

Pervaporation Separation of a Water–Ethanol Mixture by PSF–PEG Membrane

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ABSTRACT: For dehydrating a water–ethanol mixture by pervaporation, a polysulfone–And poly(ethylene glycol)–(PSF–PEG) membrane was prepared. The separation performance of water and ethanol was found to strongly depend on the diffusion selectivity of permeates. On the other hand, the solubility selectivity of water to ethanol showed only minor change with an increasing PEG composition of the PSF–PEG membrane. This study found that the PEG content in a PSF–PEG membrane showed mobility enhancement of pervaporation properties and that the diffusion difference of permeates increased with increasing PEG content. The effect

of PEG content on separation performance was a result of the improvement of the permeate diffusion properties of the PSF/PEG membrane. The diffusion difference in the membrane, not the solubility of water–ethanol in the membrane, was the dominant factor for the separation. Suitable PEG content in PSF/PEG membranes can prepare a high-performance pervaporation membrane. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2158–2164, 2003

Key words: polysulfone; poly(ethylene glycol); membrane; pervaporation

INTRODUCTION

Many polymer modification technologies^{1–5} have been applied to improving the separation performance of pervaporation membranes. Previous works have considered the balance of hydrophilic and hydrophobic moieties in glassy polymers to prepare a high-permeate-selectivity membrane. The main focus of the study of separation of water-permselective membranes has been separation based on solubility selectivity, rather than on mobility selectivity. High-water-permselective membranes can be achieved by increasing the sorption ratio of water to ethanol or the diffusion ratio of water to ethanol. If good solubility selectivity is expected, the membranes should be modified to enhance their solubility to water rather than ethanol. Generally, the introduction of a hydrophilic moiety into a glassy polymer can improve water solubility, but it is usually accompanied by excessive swelling due to hydration from the water. Therefore, the ratio of hydrophilic and hydrophobic moieties in a mem-

brane is an important factor in preparing a high-performance membrane.⁶

The solution–diffusion mechanism has been applied to describe the transport behavior of permeates in pervaporation membranes. The membrane separation performance was determined by the competition between solution and diffusion of permeates when they were transported through the membrane. Therefore, the modification technology for commercial polymer membranes has improved membrane performance by considering the balance of hydrophilic and hydrophobic moieties in pervaporation membranes. In many cases, the resistance to diffusion of the downstream layer and the sorption of the upstream layer has determined the high-permselectivity membrane.⁷ However, for most glassy polymer membranes, permeability is determined mainly by the contribution of diffusion.⁸

Previous studies have shown that glassy polymer membranes such as polyacrylonitrile (PAN), polysulfone (PSF), and polyimide (PI) have good potential to separate water from a water–ethanol mixture.^{9–11} In those works it was found that a good separation factor could be achieved by dehydration from various solvents in the pervaporation process. However, permeation flux was too low, limiting its commercial applicability in the pervaporation process. Many investigators^{12–15} have reported that improvement of permeation flux could be achieved by increasing polymer chain mobility through blending or grafting hy-

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drophilic polymers in the pervaporation process. In those works low-glass-transition temperature polymers were used to modify the glassy polymers and the separation performance, which was significantly enhanced in the pervaporation process.

The purpose of this study was to prepare polysulfone-poly(ethylene glycol) membranes to be able to separate water from a water-ethanol mixture. To understand the effect of the enhancement of polymer chain mobility on pervaporation performance of polysulfone membranes, we measured the swelling properties of various amounts of poly(ethylene glycol) in polysulfone membranes and analyzed the sorption amount in the PSF-PEG membranes. The permeation rate and degree of swelling were measured independently. Glass-transition temperature (T_g) measurement analyses were used to characterize the change in morphology of the modified membranes. The relationship between the microstructure change of PSF-PEG membranes and pervaporation properties was also investigated in this study. The effect of feed composition was studied by measuring the pervaporation properties.

EXPERIMENTAL

Materials

Udel[®] polysulfone P-3500 was obtained from Amoco Performance Products. Merck Chemical Co. (Taiwan) supplied poly(ethylene glycol) 200, ethanol, and chloroform.

