

# Preparation of *N*-Methylol Nylon-6 Membranes for Pervaporation of Ethanol–Water Mixtures

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**ABSTRACT:** *N*-methylol nylon 6 membranes were prepared by reacting nylon-6 with formaldehyde. Elemental analysis, used to analyze the composition of modified membranes, showed that the degree of substitution increased with formaldehyde content in the reaction solution. The modified nylon-6 membranes exhibited a high affinity to ethanol. Pervaporation results for the separation of ethanol–water mixtures showed that these membranes were water-selective, indicating that the diffusion property is the dominant factor. An *N*-methylol nylon-6 membrane with 33% degree of substitution showed the best membrane performance. In order to control the swelling of *N*-methylol nylon-6 membranes in the feed solutions of high ethanol content, thermal crosslinking was applied at 180°C for different times. It was found that heat treatment of 10 minutes gave the optimal permselectivity. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 855–863, 1997

**Key words:** *N*-methylol nylon-6; thermal crosslinking; pervaporation; water–ethanol mixtures

## INTRODUCTION

In a pervaporation process, it is desirable to use a polymeric membrane with the combined characteristics of high permeation rate and good selectivity. Since the efficiency of pervaporation depends to a great extent upon the membrane employed, the choice of the best membrane is critical. Lloyd and Meluch<sup>1</sup> have reviewed the selection and evaluation of different polymeric membrane materials as well as various membrane-preparation methods. Since a homopolymer usually does not exhibit the optimum properties for a given separation system, new membranes must be developed to achieve the desired membrane performance.

Numerous modified polyamide (nylon) membranes have been utilized for separation of the

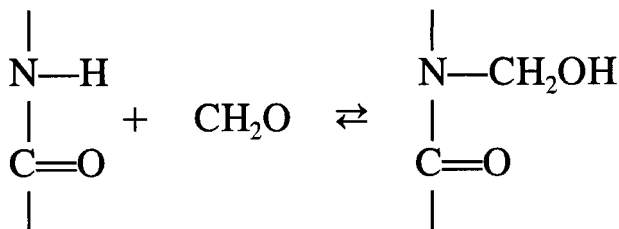
organic–water mixtures.<sup>2–7</sup> The performance of these modified polyamide membranes is better than that of the original polyamide membranes. Since polyamide materials have high crystallinity, due to their uniform chain structure and strong hydrogen bonding, the permeability of these modified polyamide membranes is quite low. The reaction of polyamide with formaldehyde in formic acid solution to yield an *N*-methylol polyamide has been studied by Cairns and associates.<sup>8,9</sup> The reaction is presented in Figure 1, where the polyamide chain is indicated simply by the amide group.

The modified polyamide has totally different physical and chemical properties than does the original polyamide.<sup>8,9</sup> Also, the modified polyamides can be thermally crosslinked, as described in Figure 2. A thermally crosslinked *N*-methoxymethylated nylon-3 membrane has been prepared and applied to pervaporation of water–alcohol mixtures.<sup>10</sup> It exhibited a water-permselective nature for all feed concentrations tested.

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**Figure 1** Reaction scheme of nylon and formaldehyde.

In this work, we prepare *N*-methylol nylon-6 membranes and their thermally crosslinked membranes to investigate their application in pervaporation for the separation of ethanol–water mixtures.

## EXPERIMENTAL

### Materials

Nylon-6 [poly(caprolactam)] used in this study was supplied by Polysciences, Inc. (Warrington, PA; cat. #6556, lot #73364). Formaldehyde solution (37%), 88 wt % formic acid, ammonium hydroxide, and acetone (BDH, Inc., Toronto, ON) were reagent grade. The ethanol–water mixtures were prepared by mixing 95 wt % ethanol from Commercial Alcohols, Inc. (Toronto, ON) and deionized water.

### Modification of Nylon-6

Modification of nylon-6 was carried out in a 500-ml three-neck reaction kettle equipped with an overhead condenser, a mechanical stirrer, an immersed glass thermometer, and two dropping funnels. A 10 wt % solution of nylon-6 in 88 wt % formic acid solution was prepared by stirring the mixture at 60°C for 2 h. Prolonged exposure of nylon-6 in warm formic acid would cause the gradual hydrolysis of amide linkages. To this solution was added different amounts of 37% formaldehyde solution (based on the unit mole ratios of formaldehyde/nylon-6 of 2, 5, 10) at 60°C. This formaldehyde was added slowly to prevent precipitation of the polymer. The reaction was continued for 2 h at 60°C. The resulting reaction solution was poured into a water/acetone (50/50) mixture to precipitate out. This product was neutralized by 0.1M aqueous ammonia and washed several times with water. The final product was vacuum-dried at room temperature for 24 h and stored.

