

Plasma-Modified Nylon 4 Membranes for Reverse Osmosis Desalination

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Synopsis

The effects of maturation time of casting solution and annealing conditions on reverse osmosis (RO) properties of nylon 4 membranes are studied. The effects of plasma treatment conditions, such as supply power, treatment time, and gases used in reactor, on the water contact angle, surface energy, water flux, and salt rejection of nylon 4 membranes are considered. The best results of 4.86×10^{-5} g/cm² s of water flux with 74.2% of salt rejection for 1 wt % NaCl aqueous feed solution can be obtained in the conditions of plasma treatment for 80 W-3 min in a reactor with O₂ on 25 wt % formic acid-4 h annealing nylon 4 membranes. The hydrophilic monomers, such as 1-vinyl-2-pyrrolidone (VP), 2-hydroxyethyl methacrylate (HEMA), and acrylic acid (AA), are plasma deposited onto the chemical and/or plasma etched nylon 4 membranes to improve the salt rejection without decrease in water flux. The salt rejection of 90.9% and water flux of 3.64×10^{-5} g/cm² s of the deposited membrane are obtained in the conditions of depositing AA monomer onto the substrate membrane which was previously treated with annealing followed with plasma etching.

INTRODUCTION

By using the improved polypyrrolidone synthesis and membrane preparation, a good separation performance of nylon 4 membranes was prepared by Huang et al.^{1,2} To improve the RO performances of nylon 4 membranes, Lai, Change, Wu, and Hsieh utilized ⁶⁰Co γ -ray irradiation to induce hydrophilic vinyl monomers to be grafted onto nylon 4 membranes; this was studied in our previous reports.³ Both the water flux and salt rejection were significantly improved. Chemical method of graft monomers onto nylon 4 membranes was also utilized for improving nylon 4 membranes by our laboratory.⁴ Glow discharge (plasma) has been utilized to increase surface energy, plasma polymerization, etching in membrane modification,⁵⁻⁸ and biomedical application.^{9,10} Buck and Davar¹¹ first reported that high salt rejection RO membrane could be obtained by the plasma polymerization. Yasuda¹² and Hollahan¹³ indicated that the nitrogen-containing monomers used for preparing membranes by plasma polymerization provided highly functional properties of RO.

The first phase of this report is to increase surface energy and hence improve the water flux of nylon 4 membranes by plasma treatment under different gases, such as Ar, N₂, O₂. The second phase is to deposit hydrophilic monomers, such as HEMA, VP, and AA onto nylon 4 membranes for improving the salt rejection. The effects of plasma treatment conditions, such as supply power, treatment time, gases used in reactor, kinds of monomers on surface energy, water flux, and salt rejection of nylon 4 membranes are

considered. The effects of maturation time of casting polymer solution and different kinds of nylon 4 membrane substrates on performances of plasma-treated nylon 4 membranes are also studied.

EXPERIMENTAL

Polymer Synthesis

Nylon 4 was synthesized by CO₂-initiated polymerization of 2-pyrrolidone using potassium 2-pyrrolidonate as a catalyst.³ The molecular weights of nylon 4 as measured by a Cannon-Fenske viscometer with *m*-creso as a solvent at 25°C were about 20,000–25,000.

Membrane Preparation

Reverse osmosis membrane was prepared from a formic acid-casting solution of nylon 4 added with *n*-PrOH as a swelling agent.^{2,3} The casting condition for the membrane was heat treatment at 70°C for 40 min to evaporate solvent and to provide a suitable pore size of membrane. The membrane's thickness was in the range of 20–25 μm.

Reverse Osmosis Properties

The RO runs were carried out in RO high-pressure testing equipment (Schleicher & Schill Co., Type RO-03). The apparatus consists of three testing cells that can test three membranes at the same time. The permeate which flowed down from the cells was collected to be measured. All the RO runs were conducted at 41 kg/cm² at a temperature of 25°C with 1.0 wt % sodium chloride aqueous solution. The water flux (WF) and the salt rejection (SR) were determined by the following equations:

$$WF = V/A \times t \text{ (g/cm}^2 \text{ s)}$$

$$SR = [(C_{f1} - C_{f2})/C_{f2}] \times 100\%$$

where *V* is the permeate volume, *A* is the effective membrane area, *t* is the operation time, and *C_{f1}* and *C_{f2}* are the feed and permeate concentrations, respectively. The sodium chloride concentrations were determined by a conductivity meter.