Membrane preparation

The polysulfone-poly(ethylene glycol) membranes were prepared according to the blend method by adding various amounts of poly(ethylene glycol) 200 and casting solution in chloroform. The casting solution was cast onto a glass plate to a predetermined thickness of 350 μm using a Gardner knife. The membrane was dried at room temperature for 30 min, then peeled off and immersed in distilled water for 12 h, and finally put into a vacuum oven for 24 h before sorption and pervaporation measurements were done.

Pervaporation experiment

A traditional pervaporation process was used.¹⁶ The pervaporation apparatus is shown in Figure 1. In pervaporation the feed solution, which was 90 wt % ethanol, was in direct contact with the membrane and was kept at 25°C. The effective membrane area was 10.2 cm^2 . The downstream pressure was maintained at about 5–8 torr. The permeation rate was determined by measuring the weight of the permeate. The composition of the feed solution permeate and of the

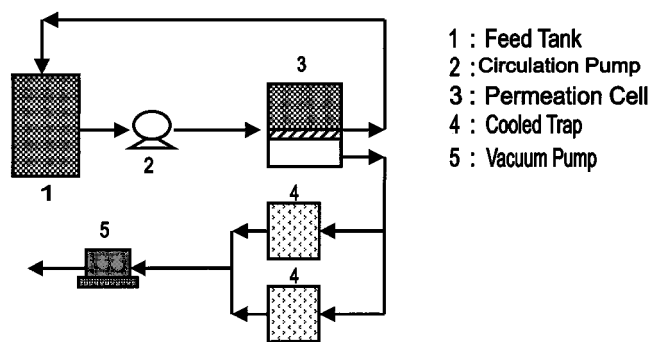


Figure 1 Schematic diagram of the pervaporation apparatus.

solution adsorbed in the membranes was measured by gas chromatography (GC; China Chromatography). The separation factor, $\alpha_{A/B}$, was calculated by the formula

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

where X_A , X_B , and Y_A , Y_B are the weight fractions of A and B in the feed and permeate, respectively (with A the more permeative species).

Sorption measurements

The membranes were immersed in the ethanol-water mixture for 24 h at 25°C. They were subsequently blotted between tissue paper to remove the excess solvent and placed in the left half of a twin-tube setup. The system was evacuated while the tube was heated with hot water for 30 min and the right tube was cooled in liquid nitrogen. The composition of the condensed liquid in the right tube was determined by GC. The separation factor of sorption was calculated by

$$\alpha_{\text{sorp}} = (Y_w/Y_e)/(X_w/X_e)$$

where X_e , X_w , and Y_e , Y_w are the weight fractions of ethanol and water in the feed and membranes, respectively.

RESULTS AND DISCUSSION

Effect of PEG additive on polymer chain flexibility

To improve permeate mobility, low-molecular-weight poly(ethylene glycol) was added into the polysulfone membranes. To explain the effect of polymer chain flexibility on the pervaporation performance of PEG-additive membranes, the effect of PEG content on the glass-transition temperature (T_g) of PSF-PEG membranes is shown as in Figure 2. It can be seen that the glass-transition temperature of PEG-additive membranes significantly decreased with increasing PEG

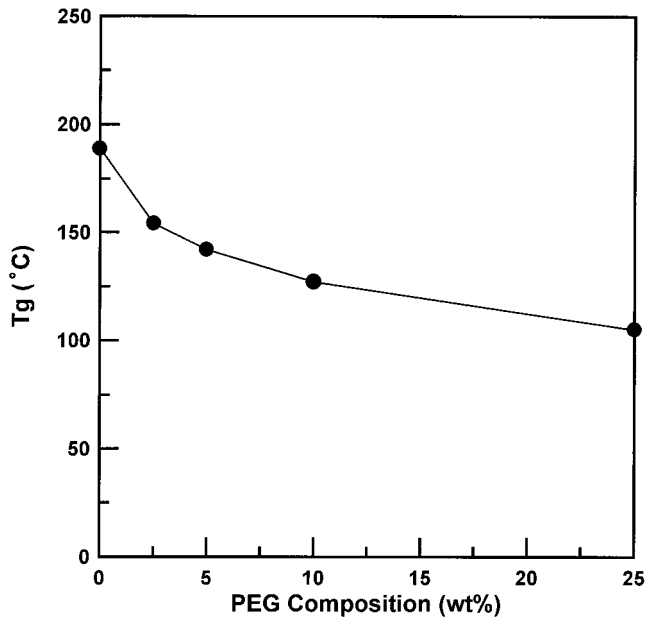


Figure 2 Effect of PEG content on glass-transition temperature of PSF-PEG membranes.

