

# Nylon 4/PVA Blend Membrane for Dialysis

J. Y. LAI,\* Y. C. CHEN, and K. Y. HSU

Department of Chemical Engineering, Chung Yuan University, Chung Li, Taiwan, Republic of China

## SYNOPSIS

To improve the hydrophilicity and enhance the transport flux of nylon 4 membrane for dialysis, this study attempts to utilize blending nylon 4 with poly(vinyl alcohol) (PVA). The instability of PVA in water can be significantly improved by esterification of PVA with formic acid when it is used as casting solvent of PVA/nylon 4 blend membrane. By this method, the stability of PVA in water can be obtained more easily than by other methods, such as chemical,  $\gamma$ -ray irradiated crosslinking, or high-temperature treatment used by previous researchers. The effects of maturation time of the casting solution, nylon 4/PVA ratios, and casting solvent compositions on esterification of PVA, salt permeability, water content, partition coefficient, diffusivity, and mechanical strength of membranes are studied. The membrane, prepared by casting solution of nylon 4/PVA = 9/1 wt % formic acid with 24-h maturation time, possesses permeabilities of NaCl and urea, 33.14 and 19.67  $\times 10^{-5}$  cm<sup>2</sup>/min, respectively.

## INTRODUCTION

Previous work on nylon 4 membrane has been carried out by Huang et al.<sup>1,2</sup> To improve the performances of nylon 4 membranes, Lai et al.<sup>3</sup> utilized <sup>60</sup>Co  $\gamma$ -ray irradiation to induce hydrophilic vinyl monomers grafted onto nylon 4 membrane for reverse osmosis desalination purposes. Jong et al.<sup>4</sup> used chemical methods to graft different hydrophilic monomers onto nylon 4 membranes for reverse osmosis, ultrafiltration, and electro dialysis. Nylon 4 membranes were plasma modified to improve the surface energy, water content, and transport fluxes for dialysis by Lai and Chou.<sup>5</sup>

The properties and performances of a composite membrane can also be improved by blending two or more polymers.<sup>6-8</sup> The purpose of this study is to improve the hydrophilicity of nylon 4 membranes by blending poly(vinyl alcohol) (PVA). The instability of PVA in water could be overcome by the esterification of PVA with formic acid, which was used as casting solution. This stabilization method is much more convenient than those of previous re-

searchers, such as chemical,<sup>9,10</sup>  $\gamma$ -ray irradiation crosslinking,<sup>11</sup> or high-temperature treatment.<sup>12</sup>

The factors affecting the degree of esterification of PVA were studied. The effects of maturation time of casting solution PVA/nylon 4 weight ratio, degree of polymerization of PVA, casting solvent composition on solute permeability, water content, partition coefficient, diffusion coefficient, and mechanical strength were studied.

## EXPERIMENTAL

### Materials

Nylon 4 was synthesized by CO<sub>2</sub>-initiated polymerization of 2-pyrrolidone using potassium 2-pyrrolidone as a catalyst.<sup>3</sup> Molecular weights of the samples, measured by a Cannon-Fenske viscometer with *m*-cresol as a solvent at 25°C, were about 28,000–36,000. Molecular weight can be determined from the empirical equation  $\eta = 2.99 \times 10^{-3} M^{0.7}$ .<sup>13</sup>

Two types of PVA used—BF-17 (degree of polymerization, DP = 1700; hydrolysis 98.5–99.2%) and BF-05 (DP = 500; hydrolysis 98.5–99.2%)—were supplied by Chang Chun Petrochemical Co., Ltd. Formic acid was laboratory grade of Shimadzu Pure Chemical Co., Ltd.

\* To whom correspondence should be addressed.

### Membrane Preparation

The casting solutions were prepared by different compositions of nylon 4 and PVA to a total 8 wt % solute in different wt % formic acid aqueous solutions (formic acid–water = 90, 60, 45 wt %) and different maturation times, respectively. It takes about 6 h to dissolve the polymer with formic acid by stirring rigorously. The membrane was formed by casting the solution onto a glass plate to a pre-determined thickness by using a Gardner knife. The glass plate was dried for 30 min at room temperature and heated for 70 min at 30°C in a well-circulated oven.

The membrane was then peeled off and soaked in distilled water for 24 h at least. The average membrane thickness was 40  $\mu\text{m}$ .

### Water Content

The membranes were allowed to soak in beakers of distilled water for 24 h at room temperature. They were then removed, blotted dry, and weighed. The membranes were then placed in a vacuum oven to dry and were reweighed.<sup>14</sup>

$$\text{Water content } (H) = \frac{W_1 - W_2}{W_2} \times 100\%$$

where  $W_1$  and  $W_2$  are the wet and dry weights of the membranes, respectively.

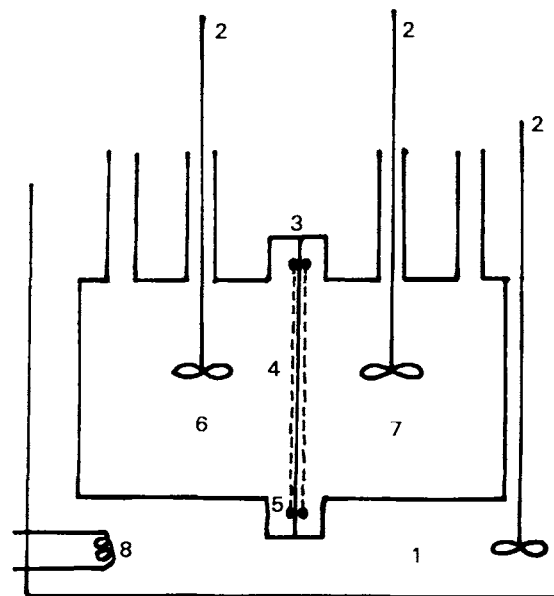
### Dialysis Permeability

The diagram of dialysis testing equipment is shown in Figure 1. A stainless cell consisting of two compartments (171  $\text{cm}^3$ ) was used. A membrane was clamped between two compartments using suitable supporting and sealing devices. One of the compartments was filled with distilled water; the other with a solution of NaCl or urea. The solutions in the compartments were stirred while measuring permeabilities and kept in water bath at  $37.0 \pm 0.5^\circ\text{C}$ .