### Membrane Preparation

Nylon-6 or *N*-methylol nylon-6 (the product from the above section) was dissolved in 88 wt % formic acid to form a homogeneous solution of 10 wt % polymer. The membrane was prepared by casting the polymer solution onto a clean glass plate using a Gardner knife with preset thickness. The casting membrane was air-dried at room temperature for 24 h in a dust-free, environmentally controlled chamber (supplied by D.F.S. Inc., North Andover, MA), then vacuum-dried at room temperature for 6 h to remove any volatile residuals. The newly formed membrane was soaked in deionized water for 24 h and peeled off for further use. The thickness of the dry membrane was approximately 30–40 μm.

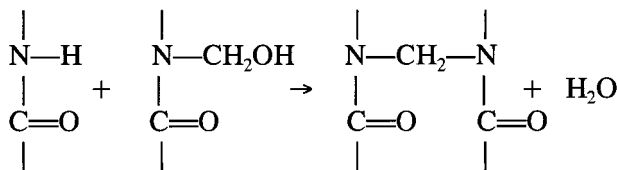
*N*-methylol nylon-6 membrane obtained from the product of reaction with formaldehyde/nylon-6 (unit mole ratio of 5; NF105, 33% substitution) was used for thermal crosslinking. The crosslinking reaction was carried out at 180°C for different periods of time (5, 10, 30, and 60 min).

### Elemental Analysis

The elemental analysis of *N*-methylol nylon-6 was performed using a Perkin-Elmer model 240C Elemental Analyzer. Prepurified helium, 99.99 mol % minimum, was used as the carrier gas. Ultra-pure oxygen, 99.99 mol % minimum, was used as the combustion gas. Sample weight of the membrane was between 2 and 3 mg.

### Sorption Measurement

The preweighed dry membranes were immersed in the bulk liquid of deionized water or ethanol at room temperature for at least 24 h. After removal from the liquid, the membrane surface was carefully wiped with tissue paper and then weighed as quickly as possible. The water sorption amount was calculated in terms of liquid weight per polymer weight.



**Figure 2** Crosslinking reaction of *N*-methylol nylon.

## Pervaporation

The pervaporation apparatus used in this study was developed previously in our laboratory.<sup>11</sup> The membrane was placed between two disks and sealed tightly. The effective membrane area in contact with the feed solution was 14.2 cm<sup>2</sup>. The feed solution in the tank was kept at 30°C and was circulated by a circulation pump. The vacuum in the permeate side was maintained at approximate 3 mmHg by using a Welch duo-seal vacuum pump. The permeate, condensed in a glass trap which was immersed in liquid nitrogen, was collected after a 2-h run to reach steady state. The flux was calculated by weighing the trapped permeate. The composition analysis of the permeate was carried out by using an Anton-Paar DMA 60 digital densitometer.

## RESULTS AND DISCUSSION

### Characterization of *N*-Methylol Nylon-6

Three types of *N*-methylol nylon-6 membranes have been prepared in this study, namely, NF102, NF105, and NF110, as shown in Table I. Using the value of C/N ratio from elemental analysis, the degree of substitution can be calculated as<sup>10</sup>

Degree of substitution, %

$$= \frac{C/N \text{ (observed)} - C/N \text{ (nylon-6)}}{C/N \text{ (N-methylol nylon-6)} - C/N \text{ (nylon-6)}} \times 100\% \quad (1)$$

As the amount of formaldehyde increases, the degree of substitution increases. The maximum

formaldehyde/nylon-6 unit mole ratio (F/N) used is 10. Beyond this amount, the reaction solution becomes very viscous and gel-like, presumably due to crosslinking. From the sorption data of the different membranes in Table I, it is evident that increasing the degree of substitution in *N*-methylol nylon-6 also promotes water and ethanol sorption. The formation of the methylol group in the polymer chain by the reaction of formaldehyde and the amide group in nylon-6 reduces the extent of interchain hydrogen bonding in nylon-6, and the introduction of the large =CH<sub>2</sub>OH group makes the *N*-methylol nylon-6 less crystallizable. The *N*-methylol nylon-6 membranes show a much higher sorption ability to ethanol. For the modified membrane with the 40% degree of substitution, the amount of sorbed ethanol in polymer can reach 200% higher in comparison with the original nylon-6. This indicates that the substitution of hydrogen by the methylol group in nylon-6 significantly improves the affinity of the polymer to ethanol.

### Pervaporation Performance of *N*-Methylol Nylon-6 Membranes

The presence of crystallites in the polymer has a significant influence on various polymer properties such as tensile strength, elasticity, impact strength, solubility, diffusivity in the polymer, etc. In pervaporation, solubility and diffusivity are especially important factors. Crystallites act as physical crosslinks that prevent a high degree of swelling on the membrane and dissolution of the feed mixture in the membrane during pervaporation. Nylon-6 is a crystalline polymer with strong interchain forces due to hydrogen bonding.