content, indicating that a more flexible polymer chain is expected for the PSF-PEG membranes. Generally, it is expected that a flexible polymer chain for a PSF-PEG will lead to an increase in permeation flux and a decrease in diffusion selectivity. The relationship between polymer chain flexibility and permeation properties of the membranes is discussed in the following section.

Figure 3 shows the effect of PEG additive on the degree of swelling of PSF-PEG membranes for a 90 wt

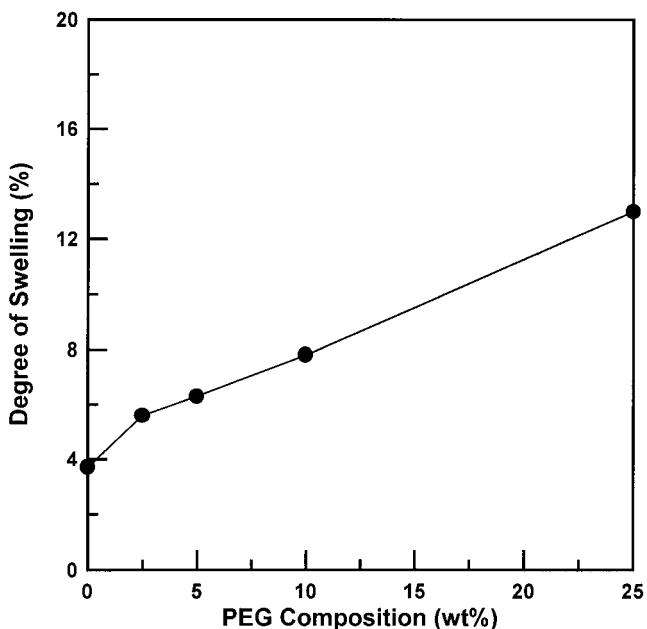


Figure 3 Effect of PEG composition on the degree of swelling of PSF-PEG membranes in 90 wt % ethanol solution.

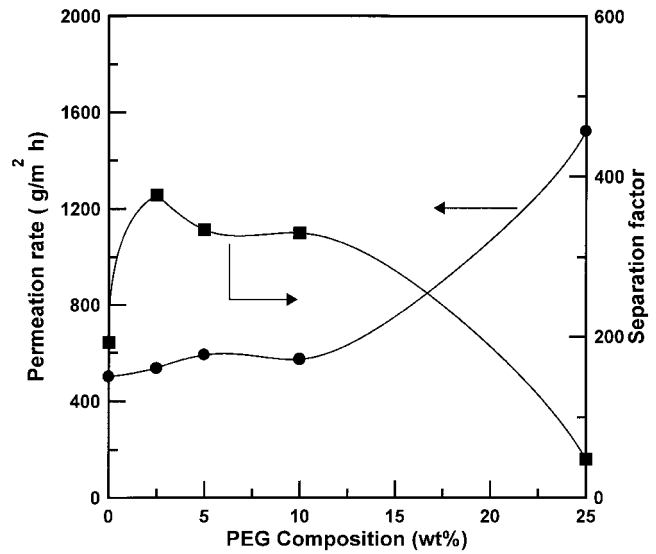


Figure 4 Effect of PEG composition on the pervaporation performance of PSF-PEG membranes for 90 wt % ethanol solution in the feed at 25°C.