The permeabilities  $P$  (in  $\text{cm}^2 \text{min}^{-1}$ ), under the assumption of neglecting liquid film resistance of both side of membrane, were calculated from<sup>15</sup>

$$\ln \frac{C'' - C'}{C'' - C' - 2C(t)} = \frac{2PA}{\delta V(t)} t$$

where  $V(t)$  is the volume of the solution at time  $t$ ,  $A$  is the effective membrane area (24.28  $\text{cm}^2$ ),  $\delta$  is the membrane thickness,  $C''$  and  $C'$  are the concen-



**Figure 1** Diagram of dialysis testing equipment: (1) water bath, (2) stirrer, (3) membrane, (4) support, (5) O-ring, (6) concentration solution, (7) dialysis solution, (8) heater.

tration of the concentrate and diluent compartments at the initial time, respectively,  $C(t)$  is the concentration of diluent compartment at time  $t$ . The concentration of NaCl was determined by a conductivity meter Model SC-15 (Suntex). The urea-permeate was added with urease to hydrolyze to  $\text{NH}_4^+$  ion and  $\text{CO}_3^{2-}$  ion. Ion concentrations,  $\text{NH}_4^+$  and  $\text{CO}_3^{2-}$ , were also determined by the conductivity meter.<sup>16</sup>

### Density

Density of the blended membranes were measured at  $25^\circ\text{C}$  using a density gradient column filled with mixtures consisting of varied solutions of carbon tetrachloride and ethanol.

### Partition Coefficient

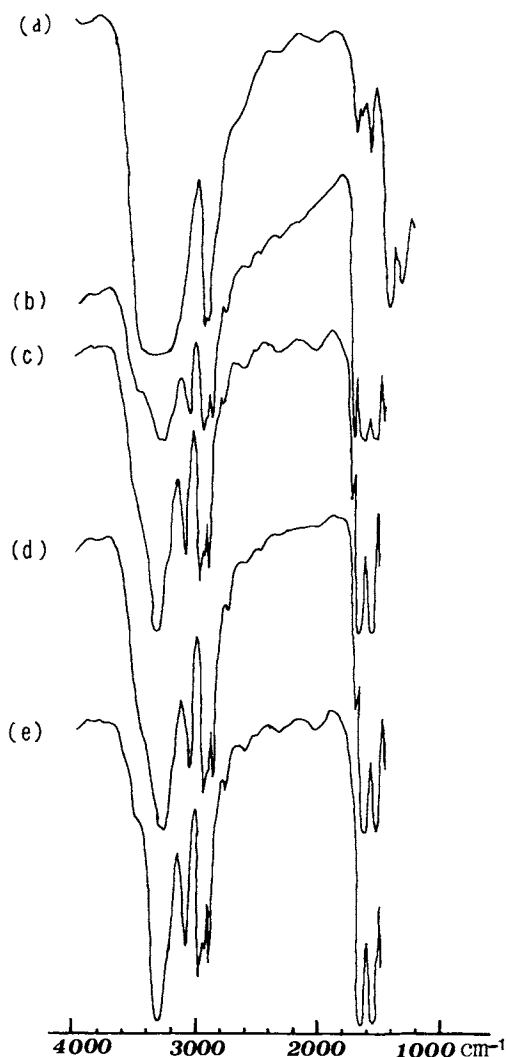
The dried membrane samples were immersed and equilibrated in a solution of the same concentration as the solution in the concentrate compartment of the cell at  $37.0 \pm 0.5^\circ\text{C}$ . After packing up the membrane sample, the extra solution on the surface of the membrane was removed by a filter paper. The membrane sample was then kept in distilled water with shaking for at least 2 h. The amount of solute extracted from the swollen membrane sample by the distilled water was determined by the previously

mentioned method. Partition coefficient  $K_2$  was calculated by the following equation:

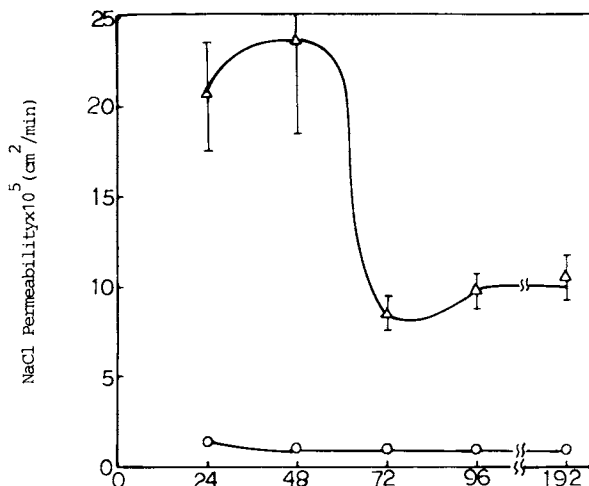
$$K_2 = \frac{\text{grams solute}/1 \text{ cm}^3 \text{ swollen membrane}}{\text{grams solute}/1 \text{ cm}^3 \text{ solution}}$$

### Mechanical Strength Measurements

The tensile strength measurement of blended membranes was carried out on the Toyo Baldwin type Tensilon/UTM-III-100 instrument. The membranes were tested by ASTM method<sup>17</sup> for their tensile strengths and elongations in their dry states.



