

Crosslinked Blended Poly(vinyl alcohol)/*N*-Methylol Nylon-6 Membranes for the Pervaporation Separation of Ethanol–Water Mixtures

ROBERT Y. M. HUANG, JYH-JENG SHIEH

Department of Chemical Engineering, University of Waterloo, Ontario, Canada N2L 3G1

Received 6 November 1997; accepted 23 March 1998

ABSTRACT: Crosslinked blended membranes of poly(vinyl alcohol) (PVA) and *N*-methylol nylon-6 were prepared either by thermal crosslinking at 180°C or by chemical crosslinking with maleic acid. The pervaporation performance for the separation of ethanol–water mixtures of these membranes was investigated in terms of feed concentration, PVA content, and crosslinking agent content. The pervaporation performance of two differently crosslinked membranes was strongly influenced by the nature of the crosslinkage. Significant improvement in the pervaporation separation index can be achieved for chemically crosslinked membranes. From the comparison between the pervaporation and sorption tests, it is suggested that, for hydrophilic membranes, sorption properties dominate the pervaporation performance at feed solutions of higher water content, while diffusion properties govern at feed solutions of higher ethanol content. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 70: 317–327, 1998

Key words: crosslinked blend membranes; *N*-methylol nylon-6; poly(vinyl alcohol); pervaporation; sorption

INTRODUCTION

In the previous works,^{1,2} we studied the membrane performances of *N*-methylol nylon-6 membranes and its blend membranes with poly(acrylic acid). Although they possess high permeability, these membranes still do not exhibit satisfactory selectivity. Poly(vinyl alcohol) (PVA), a 1,3-diglycol polymer with a monomer weight of 44, is the primary material from which the commercial GFT membranes are fabricated and has been studied intensively in pervaporation because of its excellent film-forming, highly hydrophilic, and

good chemical-resistant properties.^{3–5} However, PVA has poor stability in aqueous solutions. Two ways to improve the stability of PVA in aqueous solutions have been suggested: crystallization and crosslinking.⁶ Although PVA membranes with crystallization pretreatment can be used in aqueous solutions at low temperatures, they are still unstable at high temperatures. Crosslinking seems to be the best method to improve the stability against water and organic solvents at high temperatures. Many crosslinking methods of PVA for membrane application can be found in the literature.^{7–13}

Maleic acid, a dicarboxylic acid, is often used as a crosslinking agent for PVA.^{14,15} For example, the GFT membrane is prepared by casting an aqueous solution of PVA and maleic acid in an ultrathin film on a microporous polyacrylonitrile supporting membrane, evaporating the solvent,

Correspondence to: R. Y. M. Huang.

Contract grant sponsors: Natural Science and Engineering Research Council of Canada; Environmental Science and Technology Alliance Canada.

Journal of Applied Polymer Science, Vol. 70, 317–327 (1998)

© 1998 John Wiley & Sons, Inc.

CCC 0021-8995/98/020317-11

and heat-curing. The resulting crosslinked PVA membranes always showed excellent permselectivity for the separation of ethanol–water mixtures.¹⁶ It has also been reported that the *N*-methoxymethyl nylons react readily with maleic acid to form the crosslinked structure.¹⁷ In this work, two crosslinking methods are utilized to prepare crosslinked blended membranes of *N*-methylol nylon-6 and PVA: (1) thermal crosslinking (heated at 180°C) and (2) chemical crosslinking (reacted with maleic acid). The pervaporation performance of the resultant membranes was investigated for the separation of ethanol–water mixtures.

EXPERIMENTAL

Materials

A *N*-methylol nylon-6 with a 33% substitution degree was prepared as described previously.¹ PVA (molecular weight 133,000; 99 mol % hydrolyzed) was obtained from Polysciences Inc. Eighty-eight percent formic acid was obtained from the BDH Chemical Co. Reagent-grade maleic acid was purchased from Fisher Scientific Co.

Membrane Preparation

PVA, 5 wt %, and *N*-methylol nylon-6, 10 wt %, both in an 88 wt % formic acid solution, were mixed together in different ratios and stirred for 12 h at room temperature to form a homogeneous solution. Two cases can be distinguished:

1. Thermally crosslinked membrane: The above homogeneous solution was cast onto a clean glass plate with the aid of a Gardner casting knife and dried at room temperature for 24 h, then vacuum-dried at room temperature for 6 h. Then, the dried blend membranes were reacted by heating at 180°C for 10 min and stored in deionized water until further use.
2. Chemically crosslinked membrane: Maleic acid was added directly to the homogeneous solution described above and continuously stirred for 6 h to dissolve the maleic acid completely. The resulting solution was then filtered to remove any solid residuals. The casting and drying procedures were the same as before. The maleic acid-containing blend membranes were heated at 180°C for

10 min, then stored in deionized water for further use.

Pervaporation

Pervaporation was conducted at 30°C for the entire concentration range. For a detailed description of the experimental procedure and composition analysis, refer to previous work.¹ The permeability, separation factor, and pervaporation separation index (PSI) are calculated as follows:

$$\text{Permeability} = Q/Adt$$

$$\text{Separation factor} = (y_w/y_e)/(x_w/x_e)$$

$$\text{PSI} = (\text{permeability}) \times (\text{separation factor})$$

where Q is the collected amount of permeate at a time interval of t ; A , the effective membrane area; d , the membrane thickness; x_w and x_e , the concentrations of water and ethanol, respectively, in the feed solution; and y_w and y_e , the concentrations of water and ethanol, respectively, in the permeate.

Sorption Measurement

The dried membrane sample was immersed in ethanol–water mixtures of different concentrations to equilibrate at 30°C for at least 24 h. Subsequently, the membrane was taken out from the solution, blotted, and placed in a clean dry container that was connected to a cold trap followed by a vacuum pump. The liquid absorbed by the membrane was thus desorbed and collected in the cold trap and then weighed and analyzed for the composition. The same vacuum and trapping system as used in the pervaporation was used for the desorption process. The vacuum-dried membrane sample was also weighed for the calculation of sorption capacity.