% ethanol solution. It can be seen that the degree of swelling showed a strong dependence on the amount of PEG content in the composite membranes. The degree of swelling increased with PEG content in the PSF-PEG membranes. It was indicated that the flexibility of the polymer chain in a composite membrane would be increased by the plasticization effect of permeate in 90 wt % ethanol solution. Based on the results for the T_g and swelling properties, it can be concluded that polymer chain flexibility would be improved by added PEG into a membrane no matter if the composite membrane was dry or immersed in a 90 wt % ethanol solution.

Effect of PEG content on separation performance of pervaporation

Figure 4 shows the effect of the polyethylene content in the PSF-PEG membranes on separation performance of pervaporation. It can be seen that the permeation flux increased with increasing PEG content in the composite membranes and the separation factor increased up to 2.5 wt % of PEG content and then decreased with increasing PEG composition in the composite membranes. The results indicate that the permeation rate was significantly dependent on the PEG content in the composite membranes. This result was as expected from the T_g and degree-of-swelling measurements. The low molecular weight of the PEG additive enhanced the polymer chain mobility of the PSF-PEG membranes. As for the permeation measurements, the permeation rate of PSF-PEG membranes showed strong dependence on the PEG content in the membranes. Based on the concept of the solution-diffusion model, the permeates dissolve into the mem-

brane surface and then diffuse through it. Finally, the permeates vaporize and leave the other side of membrane. In general, a high-solubility membrane leads to high diffusivity.⁶ It was proposed that the barrier to mass transfer in the membranes was dominated by the diffusion step during pervaporation. Therefore, increased diffusion rate of permeates was sought because it contributes to an increase in the permeation rate of pervaporation membranes. The diffusion behavior of permeates in membranes was the key point in determining the permeation rate. However, the separation factor did not show the same dependence on PEG composition. The separation factor first increased and then decreased on increasing PEG content in the membranes. The loss of the separation factor may have occurred because of the increase in free volume of the blend membranes during permeate transport through the composition membranes.⁷ Although polymer chain mobility increased with an increase in the plasticization effect, the rigid polysulfone membranes were swelling easily in the feed solution from the addition of low-molecular-weight PEG in the matrix. The pervaporation separation index (PSI) is the product of the total permeation rate and separation factor, and it is a good index for determining the performance of a pervaporation membrane. Figure 5 shows the relationship of the PSI of PSF-PEG membranes with PEG content. It can be seen that the PSI value increased with increased PEG content up to 5 wt % and then decreased. Thus, it is proposed that a higher PEG content leads to a highly flexible polymer chain of PSF-PEG membrane, and therefore the PSI value decreased with increasing PEG content on the mem-

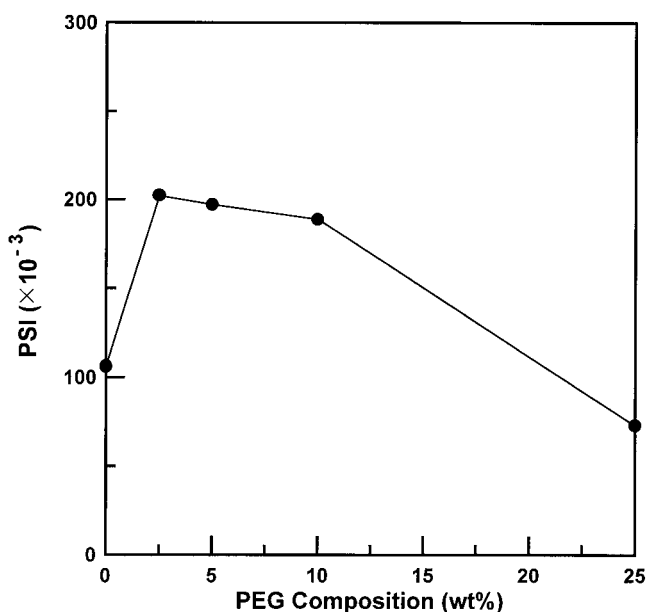


Figure 5 Effect of PEG composition on PSI value of PSF-PEG membranes for 90 wt % ethanol solution in the feed at 25°C.