Plasma Treatment

Bell jar type plasma deposition system PD-2S (made by Samco Ltd., Japan) was used in this study as in the previous report.¹⁴ The membrane was placed between two electrodes. After the system has been pumped down (less than 0.04 m kg/cm²), gases (O₂, N₂, Ar) or monomers (HEMA, VP, AA) are introduced into the reactor through the system which is allowed to equilibrate at the desired pressure. The plasma is then ignited at the required power for a fixed time interval. All monomers used to prepare reverse osmosis samples were previously degassed and thereafter kept under vacuum. The membrane was treated by gas (O₂, N₂, Ar) plasma at a pressure of 0.2 m kg/cm², and by

monomer (HEMA, VP, AA) plasma at a pressure of 0.04 m kg/cm², a frequency of 13.65 MHz, and the range of supply power from 1 to 100 W for 1–60 min.

Surface Energy

Contact angles of water, formamide, ethylene glycol, and tricresyl phosphate on the membranes were measured with a contact angle viewer model D-1060 (Kayeness, Inc.) at 25°C. The contact angle data were to estimate the surface energy by Kaeble's method.¹⁵

Annealing of Membrane

Membranes were immersed in 25% formic acid aqueous solution at temperature of 25°C for 1–5 h.

RESULTS AND DISCUSSION

Effect of Maturation Time of Nylon 4 Casting Solution

The factors, such as solvent evaporation time, heat treatment temperature, and molecular weight of polypyrrolidone, that affect the performances of nylon 4 membranes were studied in our previous paper.³ The effects of maturation time of casting polymer solution before casting and annealing conditions on transport properties of nylon 4 membranes are considered in this report.

Figure 1 shows that the flux decreases and the salt rejection increases as the maturation time increases. For longer than 700 h the water flux increases and

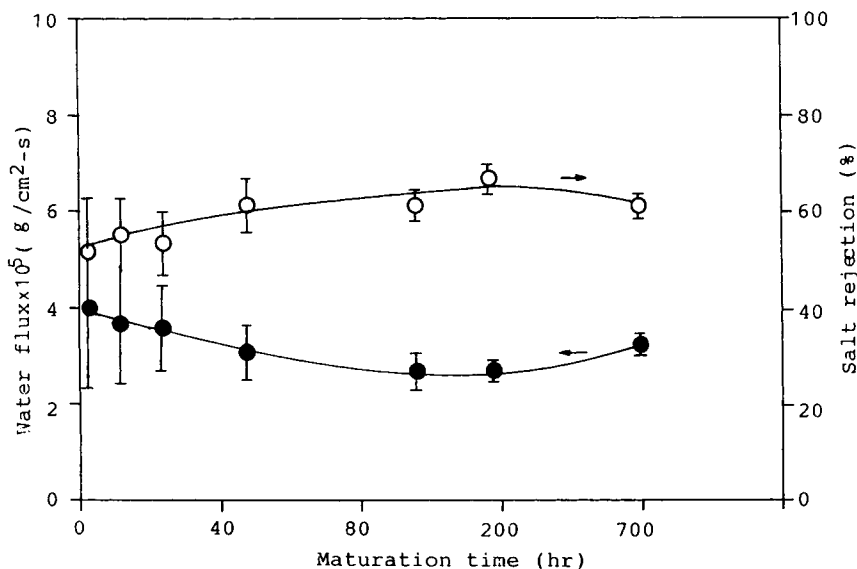


Fig. 1. Effect of maturation time of casting solution before casting on water flux (●) and salt rejection (○). Feed concentration, 1 wt % NaCl; operating pressure, 41 kg/cm²; operating temperature, 25°C.

salt rejection decreases. Higher fluctuations for both water flux and salt rejection are found at lower maturation time, and stable for longer than 100 h. It could be explained that nylon 4 molecule chains could not be extended thoroughly if the dissolving time in formic acid was not enough. From this result it suggests that the proper maturation time is over 100 h for better reproducibility of water flux and salt rejection of the membrane.

