectively. The permeation flux is high but the permselectivity is very low. When the s-PTFE membrane surface was resintered at 360°C, the permeation rate decreased to 358g/m^2·h and the water selectivity increased to 11. As expected, the surface sintering process decreased the permeation rate but increased the selectivity. The selectivity of the untreated s-PTFE membrane is too low for commercial application. After the surface resintering, the selectivity can be greatly improved. The feed composition is a very important operation variable for the pervaporation or vapor permeation process. Therefore, the effect of feed composition on the vapor permeation through the s-PTFE membrane is subsequently discussed. Because the s-PTFE membrane sintered at 360°C possesses the highest water selectivity, we chose to use it for our investigation into the effect of feed composition. The effect of feed composition on the vapor permeation performances can be observed from the data shown in Table 5. The permeation rate and separation factor increased as the feed ethanol concentration increased. The result can be explained by the plasticizing effect of ethanol. Generally, the hydrophobic membrane has a stronger interaction with alcohol than with water. When the ethanol concentration in the feed is higher, the amorphous region of the membrane is swollen to a larger degree. Hence, the polymer chain becomes more flexible; thus, the energy required for the permeant to diffuse through the membrane decreases, which results in higher permeation rate.

The higher affinity s-PTFE membrane for ethanol can be further illustrated by the differences in solubility parameters. The solubility parameter difference between alcohol and PTFE membrane ($\delta_{PTFE} - \delta_{EtOH} = 7.3$ (cal/cm^3)$^{1/2}$) was

Table 5. Performances of 360°C Surface Resintered s-PTFE Membranes for Vapor Permeation of Aqueous Ethanol Mixtures at 25°C

Feed Ethanol Concentration (wt %)	Permeation Rate (g/m^2·h)	Separation Factor
90	669	N/A
70	429	240
50	418	153
30	386	20
10	358	11

N/A. Data not applicable; 100 wt% water in the permeate.

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lower than that between water and PTFE membrane ($\delta_{PTFE} - \delta_{H2O} = 16.1$ $(cal/cm^3)^{1/2}$). That is, ethanol has a stronger interaction with PTFE than does water. However, water molecules can diffuse faster through the resintered s-PTFE membrane because it has smaller molar volume than does ethanol. Moreover, when the membrane is swollen by ethanol, water can be sorbed into the membrane more easily because of the strong interaction between water and ethanol. Hence, excessive swelling due to the nonselective solvent (ethanol) causes a selective solvent (H_2O) to permeate through the membrane and enhance the separation selectivity, resulting in the increase of the separation factor with increasing feed ethanol concentration.

CONCLUSION

The vapor permeation experiments show that the surface resintering temperature significantly affect the vapor permeation performance of the s-PTFE membranes. The membrane surface morphologies of the resintered and unmodified membranes are different and are responsible for the differences in the performance of vapor permeation. The surface resintering process can make the membrane surface denser and smoother, resulting in an increase in the water permselectivity but a decrease in the permeation rate. The effect of surface resintering can be enhanced by elevating the surface resintering temperature. Both the permeation rate and water selectivity of the PTFE membrane resintered at 360°C increased with increased ethanol concentration in the feed.

REFERENCES

1. Kober, P.A. Pervaporation, Perstillation and Percrystallization. J. Am. Chem. Soc. **1917,** *39,* 944.
2. Uragami, T.; Saito, M.; Takigawa, K. Studies on Syntheses and Permeabilities of Special Polymer Membranes 69. Comparison of Permeation and Separation Characteristics for Aqueous Alcoholic Solutions by Pervaporation and New Evapomeation Methods Through Chitosan Membranes. Makromol. Chem., Rapid Commun. **1988,** *9* (5), 361.
3. Uragami, T.; Saito, M. Studies on Syntheses and Permeabilities of Special Polymer Membranes 68. Analysis of Permeation and Separation Characteristic and New Technique for Separation of Aqueous Alcoholic Solutions through Alginic Acid Membranes. Sep. Sci. Technol. **1989,** *24* (7 & 8), 541.
4. Okamoto, K.; Tanihara, N.; Watanabe, H.; Tanaka, K.; Kita, H.; Nakamura, A.; Kusuki, Y.; Nakagawa, K. Vapor Permeation and Pervaporation Separation of Water Ethanol Mixtures through Polymic Membranes. J. Membr. Sci. **1992,** 68 (1–2), 53.

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5. Xu, Y.F.; Huang, R.Y.M. Pervaporation Separation of Ethanol Water Mixtures Using Ionically Crosslinked Blended Polyacrylic Acid (PAA)-Nylon-6 Membranes. J. Appl. Polym. Sci. **1988,** *36,* 1121.
6. Wessling, M.; Werner, U.; Hwang, S.T.; Yeom, C.K.; Huang, R.Y.M. Modeling of the Pervaporation Separation of Pervaporation of Aromatic C8-Isomers. J. Membr. Sci. **1991,** *57,* 257.
7. Yeom, C.K.; Huang, R.Y.M. Modeling of the Pervaporation Separation of Ethanol Water Mixtures Through Cross-Linked Poly(Vinyl Alcohol) Membrane. J. Membr. Sci. **1992,** *67,* 39.
8. Aptel, P.; Challard, N.; Cuny, J.; Neel, J. Application of the Pervaporation Process to Separate Azeotropic Mixtures. J. Membr. Sci. **1976,** *1,* 271.
9. Rhim, J.W.; Sohn, M.Y.; Joo, H.J.; Lee, K.H. Pervaporation Separation of Binary Organic-Aqueous Liquid-Mixtures Using Cross-Linking PVA Membranes. 1. Characterization of the Reaction Between PVA and PAA. J. Appl. Polym. Sci. **1993,** *50,* 679.
10. Huang, R.Y.M.; Yeom, C.K. Pervaporation Separation of Aqueous Mixtures Using Cross-Linked Poly(Vinyl Alcohol) (PVA). 2. Permeation of Ethanol Water Mixtures. J. Membr. Sci. **1990,** *51,* 273.
11. Yamasaki, A.; Iwatsubo, T.; Masuoka; Mizoguchi, K. Pervaporation of Ethanol/Water Through a Poly(Vinyl Alcohol)/Ciclodextrin (PVA/CD) Membrane. J. Membr. Sci. **1994,** *89* (1–2), 53.
12. Chen, J.R.; Wakida, T. Studies on the Surface Free-Energy and Surface-Structure of PTFE Film Treated with Low-Temperature Plasma. J. Appl. Polym. Sci. **1997,** *63,* 1733.
13. Mulder, M. Basic Principles of Membrane Technology; Kluwer: Dordrecht/Boston/London, 1991.
14. Aptel, P.; Cuny, J.; Jozefowicz, J.; Morel, G.; Neel, J. Liquid Transport Through Membranes Prepared by Grafting of Polar Monomers onto Poly(Tetrafluoroethylene) Films. 1. Some Fractionations of Liquid Mixtures by Pervaporation. J. Appl. Polym. Sci. **1972,** *16,* 1061.
15. Lee, K.R.; Chen, R.Y.; Lai, J.Y. Plasma Deposition of Vinyl Acetate onto Nylon 4 Membrane for Pervaporation and Evapomeation Separation of Aqueous Alcohol Mixtures. J. Membr. Sci. **1992,** *75,* 171.
16. Hirose, M.; Ito, H.; Kamiyama, Y. Effect of Skin Layer Surface-Structure on the Flux of RO Membrane. J. Membr. Sci. **1996,** *121,* 209.

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