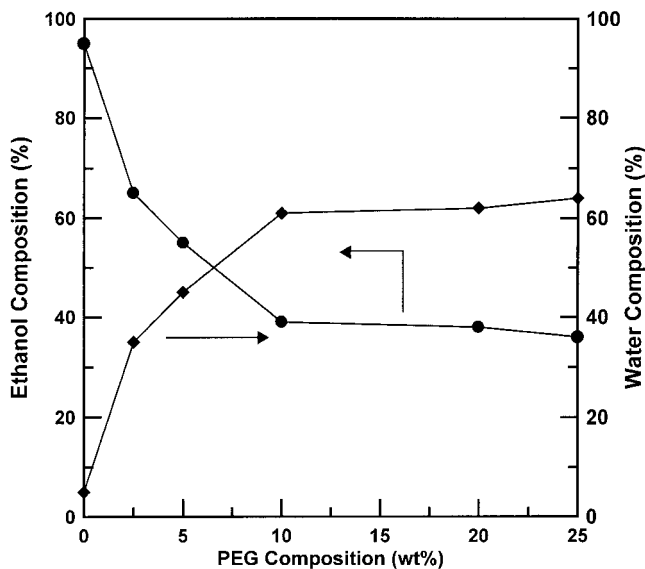


Figure 6 Effect of PEG composition on water and ethanol content in PSF-PEG membranes for 90 wt % ethanol solution in the feed at 25°C.

brane. Therefore, it can be concluded that a higher separation performance of pervaporation membranes can be obtained by adding a suitable amount of PEG on the membranes.

To clarify the factors influencing the separation performance of PSF-PEG membranes permeate content in composite membranes was measured. The effect of PEG membrane composition on ethanol and water content is shown in Figure 6. It can be seen that the water composition decreased with increasing PEG content on the membranes. The solubility selectivity was calculated by the ratio of water content to ethanol in the membrane. As shown in Figure 5, it was found that solubility decreased with increasing PEG content in the membranes. The influencing factors of separation were not only the sorption properties but also the diffusion properties of the PSF-PEG membranes. Therefore, sorption and diffusion properties should be discussed relative to the PEG content of PSF-PEG membranes. Diffusion selectivity (α^d) can be defined as the ratio of permeation selectivity (α^p) to sorption selectivity (α^s):

$$\alpha^d = \alpha^p / \alpha^s$$

Figure 7 shows the relationship between sorption selectivity and PEG content in composite membranes, and Figure 8 shows the relationship between diffusion selectivity and PEG content in composite membranes. It can be seen that the sorption selectivity decreased with increasing PEG content in the composite membranes. However, the separation factor first increased with increasing PEG content up to 5 wt %, and then decreased, indicating that the dominant influence on

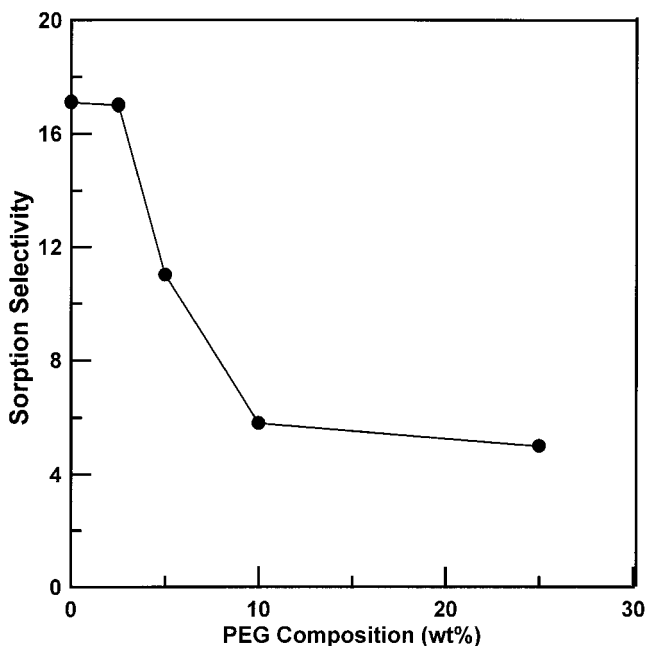


Figure 7 Effect of PEG composition on the sorption selectivity of PSF-PEG membrane for 90 wt % ethanol solution in the feed at 25°C.

the separation factor was diffusion selectivity, which decreased when PEG content increased up to 5 wt %, implying the formation of a flexible polymer chain of PEG additive membranes.