RESULTS AND DISCUSSION

Pervaporation Performance of the Thermally Crosslinked Blend Membranes

Thermal decomposition of polymer materials may occur if the crosslinking temperature is too high, whereas a too low crosslinking temperature leads to a low crosslinking rate and long reaction time. It has been observed that 10-min crosslink-

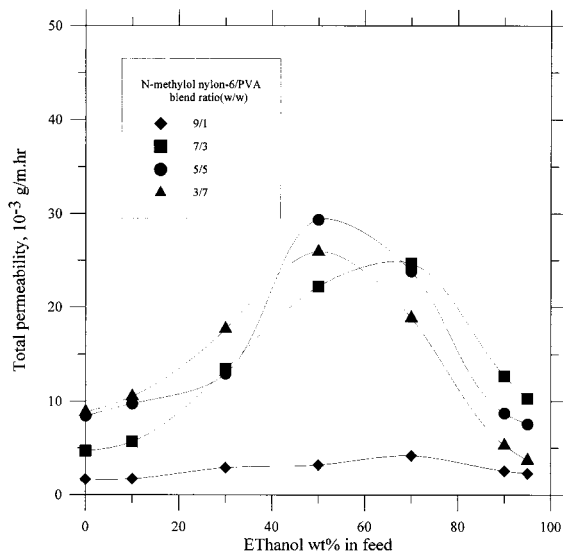


Figure 1 Total permeability versus ethanol weight percent in feed for thermally crosslinked membranes with different PVA contents; $T = 30^{\circ}\text{C}$.

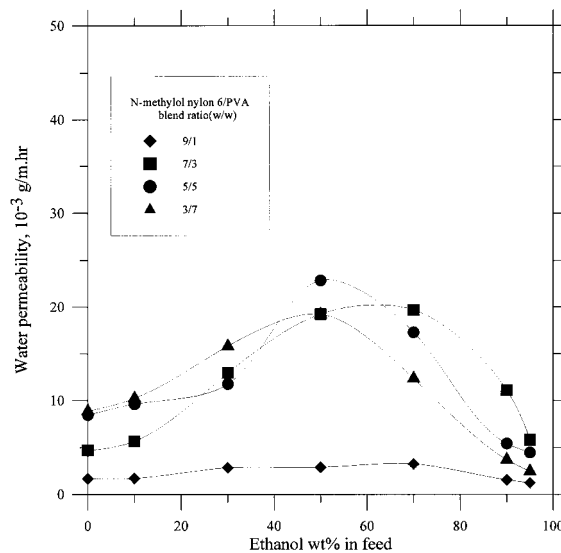


Figure 2 Water permeability versus ethanol weight percent in feed for thermally crosslinked membranes with different PVA contents; $T = 30^{\circ}\text{C}$.

ing reactions of *N*-methylol nylon-6 at 180°C gives the optimal membrane performance.¹ The crosslinking temperature used for the preparation of the commercial GFT membrane was set at 150°C .¹⁸ Katz and Wydeven¹⁰ used a crosslinking temperature of 175°C and a crosslinking time of 70 min to thermally crosslink the PVA membrane. Thus, it should be reasonable to use a crosslinking temperature of 180°C and crosslinking time of 10 min to crosslink the blend membrane of *N*-methylol nylon-6 and PVA.

The effect of the ethanol content in the feed solution on the total and individual permeability is shown in Figures 1–3. A serious deviation from ideal permeation indicates that these membranes are strongly plasticized by the ethanol–water mixtures, especially around the feed concentration at 50 wt % ethanol, where they exhibit a maximum permeability. The plasticization is caused by the absorbed solvent in the membrane, which generates a more mobile polymer chain and therefore increases the free volume and the diffusivity of component through the membrane. On the other hand, the plasticizing effect is stronger with increase in the PVA content of the blend membrane. When examining the individual permeability curves in Figures 2 and 3, it is found that not only the ethanol permeability is enhanced by the plasticizing effect of water, but also the water permeability by the plasticizing effect

of ethanol. The plasticizing effect of water might be attributed to the PVA component in the blend membrane and the plasticizing effect of ethanol to the *N*-methylol nylon 6 component. The same phenomena were observed in the case of blend membranes of *N*-methylol nylon-6 and poly(acrylic acid) (PAA).² The permeation behavior of

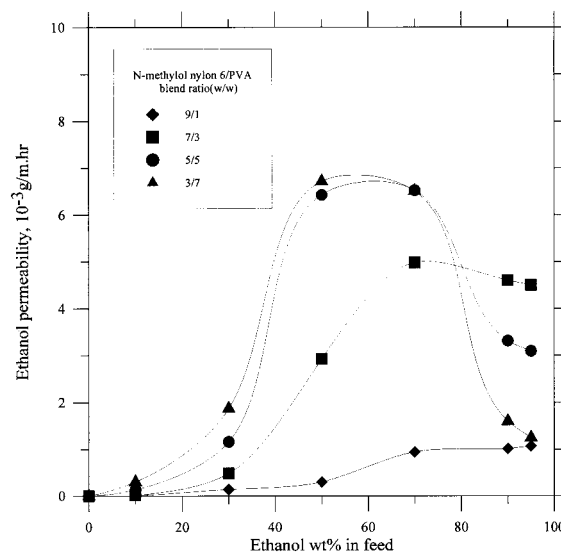


Figure 3 Ethanol permeability versus ethanol weight percent in feed for thermally crosslinked membranes with different PVA contents; $T = 30^{\circ}\text{C}$.