**Table I** Characterization of *N*-Methylol Nylon-6 Membranes

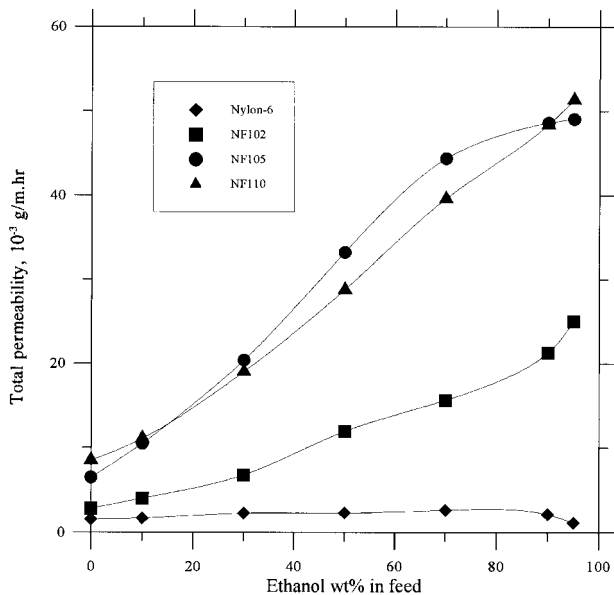
Membranes	F/N (mole ratio) <sup>a</sup>	Elemental Analysis				Degree of Substitution	Water Sorption (g/g Polymer)	Ethanol Sorption (g/g Polymer) <sup>b</sup>
		C (%)	H (%)	N (%)	C/N			
Nylon-6	0	63.39	9.81	12.38	5.14 <sup>c</sup>	0	0.11	0.09
NF102	2	63.96	9.71	12.21	5.24 <sup>d</sup>	12	0.12	0.25
NF105	5	63.85	9.53	11.79	5.42 <sup>d</sup>	33	0.18	1.87
NF110	10	63.13	9.35	11.53	5.48 <sup>d</sup>	40	0.25	2.00
<i>N</i> -Methylol nylon-6	—	58.72	9.15	9.78	6.00 <sup>c</sup>	100	—	—

<sup>a</sup> Formaldehyde/nylon-6 unit mole ration in solution.

<sup>b</sup> g of original nylon-6.

<sup>c</sup> Calculated value.

<sup>d</sup> Observed value.



**Figure 3** Total permeability versus ethanol weight percent in feed for *N*-methylol nylon-6 with different degrees of substitution;  $T = 30^{\circ}\text{C}$ .

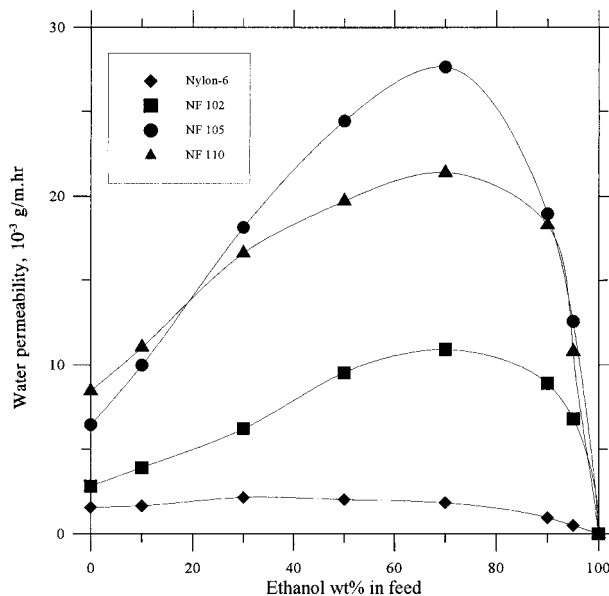
The conversion of nylon-6 into an *N*-methylol nylon-6 breaks the hydrogen bonding and crystallinity of original polyamide due to the replacement of some of the amide hydrogens by  $\text{CH}_2\text{OH}$  groups. It is expected that the modification will improve both solubility and diffusivity in the polymer.