Effect of feed concentration on pervaporation properties

The effect of ethanol composition in the feed on permeation flux and separation factor of PSF-PEG mem-

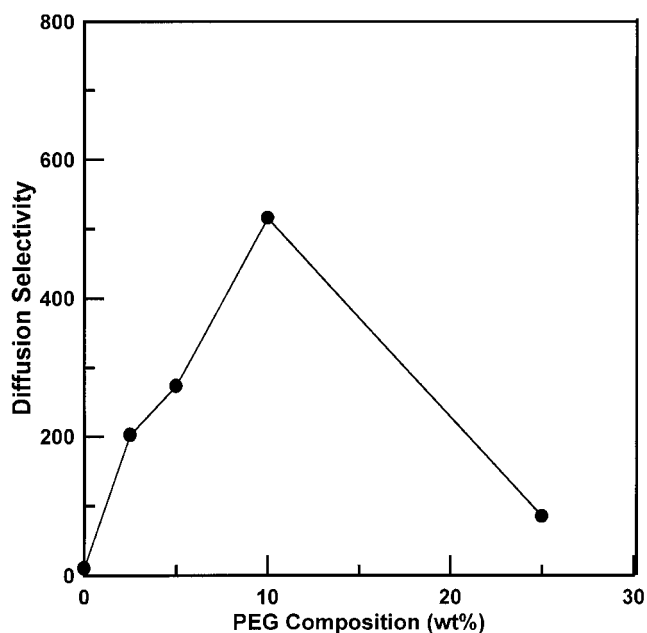


Figure 8 Effect of PEG composition on the diffusivity selectivity of PSF/PEG membrane for 90 wt % ethanol solution in the feed at 25°C.

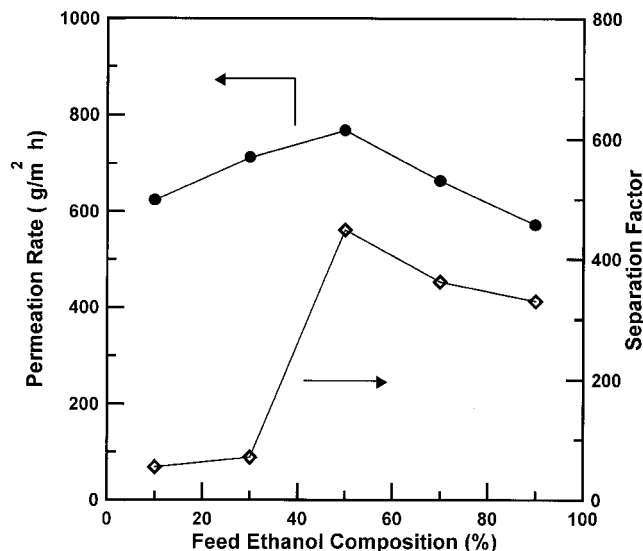


Figure 9 Effect of ethanol composition in feed on the permeation flux and separation factor of PSF-PEG membrane with 5 wt % PEG content for 90 wt % ethanol solution in the feed at 25°C.

branes with 5 wt % PEG content is shown in Figure 9. It can be seen that the permeation flux slightly increased up to 50% ethanol in the feed and then decreased with increasing ethanol composition. The permeate composition was dominated by the diffusion behavior of the permeate, which was transported through the PSF-PEG membranes. In other words, the relative ratio of the size of molecular permeates and the diffusion path of the membrane affected the permeate composition. Based on the result of Figure 9, the permeation rate and separation factor were first increased and then decreased with increasing ethanol composition. Generally, the increase in permeation rate would be accompanied with a decrease in separation factor. Thus, we measured the degree of swelling of the PSF-PEG membranes with a 5% PEG content in various concentrations of ethanol.