**Figure 2** FT-IR spectra of pure PVA with various maturation time: (a) solvent, pure water; (b) solvent, 90 wt % formic acid; maturation time, 24 h; (c) solvent, 90 wt % formic acid; maturation time, 48 h; (d) solvent, 90 wt % formic acid; maturation time, 96 h.



**Figure 3** FT-IR spectra of nylon 4/PVA-blended membranes with 10 wt % PVA maturation time 96 h: (a) pure PVA, solvent is pure water; (b) solvent is 90 wt % formic acid; (c) solvent is 60 wt % formic acid; (d) solvent is 45 wt % formic acid; (e) pure nylon 4.

### FT-IR Analysis

FT-IR spectra were obtained at  $1 \text{ cm}^{-1}$  resolution using a Bomem DA 3.002 FT-IR.

## RESULTS AND DISCUSSION

### Esterification of PVA

Utilizing the well-known fact that alcohols can be esterified with acids, this study tried to overcome the instability of nylon 4/PVA-blended membranes in water. The esterification may suppose to be  $\text{acid} + \text{alcohol} \rightleftharpoons \text{ester} + \text{water}$ . The degree of esterification was studied under different maturation times of casting solutions and different concentrations of formic acid, which used as the mutual solvent for PVA and nylon 4.

Pure PVA and nylon 4/PVA-blended membranes were shown to have different degree of esterification by the carbonyl group absorption at  $1715 \text{ cm}^{-1}$  in Figures 2 and 3, respectively. The degree of esterification was represented by the ratio of C=O absorption at  $1715 \text{ cm}^{-1}$  to H—CH absorption at  $2940 \text{ cm}^{-1}$ . As shown in Table I, the degree of esterification reached the maximum value for pure PVA membrane after matured for 18 h by using 90 wt % formic acid. The degree of esterification was found lower at a longer maturation time, presumably due to the degradation of the ester group.

**Table I Esterification of PVA and Nylon 4/PVA Blend Membranes**

Composition Nylon 4/ PVA	Formic Acid Conc. (wt %)	Maturation Time (h)	Degree of Esterification <sup>a</sup>
0/10	90	6	1.08
		12	1.12
		18	1.26
		24	1.02
		48	1.05
		96	1.06
9/1	90	6	0.985
		12	1.00
		18	1.00
		24	0.976
		48	1.00
		96	1.00
9/1	60	6	0.805
		12	0.858
		18	0.805
		24	0.875
		48	0.804
		96	0.812
9/1	45	6	0.655
		12	0.587
		18	0.581
		24	0.740
		48	0.674
		96	0.713

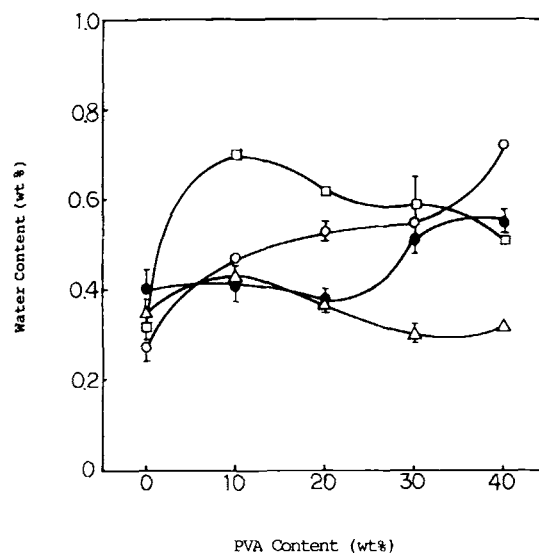
<sup>a</sup> C=O absorption at 1715 cm<sup>-1</sup>/H—CH absorption at 2940 cm<sup>-1</sup>.

For the membranes of nylon 4/PVA = 9/1, the degree of esterification decreased with decreasing formic acid concentration. The maturation time increased with decreasing formic acid concentration up to the maximum degree of esterification. With 90 wt % formic acid, it took about 6 h to reach the maximum value of esterification, but maximum esterification took 24 h with 60 and 45 wt % formic acid.

#### Effect of Maturation Time on Salt Permeability

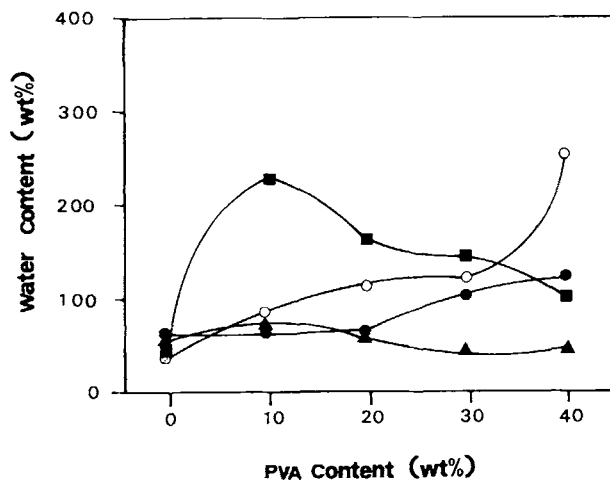
In our previous study,<sup>18</sup> a serious degradation effect existed in nylon 4 with higher formic acid concentration and a longer maturation time.