Figure 3 shows the effect of ethanol content in the feed solution on the total permeabilities of nylon-6 and *N*-methylol nylon-6 membranes. The trend for the three *N*-methylol nylon-6 membranes is very different from that of the nylon-6 membrane. The total permeability of the nylon-6 membrane increases slightly with increasing ethanol content in feed solution, then reaches a maximum before decreasing again. Thus, ethanol and water may contribute somewhat equivalently to the plasticization of the nylon-6 membrane, resulting in a maximum permeability at a certain feed composition. However, for the *N*-methylol nylon-6 membranes, the total permeability increases with increasing ethanol content in feed solution. The total permeability is greatly improved by the introduction of  $\text{CH}_2\text{OH}$  groups into nylon-6, leading to a reduction of crystallinity and hydrogen-bonding in *N*-methylol nylon-6. The flux enhancement at high ethanol concentrations is one order of magnitude larger than in the case of the nylon-6. This shows that the *N*-methylol nylon-6 membranes exhibit a greater affinity to ethanol than to water. The investigation of the effect

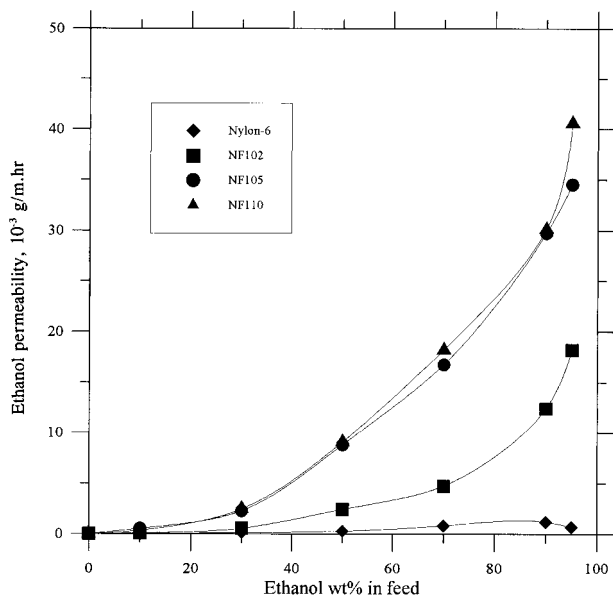
of feed composition on the individual component permeability will give more detailed insight about the interaction between the polymer and the permeants.

Generally speaking, for a hydrophilic membrane, the water permeability decreases as the ethanol content in the feed increases because the driving force for water transport decreases. However, as shown in Figure 4, the opposite trend is found for *N*-methylol nylon-6 membranes. The water permeabilities attain a maximum value at about 70 wt % ethanol. As can be seen from the sorption data in Table I, *N*-methylol nylon-6 membrane has a strong affinity to ethanol, which leads to extensive swelling of the membrane. Therefore, at higher ethanol content, the free volume inside the membrane increases significantly due to plasticization of ethanol, which is favorable to sorption and diffusion, and resulting in the parabolic permeability curve of water. On the other hand, nylon-6 membrane shows much less plasticization in water-ethanol mixtures but still has a kind of parabolic water permeability curve, which means that the presence of ethanol also provides a small plasticizing effect for water permeating through the membrane.

The dependence of ethanol permeability on the ethanol content in the feed solution, as shown in Figure 5, seems to follow an exponential curve for *N*-methylol nylon-6 membranes. Owing to the



**Figure 4** Water permeability versus ethanol weight percent in feed for *N*-methylol nylon-6 with different degrees of substitution;  $T = 30^{\circ}\text{C}$ .

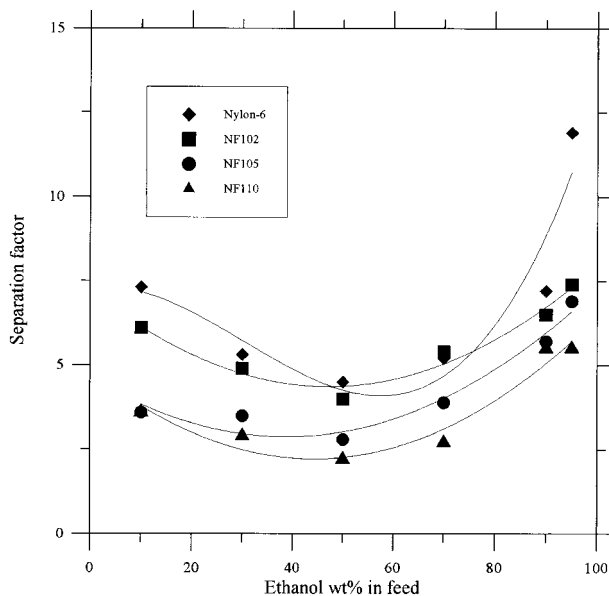


**Figure 5** Ethanol permeability versus ethanol weight percent in feed for *N*-methylol nylon-6 with different degrees of substitution;  $T = 30^{\circ}\text{C}$ .