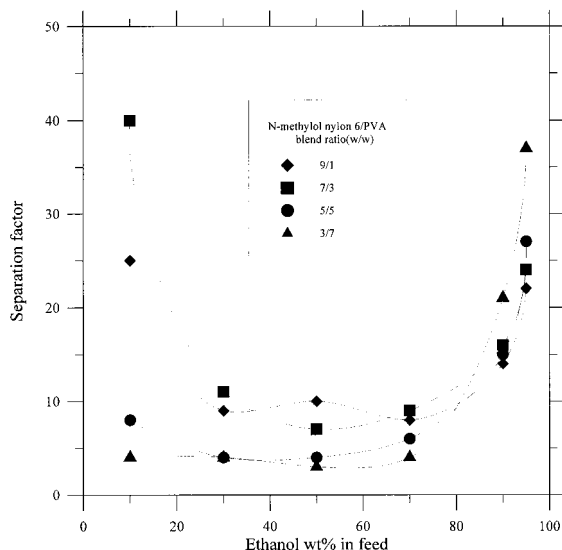


Figure 4 Separation factor versus ethanol weight percent in feed for thermally crosslinked membranes with different PVA contents; $T = 30^{\circ}\text{C}$.

a blended membrane system has been classified into three categories¹⁵:

1. Blends in which the permeation is controlled by the transport property of one of the components of the membrane;
2. Blends in which permeation is governed by the transport through the modified structure of the main polymer;
3. Blends in which both polymers contribute significantly to permeation.

The *N*-methylol nylon-6-based blend system investigated in this article seems to fall into the third category.

Basically, the PVA/*N*-methylol nylon 6 blend membranes are water-selective. The effect of ethanol concentration on the separation factor is described in Figure 4. For the membranes with PVA content less than 50 wt %, the separation curves show a reverse parabolic shape and high selectivity occurs at both ends of the concentration. On the other hand, the blend membranes with higher PVA content (more than 50 wt %) show more selectivity to water at a higher ethanol concentration than at a lower ethanol concentration, which is similar to the behavior observed in the pure PVA membranes.

The total permeability as a function of PVA content in the blend system is shown in Figure 5.

Two different trends are observed: At high water concentration (10 wt % ethanol in feed), the permeability increases with increasing PVA content. This could be explained by the strong hydrophilicity of PVA which functions extensively in solutions of high water concentration. However, at a low water concentration (95 wt % ethanol in feed), the permeability increases first with increase of the PVA content and then decreases. This may be explained as follows: If a small amount of PVA (less than 30 wt %) is added, the water solubility in the blend membrane will increase. The water in the membrane acts as a plasticizer which enables the permeant to more easily permeate through the membrane and, hence, increases the permeability. In this region, the plasticizing effect of water plays a dominant role. On the other hand, at high PVA content (more than 30 wt %), the membrane structure become more organic-resistant (like the chemical nature of PVA); therefore, diffusion is more difficult and the permeability decreases. The chemical nature of PVA takes control in this region.

Figure 6 shows the variation of the separation factor with PVA content at feed solutions of high and low ethanol concentrations. At high ethanol concentrations, the separation increases monotonously with increase of the PVA content, while there is a maximum separation factor in the case of the feed solution with a low ethanol concentra-

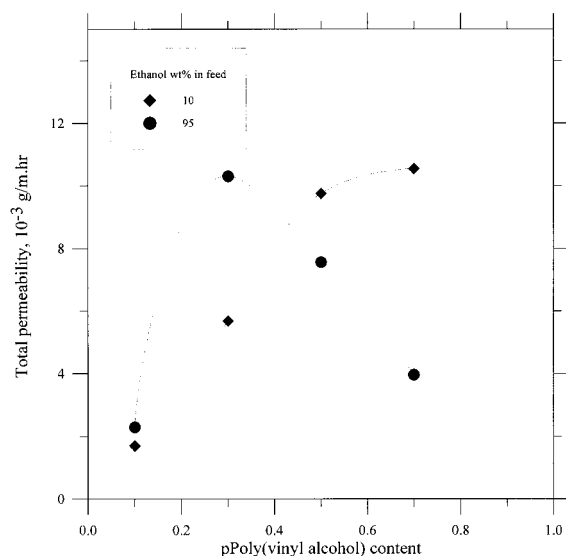


Figure 5 Total permeability versus PVA content in thermally crosslinked membranes at two different feed concentrations; $T = 30^{\circ}\text{C}$.

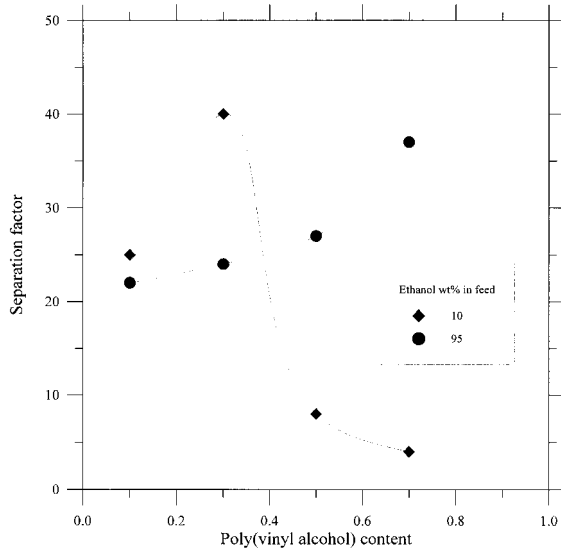


Figure 6 Separation factor versus PVA content in thermally crosslinked membranes at two different feed concentrations; $T = 30^{\circ}\text{C}$.

tion. As explained in Figure 5, the selectivity first increases due to the improved water permeation resulting from the increase of PVA in the membrane, but this advantage eventually fails due to the serious swelling caused by adding more PVA, thus degrading the membrane separation performance at solutions of high water content.

The pervaporation separation index (PSI) serves as a good guideline to select the membrane materials with an optimal combination of permeability and selectivity.¹ Therefore, the PSI value is taken as the criterion for determining the optimal PVA content in the membrane. Figure 7 is a plot of PSI value versus PVA content in the blend membrane at two different feed solutions. It shows that the PSI has a maximum value at 30 wt % PVA in the blend membrane. The blend membrane at this composition apparently has the optimal hydrophilic/hydrophobic balance for this blend system.