The study of maturation time effect on salt permeability was therefore carried out with 60 wt % formic acid as a solvent. Figure 4 shows that the sodium chloride permeabilities decreased with in-



**Figure 4** Effect of maturation time on salt permeability: (Δ) 40 wt % PVA content, 60 wt % formic acid, PVA DP = 1700; (○) pure nylon 4, 60 wt % formic acid.

creasing maturation time and leveled off after 48 h for pure nylon 4 dialysis membranes. The explanation is that the mobility of nylon 4 polymer segments increased in 48 h. In the blended membranes the mobility of nylon 4 polymer segments was restrained by the addition of PVA and required a longer time, nearly 72 h, to reach the maximum value.

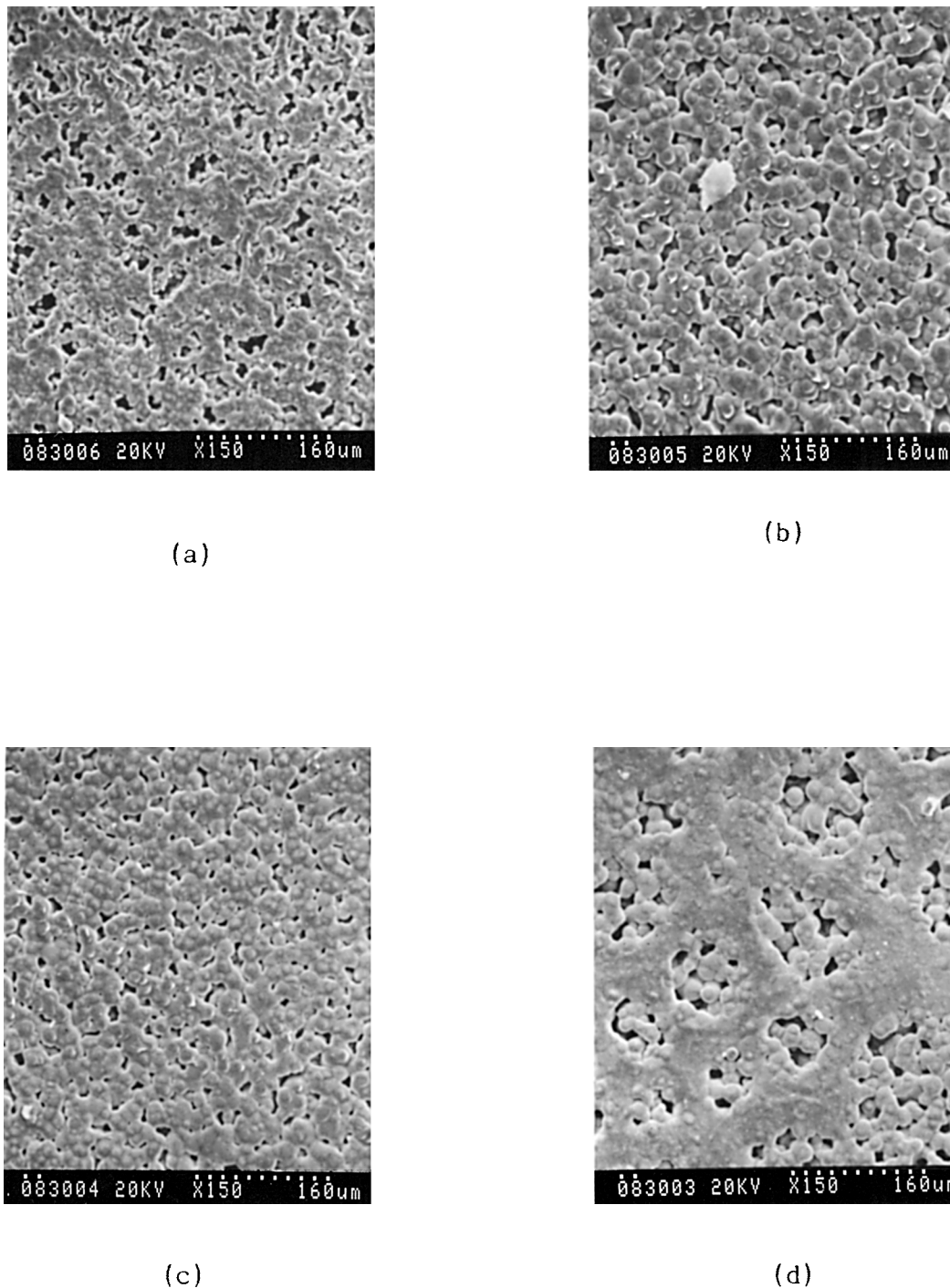


**Figure 5** Effect of PVA content and maturation time on water content. PVA DP = 1700, maturation time 24 h. Formic acid concentration: (▲) 90 wt %; (○) 60 wt %; (■) 45 wt %; (●) maturation time 96 h, formic acid 60 wt %.

**Water Content**

The salt permeability of dialysis membrane in general is higher for more hydrophilic membranes.<sup>19-21</sup>

The factors that affect the water content of the blended membranes considered in this study were the formic acid concentration of casting solvent and composition of the membranes.