high ethanol affinity of *N*-methylol nylon-6, the *N*-methylol nylon-6 membranes swell more significantly in a feed solution with higher ethanol content, thereby making it easier for the ethanol (as well as water) to permeate through the membranes. It is generally accepted that membrane swelling due to a permeating species increases its diffusivity through the membrane. In a swollen polymer, the mobility of the polymer chains is accelerated and the free volume available for diffusion is increased. When the concentration dependence of diffusivity follows an exponential relationship, a similar exponential increase in permeability will result. In the *N*-methylol nylon-6/water/ethanol system, the polymer shows a great affinity to ethanol so that the positive deviation of water permeability from ideal behavior is attributed to membrane plasticization by ethanol and the negative deviation of ethanol permeability from ideality is the result of concentration-dependent diffusivity. Ideal permeation would indicate that there is no interaction between permeant and membrane so that the permeability of a component is proportional to its concentration in the feed solution (driving force). For the nylon-6 membrane the ethanol permeability is low and has a maximum value. The low permeability exists because nylon-6 possesses higher hydrogen bonding force and degree of crystallinity which diminish the sorption and diffusion properties of

membrane. The maximum value is due to the plasticizing effect of water in the membrane.

Figure 6 shows the separation factor of membranes as a function of ethanol concentration in the feed. All the separation curves are concave upward. A minimum separation factor exists between 20 and 40 wt % ethanol. Similar behavior was also observed in the separation of ethanol-water mixtures using blended polyacrylic acid/nylon-6 membranes.<sup>4</sup> The separation factor of nylon-6 membrane is slightly higher than the other membranes although nylon-6 has high crystallinity. It seems that the crystallinity does not play a critical role in separation properties. As is well known, the crystalline region in the membrane is almost impermeable and the permeation occurs only in the amorphous region. Thus the permselectivity of a membrane is determined by the nature of the amorphous structure. The existence of the crystalline region in a membrane decreases the permeability but does not favor the selectivity. Although the *N*-methylol nylon-6 membranes show high affinity to ethanol, they still are water-selective. The introduction of the *N*-methylol group into nylon-6 is more favorable for ethanol sorption than for water sorption in membrane, as indicated in Table I, but the pervaporation performance of a membrane depends not only on sorption but also on diffusion. The breaking of hydrogen bonding and



**Figure 6** Separation factor versus ethanol weight percent in feed for *N*-methylol nylon-6 with different degrees of substitution;  $T = 30^{\circ}\text{C}$ .

crystallinity facilitates the diffusion of water through modified membrane, as does the plasticizing effect of ethanol in the membrane. When the effect of the diffusion factor surpasses the effect of the sorption factor, the membranes remain water-selective.

Figure 7 shows the effect of degree of  $\text{CH}_2\text{OH}$  substitution in *N*-methylol nylon-6 on the pervaporation performance at a feed solution of 90 wt % ethanol. The permeability increases while the separation factor decreases, when the degree of substitution increases. As mentioned above, the addition of  $\text{CH}_2\text{OH}$  groups will reduce the crystallinity and the interchain hydrogen bonding, which favor the sorption and diffusion properties in the *N*-methylol nylon-6 membranes and therefore, promote higher permeability. At the same time, the ethanol affinity of *N*-methylol nylon-6 also increases by increasing the degree of substitution, which enables ethanol to permeate more easily than water and decreases the selectivity. Since a trade-off between permeability and selectivity always exists, a pervaporation separation index (PSI) has been defined to characterize the membrane performance<sup>12</sup>:

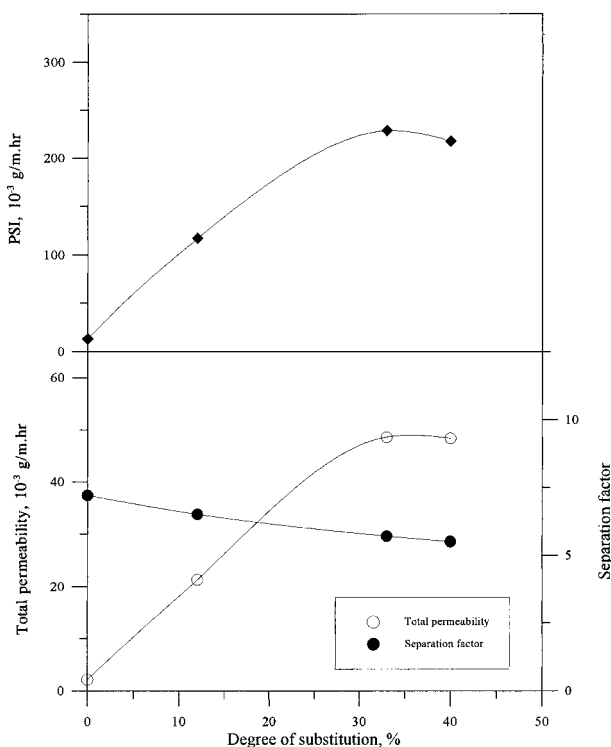
$$\text{PSI} = P(\alpha - 1) \quad (2)$$