Pervaporation Performance of Chemically Crosslinked Blend Membranes

Maleic acid can react with the pendant hydroxy groups in PVA⁷ and *N*-methoxymethyl nylons.¹⁷ It is expected that the crosslinkage in a chemically crosslinked membrane can be attributed to maleic acid, unlike a thermally crosslinked membrane where the hydrophobic crosslinkages such

as $-\text{CH}_2-$ and $-\text{O}-$ are formed. Maleic acid has proven to be a very effective crosslinking agent to improve the performance of dehydration membranes. The use of maleic acid as a crosslinking agent in the blend system of *N*-methylol nylon-6 and PVA will be investigated next.

The variation of permeability (total, water, and ethanol, respectively) as a function of ethanol content in the feed for a blend membrane of PVA and *N*-methylol nylon-6 (blend ratio 5/5 by weight), crosslinked with different amounts of maleic acid, is shown in Figures 8–10. In general, the water permeability is about one order higher than is the ethanol permeability and these three figures exhibit similar trends in that a maximum permeability occurs at a feed ethanol content between 60 and 70 wt %. Basically, these crosslinked blend membranes are water-selective and their permeability is enhanced notably by the strong plasticizing effects of both water and ethanol, especially for the plasticizing effect of ethanol on water permeability. The water permeability at a feed solution of 95 wt % ethanol is about three to four times higher than it is for a pure water feed. PVA is a highly hydrophilic polymer material and the pervaporation flux of its crosslinked membrane decreases with increasing ethanol content in the feed.¹⁹ However, when blended with the more hydrophobic *N*-methylol nylon-6, the membrane performance changes. The presence of the more

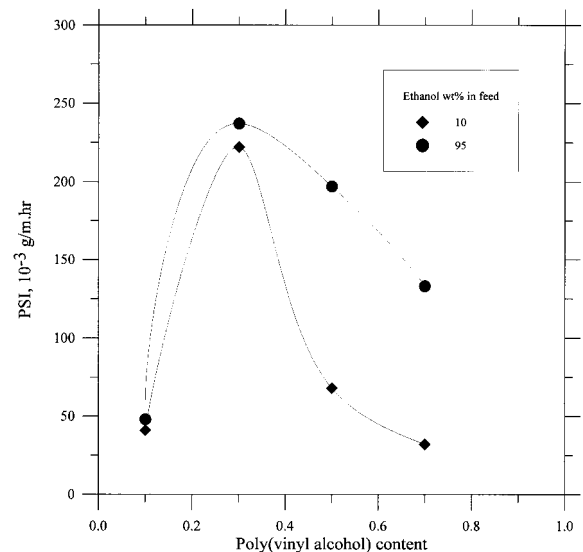


Figure 7 Pervaporation separation index versus PVA content in thermally crosslinked membranes at two different feed concentrations; $T = 30^{\circ}\text{C}$.

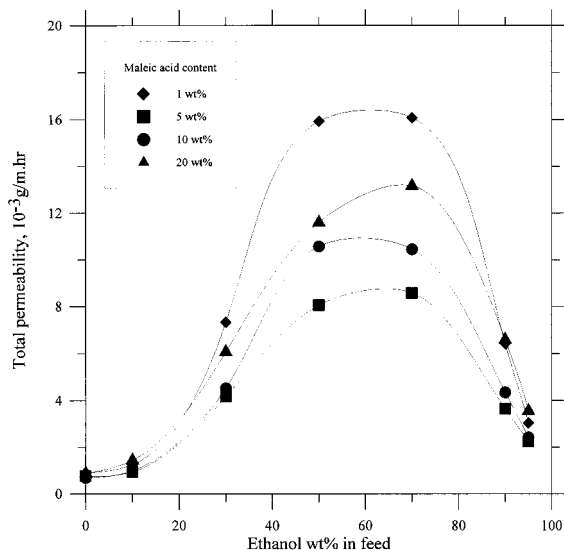


Figure 8 Total permeability versus ethanol weight percent in feed for chemically crosslinked membranes with different maleic acid contents; $T = 30^{\circ}\text{C}$.

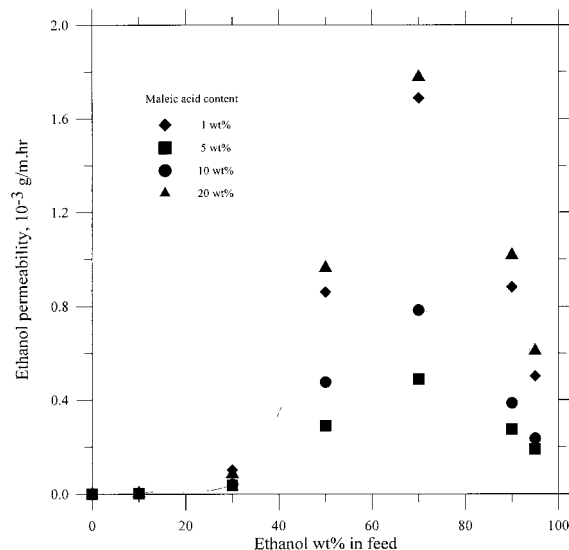


Figure 10 Ethanol permeability versus ethanol weight percent in feed for chemically crosslinked membranes with different maleic acid contents; $T = 30^{\circ}\text{C}$.

hydrophobic component in the blend membranes raises the water permeability at a feed solution of higher organic content due to the plasticization of ethanol, while still maintaining good separation properties. Figure 11 shows a plot of the separation factor versus the ethanol content in the feed for the different crosslinked blend membranes. The separation factor has the highest value (100–

200) at 95 wt % ethanol. As explained above, the water permeability is enhanced significantly by the plasticizing effect of ethanol at a feed solution of high ethanol content, which is induced by the presence of a more hydrophobic component (*N*-methylol nylon 6). A slightly higher separation factor is also found at a lower ethanol feed solution which might be attributed to the hydrophilic