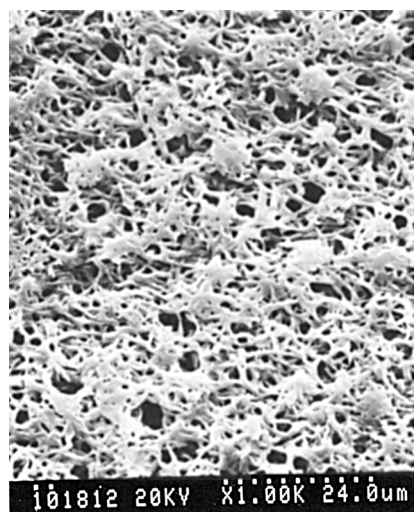


**Figure 6** Scanning electron micrographs of the air side surface for nylon 4/PVA-blended membranes: formic acid concentration 90 wt %, maturation time 24 h, PVA DP = 1700; PVA content: (a) 10 wt %, (b) 20 wt %, (c) 30 wt %, (d) 40 wt %.

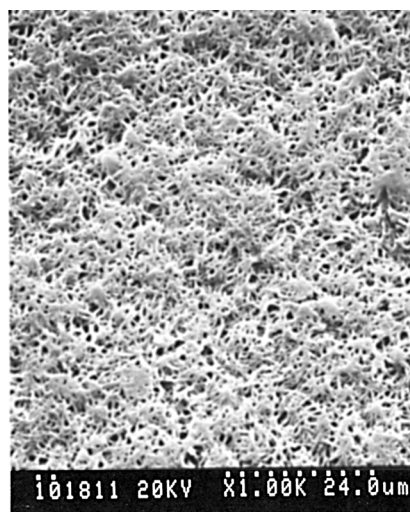
Figure 5 shows the water content of the membrane of nylon 4 membrane of nylon 4/PVA = 9/1 with 90 wt % formic acid, which is greater than that of pure nylon 4 membranes because of the lower phase separation. As the PVA content increases, the water content of the blended membrane decreases, due to the high degree of esterification of

PVA and hence a denser structure. The morphologies of the blended membranes with varying contents of PVA are shown in Figure 6.

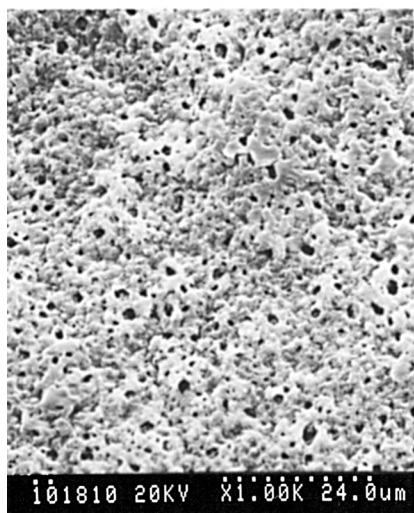
With 60 wt % formic acid, the water content increases with increasing PVA content. This trend caused by the combination effects of phase separation and lower degree of esterification of PVA is



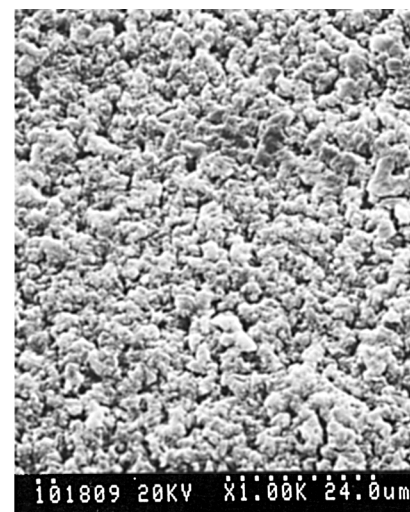
(a)



(b)



(c)



(d)

**Figure 7** Scanning electron micrographs of the air side surface for nylon 4/PVA-blended membranes: formic acid concentration 45 wt %, maturation time 24 h, PVA DP = 1700; PVA content: (a) 10 wt %, (b) 20 wt %, (c) 30 wt %, (d) 40 wt %.

different from that of the previously mentioned membranes with 90 wt % formic acid.

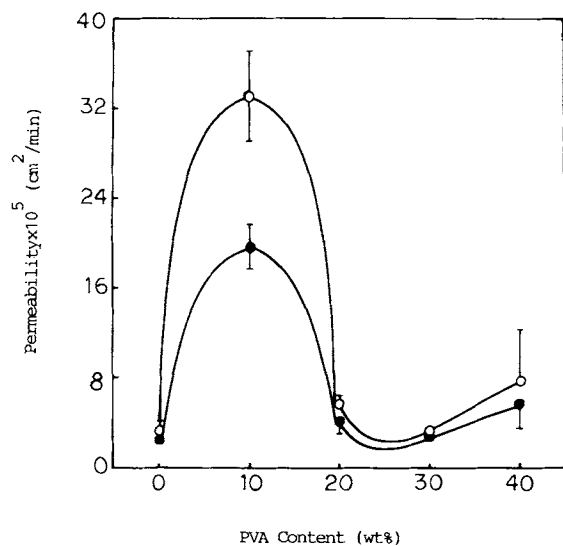
As shown in Figure 7, the membrane packing was more porous for higher nylon 4 content with 45 wt % formic acid used as casting solvent. We found the mobility of nylon 4 segments becomes lower since water is a poor solvent to nylon 4, which was the matrix of 45 wt % aqueous formic acid. This phenomenon explains the relationships between water content and PVA content.