where  $P$  is the permeability and  $\alpha$  is the separation factor. The upper part of Figure 7 is a plot of the PSI versus the degree of substitution. The PSI rises with an increase in the degree of substitution and then decreases when the degree of substitution is above 33%. From this result, it appears that an *N*-methylol nylon-6 membrane with 33% degree of substitution shows the best membrane performance for the separation of 90 wt % ethanol aqueous solution. Accordingly, we have chosen the NF105 membrane (*N*-methylol nylon-6 with 33% substitution) as the thermal-crosslinking material to investigate the effect of crosslinking time on the pervaporation performance.

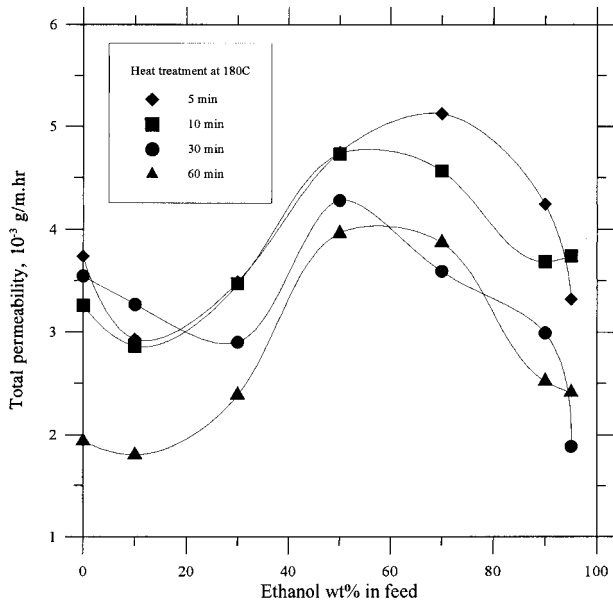
### Pervaporation Performance of Crosslinked *N*-Methylol Nylon-6 Membranes

Because the *N*-methylol nylon-6 swells extensively in ethanol-water mixtures, especially at high ethanol content, an introduction of crosslinks into this material may make the membrane more stable. Generally speaking, as crosslinking density in a polymer increases, the resulting membranes have a more compact network structure, resulting in less chain mobility, more limited chain motion, less free volume, and swelling.<sup>13</sup> This principle can be applied to the membrane separation processes in terms of solubility and diffusivity: as the degree of crosslinking increases, the solubility of the liquid mixture in the membrane is depressed and the diffusivity which is governed by the free volume decreases due to the rigidity of polymer chains. Thus the permeability of the membrane should decrease while the selectivity should increase.<sup>14</sup>

Figure 8 shows the concentration dependence of total permeability for the thermally crosslinked *N*-methylol nylon-6 membranes. All the permeability curves are sigmoidal. The dependence is completely different from that of uncrosslinked membranes as shown in Figure 3. A maximum in permeability is observed for all crosslinked membranes, which suggests both water and ethanol contribute to plasticizing a crosslinked membrane. Xu and Huang<sup>4</sup> have investigated the permeation of ethanol-water mixtures in blended polyacrylic acid/nylon-6 membranes which show a downward-parabolic shape in their permeation rate curves and an upward-parabolic shape in their separation factor curves. This can be a good

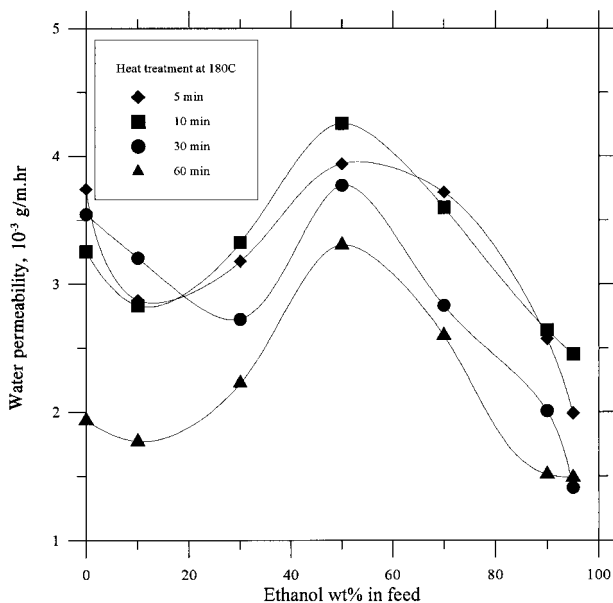


**Figure 7** Total permeability, separation factor, and PSI versus degree of substitution;  $T = 30^\circ\text{C}$ ; feed concentration: 90 wt % ethanol.