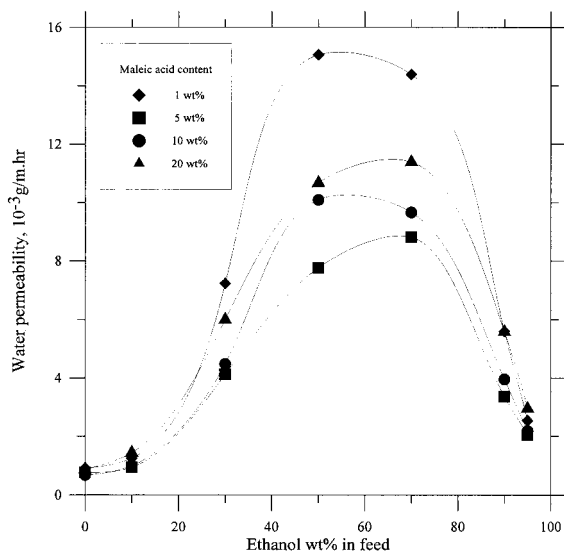


Figure 9 Water permeability versus ethanol weight percent in feed for chemically crosslinked membranes with different maleic acid contents; $T = 30^{\circ}\text{C}$.

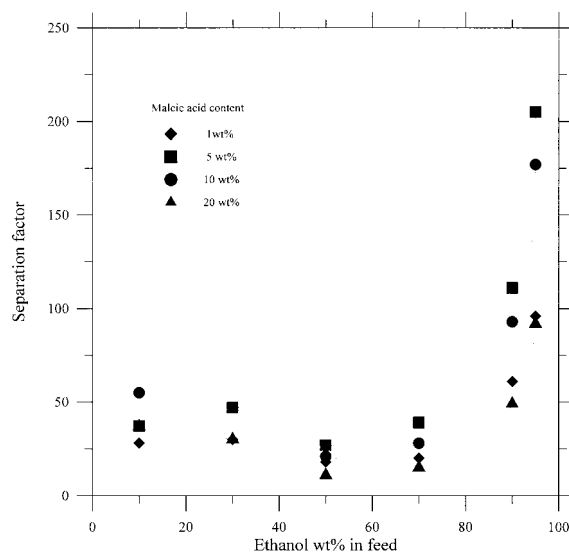


Figure 11 Separation factor versus ethanol weight percent in feed for chemically crosslinked membranes with different maleic acid contents; $T = 30^{\circ}\text{C}$.

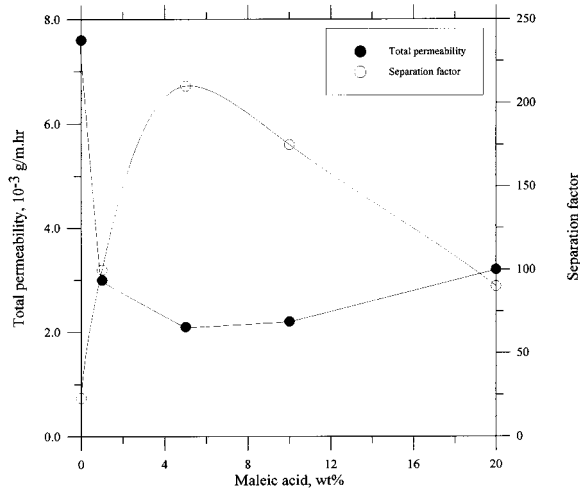


Figure 12 Total permeability and separation factor versus maleic acid content in chemically crosslinked membranes at a feed solution of 95 wt % ethanol; $T = 30^{\circ}\text{C}$.

component, that is, PVA, as explained in the above section.

The effect of the content of the crosslinking agent (maleic acid) on the membrane performance at a feed solution of 95 wt % ethanol is shown in Figure 12. The maximum separation factor and minimum permeability are observed at 5 wt % maleic acid. Generally speaking, as the crosslinking density in the polymer increases, the resulting membrane has a more compact network structure, resulting in less chain mobility and more limited chain motion, so that the free volume in the polymer decreases. According to the solution-diffusion transport mechanism, this decreases both solubility and diffusivity, leading to lower permeability and better separation. But the results in this figure show a parabolic curve shape with the crosslinking agent content. The reason for this can be explained in terms of the dispersion of the excess unreacted crosslinking agent in the membrane with more than 5 wt % maleic acid.²⁰ The reactivity of a functional group on a polymer chain is affected by adjacent neighboring groups. The chain can adversely affect the reactivities of groups on neighboring repeat units for steric effects attributable to the newly formed groups. Thus, as the reaction proceeds, the accessibility of a crosslinking agent to a functional group on a polymer chain can be restrained even below the stoichiometric quantity of the crosslinking agent. The excess crosslinking agent which

does not participate in the reaction becomes dispersed in the membrane, causing increase in the number of chain end groups in the membrane, which results in increase in the free volume. Thus, the membrane with more than 5 wt % maleic acid displays increase in the permeability and decrease in the separation factor with increasing crosslinking agent content.

As shown in Figure 13, a maximum PSI value is obtained at 5 wt % maleic acid, suggesting that the blend membrane with 5 wt % maleic acid as the crosslinking agent gives the best membrane performance. Therefore, all the blend membranes used for the following discussion are crosslinked with 5 wt % maleic acid.