Figure 10 shows the effect of various concentrations of ethanol on the degree of swelling of PSF-PEG membrane with 5% PEG content. It can be seen that the degree of swelling slightly increased with increasing ethanol concentration in feed and then decreased by further increasing ethanol concentration. It was indicated that the blend membrane more easily swelled in the range of 30%–70% ethanol in the feed solution. As shown in Figure 9, the permeation behavior shows expectation behavior. However, the separation factor showed a different trend. The degree of swelling increased with increasing PEG content in PSF-PEG membranes. It was indicated that the flexibility of the polymer chain in the composite membrane would be increased by the plasticization effect of permeate in 90 wt % ethanol solution. Based on the result of the T_g and swelling properties, it can be concluded that poly-

mer chain flexibility would be improved by adding PEG into the membranes, no matter whether the composite membrane was dry or immersed in 90 wt % ethanol solution. Therefore, permeate diffusion behavior in PSF-PEG membrane may play an important role in pervaporation.

To further distinguish the transport behavior in the composite membrane, the sorption test was conducted with different ethanol compositions in the feed. Figure 11 shows the effect of ethanol concentration in the feed on the sorption selectivity and diffusivity of PSF-PEG membranes with 5 wt % PEG content, indicating that the sorption selectivity increased with increasing ethanol concentration in the feed solution. On the other hand, the diffusivity selectivity was calculated by dividing the separation factor into solubility selectivity. Both sorption solubility selectivity and diffusion selectivity increased with increasing ethanol concentration up to 50 wt % in the feed, and then sorption selectivity increased but diffusivity selectivity decreased. It is interesting to note that both sorption and diffusion selectivity increased at low ethanol concentrations in the feed. However, the selectivity of sorption behavior showed different trends from the diffusion behavior at higher ethanol concentrations. As with the above observation, these results can be explained by the sorption measurement at different ethanol concentrations in the feed. The sorption measurement showed that the sorption ethanol concentration increased with increasing ethanol concentration in the feed. It can be seen that the increase in sorption selectivity because of the water molecules was better for permeate than

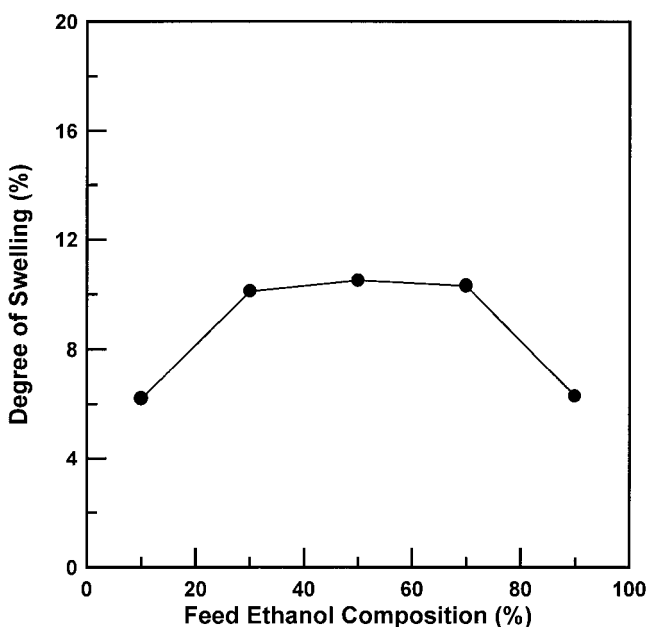


Figure 10 Effect of various ethanol compositions in feed on degree of swelling of PSF-PEG membrane with 5 wt % PEG content at 25°C.