### Effect of PVA Content and Formic Acid

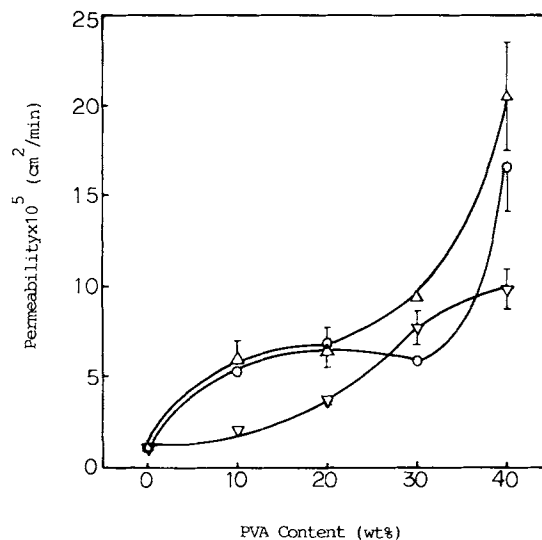
#### Concentration on Permeability

Figure 8 shows the NaCl and urea permeabilities for membranes prepared with 90 wt % formic acid are maximum for 10 wt % PVA content and lower for higher PVA concentration up to 30 wt % due to a high degree of esterification. For 40 wt % PVA, the phase separation plays an important role and causes higher solute permeabilities. The trend of permeability versus PVA content is similar to that of water content versus PVA content, the highest permeabilities of NaCl and urea are  $33.14$  and  $19.67 \times 10^{-5} \text{ cm}^2/\text{min}$ , respectively.

For 60 wt % formic acid, as shown in Figure 9, the permeabilities of NaCl and urea are higher as PVA content increases. The trend is quite different from that of the membrane using 90 wt % formic acid. The reason is that degree of esterification of

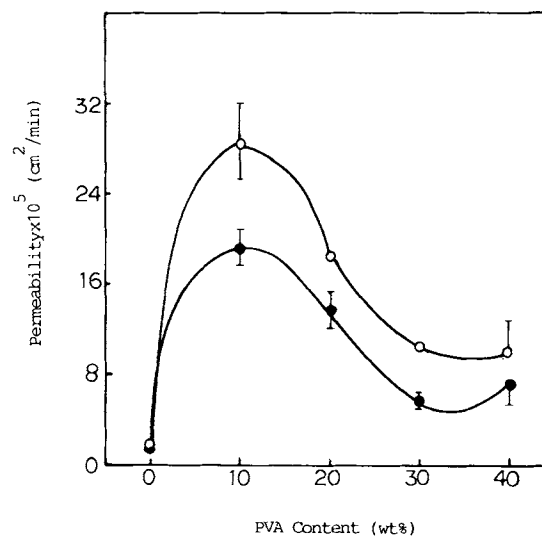


**Figure 8** Effect of PVA content on solutes permeabilities: PVA DP = 1700, maturation time 24 h, formic acid 90 wt %: (○) NaCl, (●) urea.

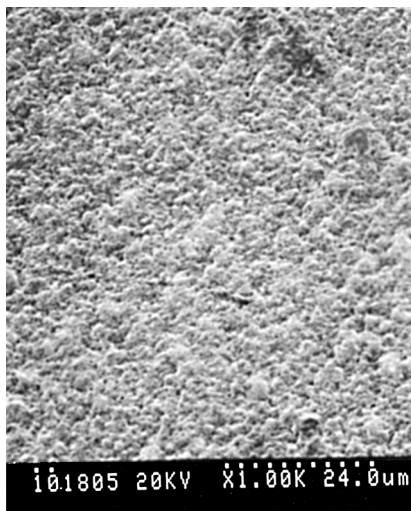


**Figure 9** Effect of PVA content and maturation time on solutes permeabilities: PVA DP = 1700, formic acid 60 wt %: (a) maturation time 24 h; ( $\Delta$ ) NaCl, (○) urea; (b) maturation time 96 h; ( $\nabla$ ) NaCl.

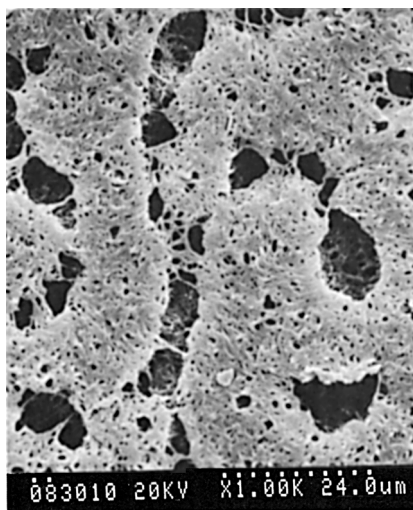
the membrane using 60 wt % formic acid is not as high as that using 90 wt % formic acid. This makes the membrane that used 60 wt % formic acid possess a higher water content and hence higher salt permeabilities as PVA content increases. The permeability of the blended membrane having 96-h maturation time is lower than that for 24 h. This can be explained by assuming that the mobility of polymer segments are increased with increasing matu-



**Figure 10** Effect of PVA content on solutes permeabilities: PVA DP = 1700, formic acid 45 wt %, maturation time 24 h: (○) NaCl, (●) urea.