**Figure 8** Total permeability versus ethanol weight percent in feed for NF 105 (degree of substitution = 33%) with different heat treatment times;  $T = 30^{\circ}\text{C}$ .

example of a membrane system in which both components act as plasticizing agents to a similar extent on the membrane. The total permeabilities of crosslinked membranes (heat treatment for 5 min) are about 10 times lower than the unmodified one (NF105) at 95 wt % ethanol, which is due

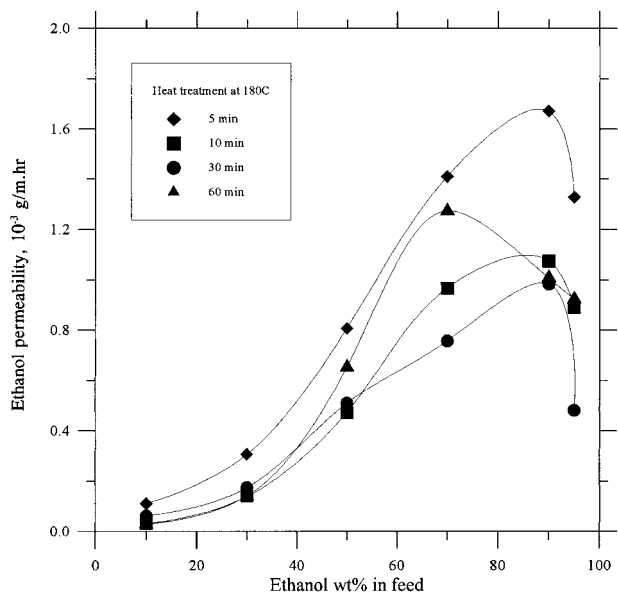


**Figure 9** Water permeability versus ethanol weight percent in feed for NF 105 (degree of substitution = 33%) with different heat treatment times;  $T = 30^{\circ}\text{C}$ .

to the decrease in diffusivity and solubility as a result of crosslinking.

A similar behavior is also observed for the water permeability, as shown in Figure 9. The decrease in water permeability at lower ethanol contents indicates little plasticizing effect of ethanol in this concentration range and shows that permeability is mainly determined by diffusion. Membrane plasticization due to ethanol only occurs at higher ethanol content, leading to a maximum water permeability around 50 wt % ethanol. The water permeability of crosslinked membrane (heat treatment for 5 min) is about 5 times lower than that of uncrosslinked membrane in a 95 wt % ethanol solution.

The variation of ethanol permeability with the ethanol content in feed solution is shown in Figure 10. It also shows a maximum permeability which, as we have already discussed, is the result of membrane plasticization. The extent of the decline in ethanol permeability for the crosslinked membranes (heat treatment for 5 min) is much more serious compared with that of water permeability, i.e., almost 20 times lower than the ethanol permeability of uncrosslinked membranes at 95 wt % ethanol. The diffusivity of a component through a membrane is influenced by its molecular size. Ethanol molecules have a larger size than water molecules. After the membrane is crosslinked, a three-dimensional structure has formed

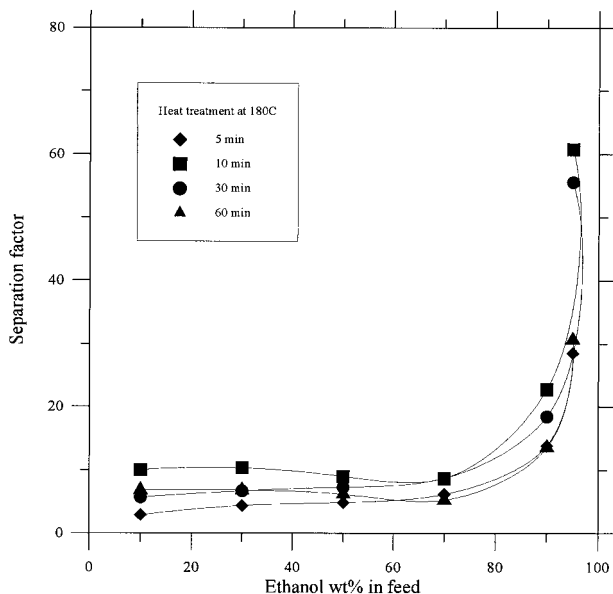


**Figure 10** Ethanol permeability versus ethanol weight percent in feed for NF 105 (degree of substitution = 33%) with different heat treatment times;  $T = 30^{\circ}\text{C}$ .