Figures 14–16 give the pervaporation results of the crosslinked (5 wt % maleic acid) blend membrane of PVA and *N*-methylol nylon 6 with different blend ratios. The trend of the permeability (total, water, and ethanol, respectively) against the ethanol content in the feed is similar to Figures 8–10. All the curves show a maximum value at about 70 wt % ethanol in the feed. It is noticeable that the ethanol permeability decreases abruptly with a PVA content of more than 30 wt %, while the water permeability decreases more gradually. This leads to a high separation factor of the blend membrane with a PVA content of more than 30 wt %. Figure 17 shows the effect of ethanol concentration on the separation factor

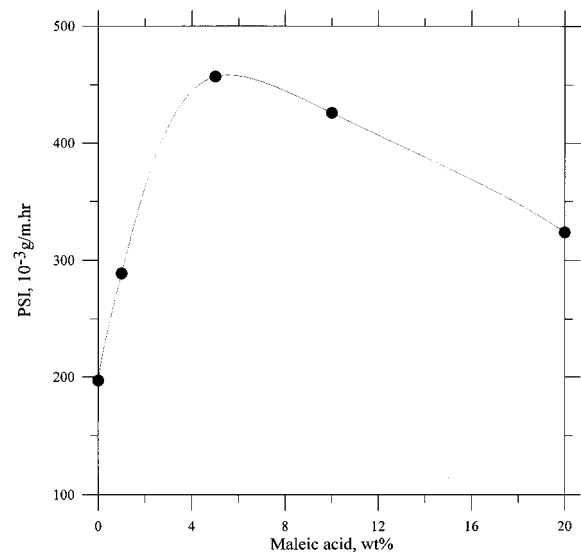


Figure 13 Pervaporation separation index versus maleic acid content in chemically crosslinked membranes at a feed solution of 95 wt % ethanol; $T = 30^{\circ}\text{C}$.

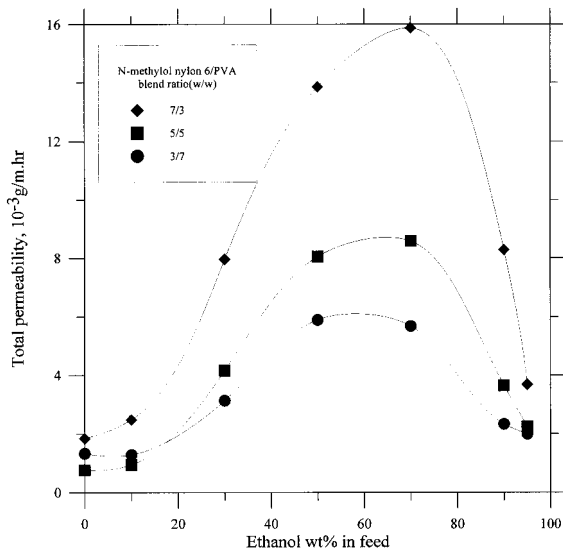


Figure 14 Total permeability versus ethanol weight percent in feed for chemically crosslinked membranes with different PVA contents; $T = 30^{\circ}\text{C}$.

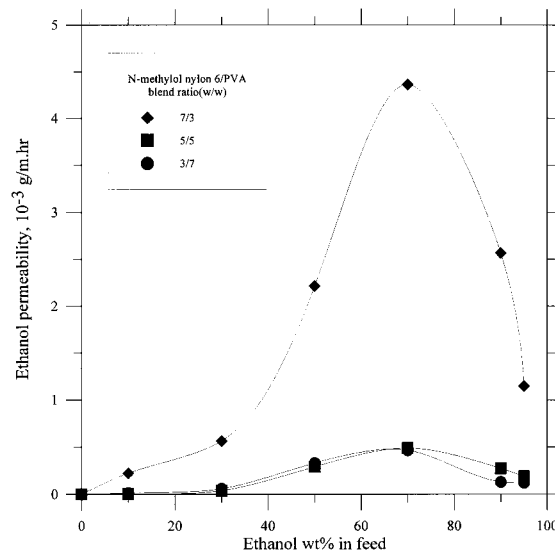


Figure 16 Ethanol permeability versus ethanol weight percent in feed for chemically crosslinked membranes with different PVA contents; $T = 30^{\circ}\text{C}$.

for the three membranes with different blend ratios. The separation factor does not change very much until the ethanol content reaches 70 wt %, but a sudden increase of the separation factor is observed when the ethanol content exceeds 70 wt %. The reason is that at a high ethanol content the membrane structure becomes more compacted due to the presence of hydrophilic

PVA, so the difference of solubility and diffusivity between water and ethanol in the membrane becomes more critical.

Figure 18 shows the effect of PVA content in the blend membrane on the pervaporation performance. These membranes are crosslinked with 5 wt % maleic acid and run at a feed solution of 95 wt % ethanol. A trade-off between the perme-

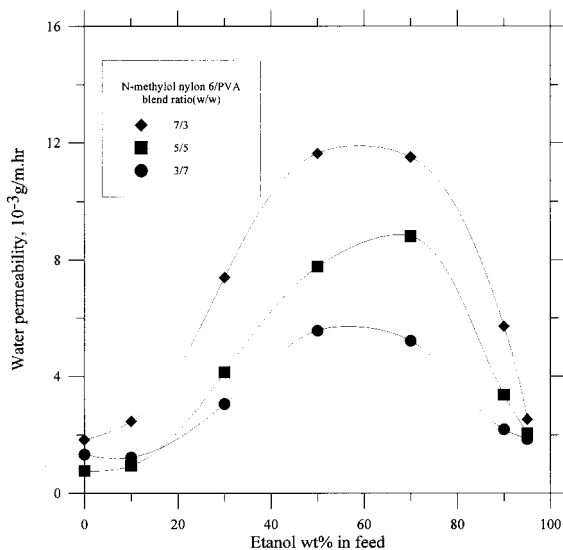


Figure 15 Water permeability versus ethanol weight percent in feed for chemically crosslinked membranes with different PVA contents; $T = 30^{\circ}\text{C}$.