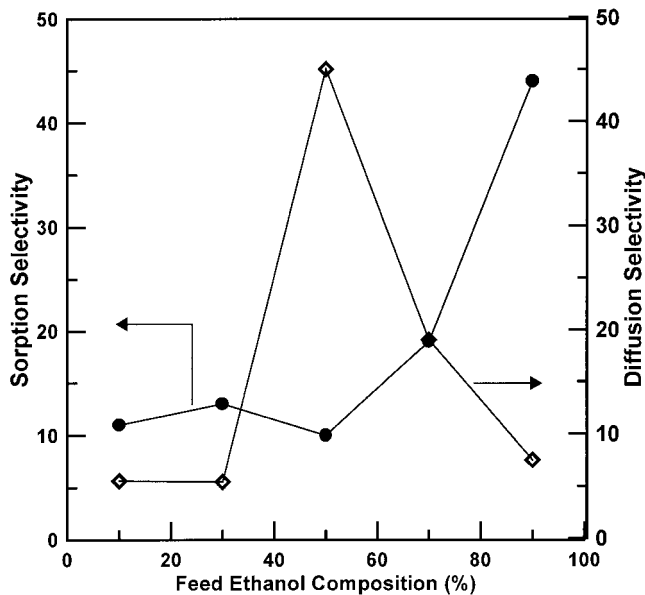


Figure 11 Effect of water concentration in the feed on sorption selectivity and diffusion selectivity of PSF/PEG membrane with 5 wt% PEG content at 25°C.

ethanol in the sorption mechanism. However, sorption selectivity decreased in the range of the higher ethanol concentration because of the polar-polar interaction between the polymer matrix and the water and ethanol molecules. The polar interaction between ethanol and the polymer matrix was stronger than that of water and membranes. Therefore, diffusion selectivity of water to ethanol increased with increasing ethanol concentration in feed. Although the ethanol concentration increased further, the polar interaction between water and ethanol was stronger than that of water and the polymer matrix. Therefore, the coupling effect appeared at higher ethanol concentrations and induced a decrease in diffusion selectivity.

Aging life of separation performance of PSF/PEG membrane

To consider the durability of the PSF-PEG composite membrane, the aging life test of separation performance of PSF-PEG membrane was done. If the wash-out effect appeared during the pervaporation process, then the micropore of PSF-PEG membrane would exist with the PEG washed out of blend membranes. If the PEG washout appeared during pervaporation, the membrane would lose its separation performance and have a poor separation factor. As is shown in Figure 12, the effect of operation time in 90% ethanol in the feed on the separation performance of the PSF-PEG membrane with 5 wt % PEG content was investigated. It can be seen that permeate concentration was nearly constant during the testing time. This could be evi-

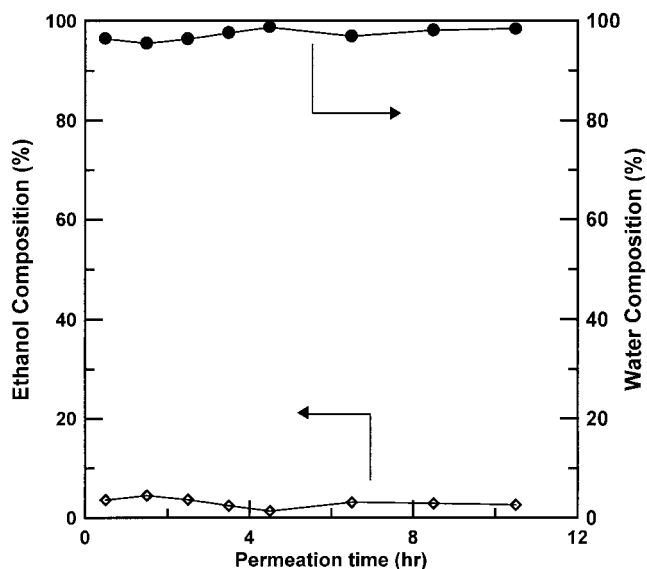


Figure 12 Effect of the aging life of PSF-PEG membrane with 5 wt % PEG on permeation composition at 25°C.

dence that the PEG in the blend membrane did not wash out during the pervaporation test.

CONCLUSION

The PEG additive successfully improved the pervaporation performance of polysulfone membrane. The T_g and swelling measurements provided evidence that polymer chain flexibility would be improved by adding PEG into membranes, whether the blend membrane was dry or immersed in 90 wt % ethanol solution. According to the permeation measurement, the

diffusion behavior of permeate on membranes was the key point determining the permeation rate. The polar-polar interaction among polymer, water, and ethanol played an important role in diffusion selectivity by adding a suitable amount of PEG in the membranes. The aging life test of PSF-PEG membrane showed that the permeate concentration was almost constant at the testing time of pervaporation.

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