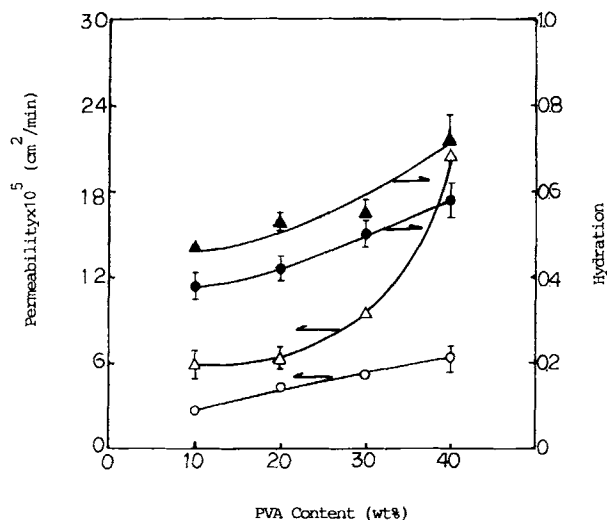
(a)



(b)

**Figure 11** Scanning electron micrographs of the air side surface for 40 wt % PVA-blended membranes, formic acid 60 wt %, maturation time 24 h: PVA DP (a) 500, (b) 1700.

ration time and thus decrease the salts permeabilities. The permeabilities of NaCl and urea are 20.84 and  $16.57 \times 10^{-5} \text{cm}^2/\text{min}$ , respectively, for blended

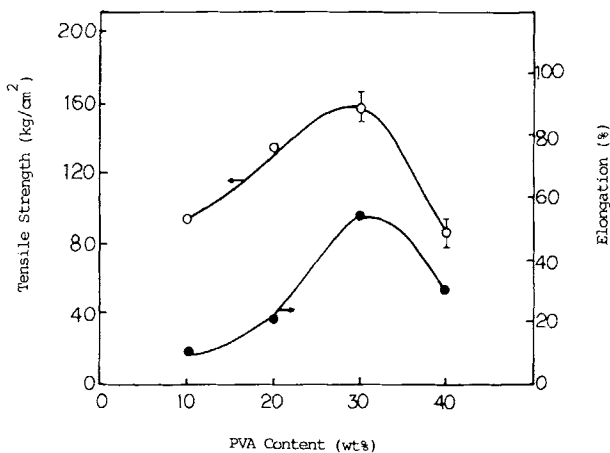


**Figure 12** Effect of PVA molecular weight on water content and solute permeability: formic acid 60 wt %, maturation time 24 h: (a) (O, ●) PVA DP = 500, (b) (Δ, ▲) PVA DP = 1700.

membrane with 40 wt % PVA for 24-h maturation time.

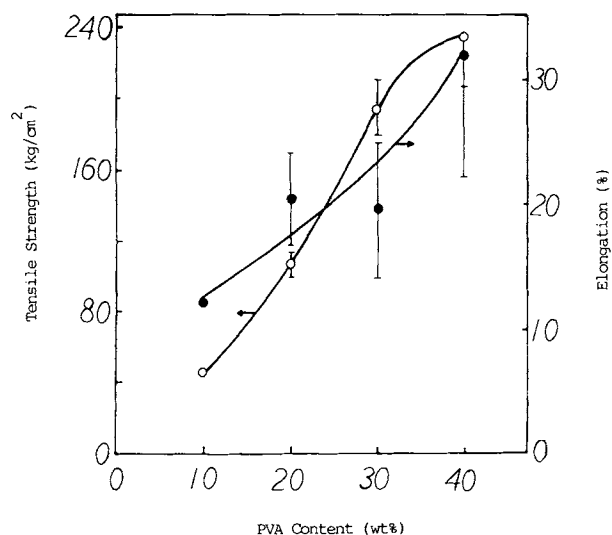
As mentioned earlier, the membrane was more porous for higher nylon 4 content as 45 wt % formic aqueous solution was used. This fact makes the permeabilities decrease as PVA concentration increases, as shown in Figure 10. The highest permeabilities of NaCl and urea are  $28.69$  and  $19.32 \times 10^{-5} \text{cm}^2/\text{min}$ , respectively, for membranes of nylon 4/PVA = 9/1.

The correlation between solute permeabilities and PVA content in the blended membrane is quite similar to that between water content and PVA content. This study indicates that salt permeability is well



**Figure 13** Effect of PVA content on mechanical strength: PVA DP = 1700, formic acid 90 wt %, maturation time 24 h.





**Figure 14** Effect of PVA content on mechanical strength: PVA DP = 1700, formic acid 45 wt %, maturation time 24 h.

related to the hydrophilicity of nylon 4/PVA-blended membrane.

#### Effect of PVA Molecular Weight on Water Content and Solute Permeability

Two different molecular weights of PVA, namely, DP = 500 and 1700, were considered for this study. As shown in Figure 11, the membrane prepared with lower molecular weight of PVA possesses better homogeneity. Figure 12 shows the water content and solute permeabilities are found lower for the membrane with better homogeneity.

#### Mechanical Strength of Blended Membrane

Figure 13 shows that the tensile strength and elongation of the membranes prepared with 90 wt %

formic acid increase with increasing PVA content up to 30 wt % and then decrease for higher PVA content. This can be explained by the high degree of esterification, which affects the increase of mechanical strength and that the phase separation plays an important role for the membranes with higher PVA content.

As shown in Figure 14, the tensile strength and elongation of the membrane prepared with 45 wt % formic acid increases with increasing PVA content or with decreasing nylon 4 content. Since water, which is the solvent in the 45 wt % formic acid aqueous solution, is a poor solvent of nylon 4, the lower homogeneity of the blended membrane would be caused by higher content of nylon 4.

Using 60 wt % formic acid as casting solvent, for longer maturation time, the mechanical strength of the blended membranes could be improved. This is shown in Table II.

#### Partition Coefficient and Diffusion Coefficient

The relation among solute permeability, partition coefficient, and diffusion coefficient is expressed in the following equation:

$$D_{2,13} = P_{2,13}/K_2 \quad (1)$$

where the subscripts 1, 2, 3, and 13 refer to water, solute, polymer, and water-swollen polymer, respectively. The diffusion coefficients,  $D$ , were calculated by using Eq. (1). The  $P$ ,  $K$ , and  $D$  values for some typical blended membranes are listed in Table III. The solute permeability is relatively high compared to those observed by the previous researchers.<sup>22-24</sup> There is one result worth mentioning that both partition coefficient and diffusion coefficient are lower for the membranes with longer maturation time.