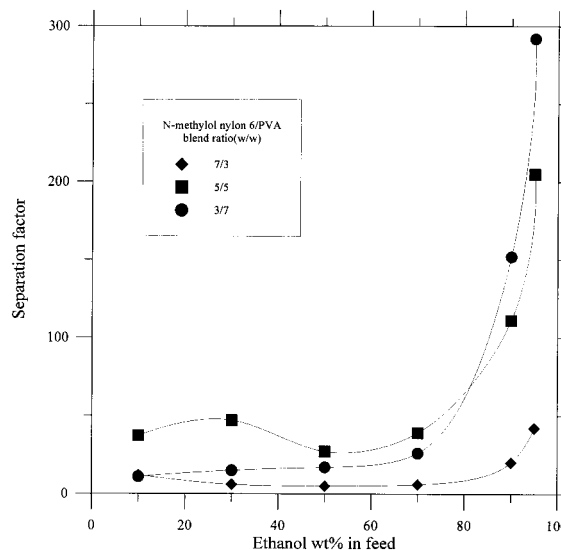


Figure 17 Separation factor versus ethanol weight percent in feed for chemically crosslinked membranes with different PVA contents; $T = 30^{\circ}\text{C}$.

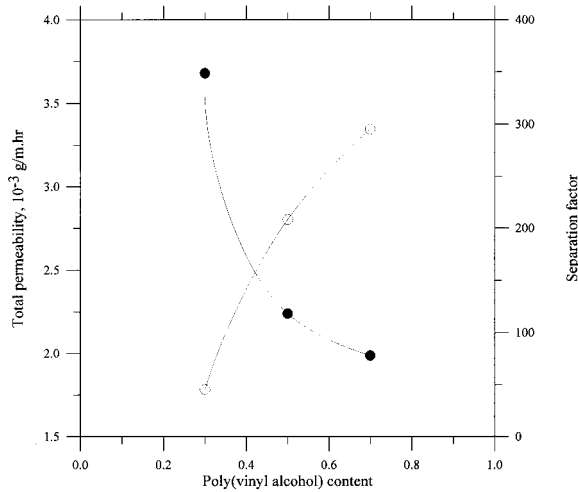


Figure 18 Total permeability and separation factor versus PVA content in chemically crosslinked membranes at a feed solution of 95 wt % ethanol; $T = 30^{\circ}\text{C}$.

ability and separation factor is observed, that is, the permeability decreases, while the separation factor increases as the PVA content increases. The hydrophilicity of the blend membrane increases with increasing PVA content; therefore, the membrane structure becomes more rigid at a high organic content, causing a decrease in permeability and increase in the separation factor. A plot of PSI against PVA content in the membrane is given in Figure 19. The PSI value increases

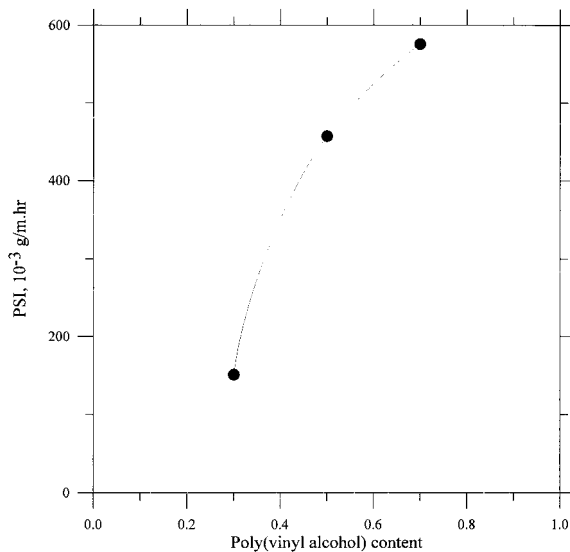


Figure 19 Pervaporation separation index versus PVA content in chemically crosslinked membranes at a feed solution of 95 wt % ethanol; $T = 30^{\circ}\text{C}$.

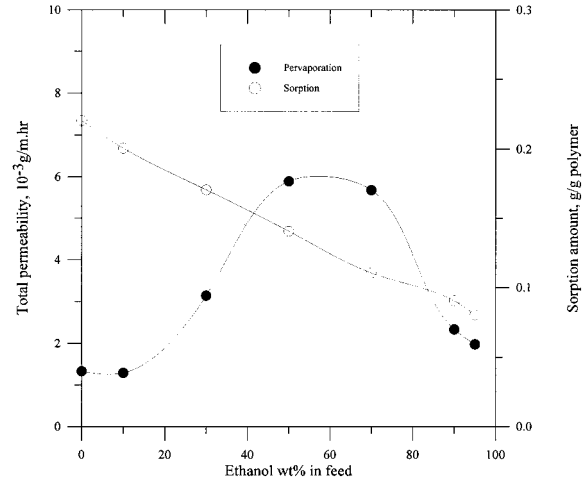


Figure 20 Total permeability and sorption amount versus ethanol weight percent in feed for chemically crosslinked membranes (blend ratio of PVA/*N*-methylol nylon-6 = 7/3 by weight); $T = 30^{\circ}\text{C}$.

rapidly with increasing PVA content. Compared with Figure 7, one can clearly see that the chemically crosslinked membrane shows a better performance than does the thermally crosslinked membranes due to the different nature of the crosslinks.

Comparison of Sorption and Pervaporation Performance

Preferential sorption has been considered as a prerequisite for preferential permeation.^{21,22} It is claimed that the component absorbing preferentially should permeate through the membrane preferentially. According to the solution-diffusion model, both sorption and diffusion aspects should be taken into account. To illuminate the relationship between sorption and pervaporation, we conducted sorption measurements at 30°C over the entire concentration range for a chemically crosslinked membrane with 70 wt % PVA content. Figures 20 and 21 show the results. As the concentration of ethanol in the bulk liquid solution increases, the sorption of the total solution in the membrane decreases almost linearly, suggesting that the membrane is hydrophilic. On the other hand, the pervaporation curve shows a different trend. The permeability increases to a maximum and then decreases with increase of the ethanol content. This indicates that, in addition