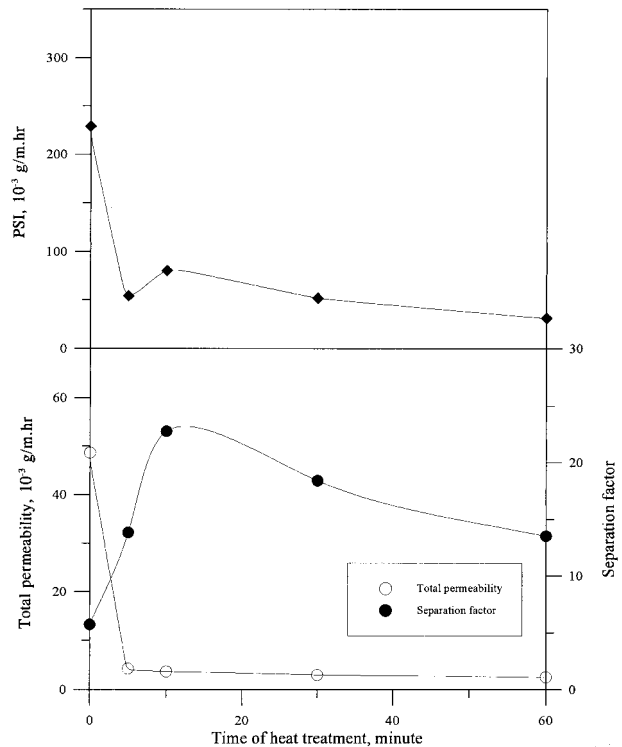
in the membrane and larger molecules have more difficulty in finding an available diffusion path than do smaller molecules. Therefore, the permeability of a component having larger molecular size will decrease more significantly than one having smaller molecular size.

Figure 11 shows the effect of feed concentration on the separation factor for crosslinked membranes. The separation factor does not change very much at lower ethanol concentration but increases abruptly at high ethanol concentration (over 80 wt %).

Figure 12 depicts the pervaporation performance as a function of crosslinking time. As the crosslinking time increases, the total permeability decreases rapidly and then levels off after 10 min. The separation factor rises with an increase of crosslinking time to a maximum value at 10 min, but then decreases slightly thereafter. This might indicate that the crosslinking reaction has been completed in 10 min. Further exposure of membrane at high temperature may degrade the membrane performance. The importance of crosslinking with respect to solubility and diffusivity aspects has already been described. The decrease in solubility and diffusivity due to the crosslinking structure reduces the permeability, while the extent of diffusivity difference between a small molecule (water) and large molecule (ethanol) will become larger. The



**Figure 11** Separation factor versus ethanol weight percent in feed for NF 105 (degree of substitution = 33%) with different heat treatment times;  $T = 30^{\circ}\text{C}$ .



**Figure 12** Total permeability, separation factor, and PSI versus heat treatment time for NF 105 (degree of substitution = 33%);  $T = 30^{\circ}\text{C}$ ; feed concentration: 90 wt % ethanol.

pervaporation separation index as a function of crosslinking time is also described in the upper part of Figure 12. For these crosslinked membranes, a crosslinking time of 10 min gives the best membrane performance, whereas the uncrosslinked membrane is better than all crosslinked membranes in terms of the PSI value, which is due to its very high permeability.

## CONCLUSIONS

*N*-methylol nylon-6 membranes with different degrees of substitution were prepared. Both uncrosslinked and thermally crosslinked membranes were used for the separation of water-ethanol mixtures by pervaporation, and the following conclusions can be drawn:

1. *N*-methylol nylon-6 with different degrees of substitution can be prepared by adjusting the amount of formaldehyde. These modified nylon-6 membranes show a great affinity to ethanol. The crosslinking reac-



tion of *N*-methylol nylon-6 can be done at 180°C and completed in 10 min.

2. Membrane permeability is greatly enhanced by the introduction of a larger CH<sub>2</sub>OH group which reduces the crystallinity and hydrogen bonding in nylon-6. As the degree of substitution increases, the permeability increases and separation factor decreases. The positive deviation of water permeability is caused by membrane plasticization due to ethanol, while the negative deviation of ethanol permeability is governed by diffusion property.
3. Both water and ethanol act to similar extents as plasticizing agents in thermally crosslinked *N*-methylol nylon-6 membrane. Maxima in total and individual component permeabilities can be observed. Crosslinks cause a decrease in permeability and an increase in separation factor.
4. At 30°C and 90 wt % ethanol, a permeability of  $48 \times 10^{-3}$  g/m.h and a separation factor of 6 are obtained by using NF105 (*N*-methylol nylon-6 with 33% substitution), and a permeability of  $4 \times 10^{-3}$  g/m.h and separation factor of 23 are obtained by using thermally crosslinked NF105 membrane.

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