**Table II** Effect of PVA Content and Maturation Time on Mechanical Strength

Composition Nylon 4/PVA	Maturation Time (h)	Tensile Strength Time (kg/cm <sup>2</sup> )	Elongation (%)
9/1	24	266.78 ± 23.01	38.63 ± 6.05
	96	422.39 ± 79.02	69.28 ± 22.00
7/3	24	230.36 ± 7.54	36.22 ± 1.18
	96	422.61 ± 49.43	88.96 ± 24.11
6/4	24	97.42 ± 6.08	102.25 ± 4.34
	96	259.05 ± 40.73	105.47 ± 3.00

Formic acid conc.: 60 wt %; PVA DP = 1700.

**Table III Permeability  $P_{2,13}$ , Partition Coefficient  $K_2$ , and Diffusion Coefficient  $D_{2,13}$  of Sodium Chloride for Various Nylon 4/PVA Blended Membranes**

PVA <sup>a</sup> Content (wt %)	Formic Acid		$P_{2,13} \times 10^5$ (cm <sup>2</sup> /min)	$K_2$	$D_{2,13} \times 10^5$ (cm <sup>2</sup> /min)
	Conc. (wt %)	Maturation Time (h)			
10	90	24	33.14 ± 3.84	0.712 ± 0.044	46.94 ± 7.68
10	90	96	1.86 ± 0.89	0.326 ± 0.030	5.66 ± 2.50
20	90	24	5.73 ± 0.71	0.506 ± 0.060	11.38 ± 1.31
40	60	24	20.84 ± 4.16	1.276 ± 0.122	16.31 ± 2.67
40	60	96	9.16 ± 1.07	0.657 ± 0.121	14.37 ± 4.32
20	60	24	6.76 ± 0.56	0.781 ± 0.162	8.79 ± 1.21

<sup>a</sup> PVA DP = 1700.

The authors wish to thank the National Science Council of The Republic of China for financial support.

## REFERENCES

- R. Y. M. Huang, U. Y. Kim, J. M. Dickson, D. R. Lloyd, and C. Y. Peng, *J. Appl. Polym. Sci.*, **26**, 1135 (1981).
- R. Y. M. Huang, U. Y. Kim, J. M. Dickson, D. R. Lloyd, and C. Y. Peng, *J. Appl. Polym. Sci.*, **26**, 1907 (1981).
- J. Y. Lai, T. C. Chang, Z. J. Wu, and T. S. Hsieh, *J. Appl. Polym. Sci.*, **32**, 4709 (1986).
- A. Jong, T. C. Chang, and J. Y. Lai, *J. Appl. Polym. Sci.*, **36**, 87 (1988).
- J. Y. Lai and C. C. Chou, *J. Appl. Polym. Sci.*, **37**, 1465 (1989).
- S. R. Murff, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **29**, 3231 (1984).
- Q. T. Nguyen, L. L. Blanc, and J. Neel, *J. Membr. Sci.*, **22**, 245 (1985).
- R. Y. M. Huang, A. Moreira, R. Notarfonzo, and Y. F. Xu, *J. Appl. Polym. Sci.*, **35**, 1191 (1988).
- Y. J. Chang, C. T. Chen, and A. V. Tobolsky, *J. Polym. Sci. Polym. Phys. Ed.*, **12**, 1 (1974).
- O. M. Ebra-Lima and D. R. Paul, *J. Appl. Polym. Sci.*, **19**, 1381 (1975).
- M. G. Katz and T. Wydeven, *J. Appl. Polym. Sci.*, **26**, 2935 (1981).
- K. Koyama, M. Okada, and M. Nishimura, *J. Appl. Polym. Sci.*, **27**, 2783 (1982).
- H. Schnell and L. Bottenbruch, *Makromol. Chem.*, **57**, 1 (1962).
- V. Shantora and R. Y. M. Huang, *J. Appl. Polym. Sci.*, **26**, 3223 (1981).
- S. Takigami, Y. Maeda, and Y. Nakamura, *J. Appl. Polym. Sci.*, **24**, 1419 (1979).
- R. J. Williams and E. M. Lansford, *The Encyclopedia of Biochemistry*, Reinhold, New York, 1967, p. 820.
- L. E. Nielsen, Ed., *Mechanical Properties of Polymers and Composites*, Dekker, New York, 1974, Vol. 1, p. 292.
- J. Y. Lai and Y. C. Chao, *J. Appl. Polym. Sci.*, **39**, 2293 (1990).
- H. Yasuda, C. E. Lamaze, and L. D. Ikenberry, *Makromol. Chem.*, **118**, 19 (1968).
- H. Yasuda, L. D. Ikenberry, and C. E. Lamaze, *Makromol. Chem.*, **125**, 108 (1969).
- H. Yasuda and C. E. Lamaze, *J. Macromol. Sci. Phys. B*, **5**(1), 111 (1971).
- S. Takigami, Y. Maeda, and Y. Nakamura, *J. Appl. Polym. Sci.*, **24**, 1429 (1979).
- S. C. Yoon and M. S. Jhon, *J. Appl. Polym. Sci.*, **27**, 3133 (1982).
- S. N. Bhattacharyya and D. Maldas, *J. Appl. Polym. Sci.*, **30**, 159 (1985).

Received August 3, 1989

Accepted January 14, 1991