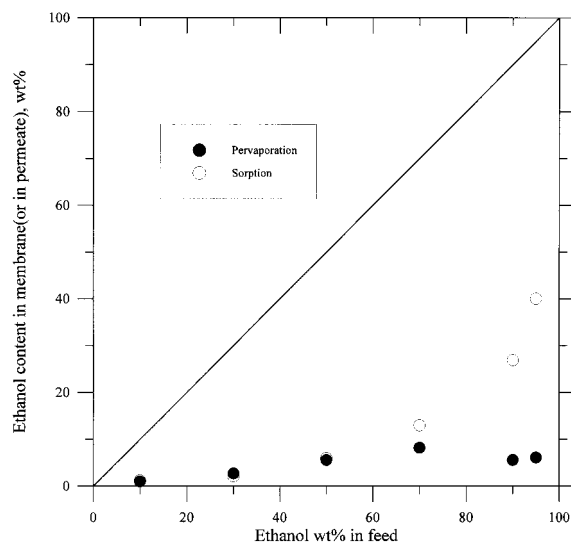


Figure 21 Ethanol weight percent in membrane (or in permeate) versus ethanol weight percent in feed for chemically crosslinked membranes (PVA content = 0.7); $T = 30^{\circ}\text{C}$.

to sorption, the diffusion of the permeant through the membrane also plays a very important role in the pervaporation due to the complicated polymer–permeant and permeant–permeant interactions which cause the membrane plasticization. Figure 21 shows the separation characteristics for both pervaporation and sorption. At lower organic concentration (<50 wt % ethanol), two curves are almost identical, while at high organic concentration (>50 wt % ethanol), they deviate from each other. At higher water concentrations, the hydrophilic membrane swells so extensively that selective diffusion does not exist and the separation depends mainly on sorption properties. At high organic concentration, membrane swelling diminishes so that the major part of the membrane is almost in a dry state and separation now depends mainly on diffusion which leads to a better separation performance.

CONCLUSIONS

In this study of the pervaporation performance of crosslinked blend membranes of PVA/*N*-methylol nylon-6 for the separation of ethanol–water mixtures, the following conclusions can be drawn:

1. Both water and ethanol show a strong plasticizing effect on the thermally crosslinked membranes. These membranes show higher selectivity at both extremes of the concentration range. The best membrane performance can be obtained from the crosslinked blend membrane with 30 wt % PVA, having a total permeability of $10 \times 10^{-3} \text{ g m}^{-1} \text{ h}^{-1}$ and a separation factor of 22.
2. A significant improvement in membrane performance is achieved by using maleic acid as the crosslinking agent. The pervaporation performance for the separation of water–ethanol mixtures was investigated in terms of the crosslinking agent content and the PVA content in the membrane. It was found that membranes crosslinked with 5 wt % maleic acid give the optimal membrane performance, while the membrane performance improves with increase of the PVA content in the membrane. For a feed solution of 95 wt % ethanol, a membrane with 5 wt % maleic acid as a crosslinking agent and 70 wt % PVA content gives a permeability of $2 \times 10^{-3} \text{ g m}^{-1} \text{ h}^{-1}$ and a separation factor of 300.
3. From the comparison in results from the sorption and pervaporation tests on chemically crosslinked membranes, the diffusion is a controlling process when the feed solution has a low water content, while the sorption property takes control when the feed solution has a high water content.

REFERENCES

1. J.-J. Shieh and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **65**, 855 (1997).
2. R. Y. M. Huang and J.-J. Shieh, *Sep. Sci. Technol.*, **32**, 2765 (1997).
3. R. Y. M. Huang and N. R. Jarvis, *J. Appl. Polym. Sci.*, **14**, 2341 (1970).
4. V. Shantora and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **26**, 3223 (1981).
5. M. Satoh, W. Z. Zhang, A. Nodera, and J. Komoyama, *J. Membr. Sci.*, **35**, 311 (1988).
6. J. W. K. Sptizen, Ph.D. dissertation, Twente University, The Netherlands, 1988.
7. R. Nobrega, A. C. Habert, M. E. F. Esposito, and C. P. Borges, in *Proceedings of the 3rd International Conference on Pervaporation Processes in the Chemical Industry*, R. Bakish, Ed., Bakish Material Corp., Englewood, NJ, 1988, p. 326.

8. R. W. Kormeyer and N. A. Peppas, *J. Membr. Sci.*, **9**, 211 (1981).
9. W. Ying, *Desalination*, **46**, 335 (1983).
10. M. G. Katz and T. Wydeven, Jr., *J. Appl. Polym. Sci.*, **26**, 2935 (1981).
11. M. G. Katz and T. Wydeven, Jr., *J. Appl. Polym. Sci.*, **27**, 79 (1982).
12. S. Peter and S. Stefan, in *Synthetic Membrane, Hyper- and Ultrafiltration Uses*, Vol. II, Turbak, Ed., American Chemical Society, Washington, DC, 1981.
13. T. Hirotsu, K. Ichimura, K. Mizoguch, and E. Nakamura, *J. Appl. Polym. Sci.*, **36**, 1717 (1988).
14. J. W. Rhim, Ph.D. dissertation, University of Waterloo, Canada, 1989.
15. Y. Maeda and M. Kai, in *Pervaporation Membrane Separation Processes*, R. Y. M. Huang, Ed., Elsevier, Amsterdam, 1991.
16. S. Takegami, H. Yamada, and S. Tsujii, *Polym. J.*, **11**, 1239 (1992).
17. T. L. Cairns, H. W. Gary, A. K. Schneider, and R. S. Schreiber, *J. Am. Chem. Soc.*, **71**, 655 (1949).
18. H. E. A. Brusckke, *Ger. Pat. DE 3,200,570 A1* (1983).
19. R. Y. M. Huang and C. K. Yeom, *J. Membr. Sci.*, **51**, 273 (1990).
20. C. K. Yeom and R. Y. M. Huang, *Angew. Makromol. Chem.*, **184**, 27 (1991).
21. M. H. V. Mulder, T. Franken, and C. A. Smolders, *J. Membr. Sci.*, **22**, 155 (1985).
22. Y. Z. Zhang, K. D. Zhang, and J. P. Xu, *J. Membr. Sci.*, **80**, 297 (1993).