Effect of Annealing

Haruvy et al.^{16,17} reported that the water flux increased and salt rejection decreased after nylon 6 graft acrylamide membrane was immersed in 65% formic acid aqueous solution. In our laboratory nylon 4 membrane was immersed in a 25% formic acid aqueous solution which is about the maximum concentration at which the membrane cannot be dissolved. In Figure 2, it indicates that the water flux does not increase evidently before 2 h of annealing time, and then increases rapidly. The salt rejection of the annealing treated membrane keeps constant for 4 h, which is almost same as the original unannealing nylon 4 membrane, and then it decreases significantly. Before 2 h in this annealing process it is in the period of protonation, and after 2 h in the period of hydrolysis.¹⁸⁻²⁰ This is verified by the SEM study, as shown in Figures 3(a) and (b).

The optimal annealing time is 4 h for significant improvement of water flux without decrease of salt rejection from this study.

Effect of Gas Plasma Treatment

The surface energy and water contact angle of nylon 4 membrane are 43.1 dyn/cm and 75°, respectively. As shown in Figure 4, the water contact angles decrease to 27–30° under a 40–100-W supply power with 5–20-min plasma

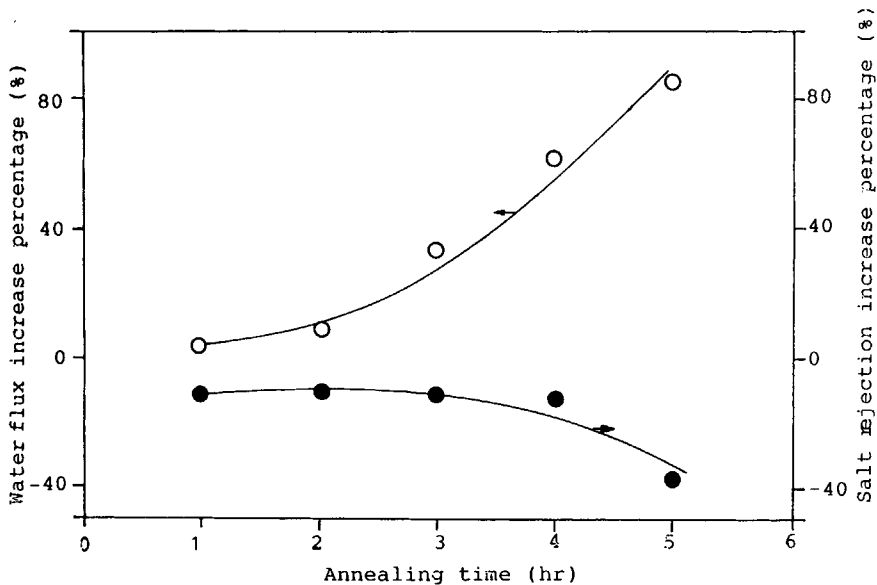
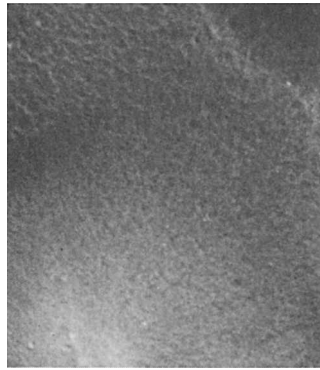
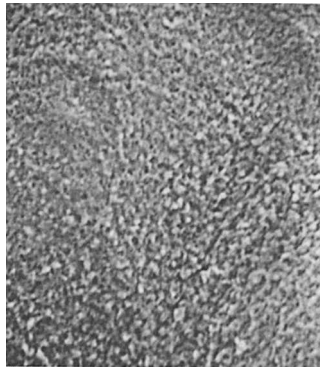


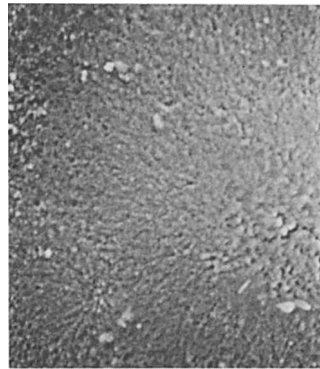
Fig. 2. Effect of annealing time of nylon 4 membrane on water flux (○) and salt rejection (●). Annealing with 25% formic acid aqueous solution at 25°C.



(a)



(b)



(c)

Fig. 3. SEM ($\times 10,000$) of chemical annealing and plasma etching: (a) annealing 1 h; (b) annealing 4 h; (c) O_2 , 80 W, 3 min, 0.2 m kg/cm^2 .

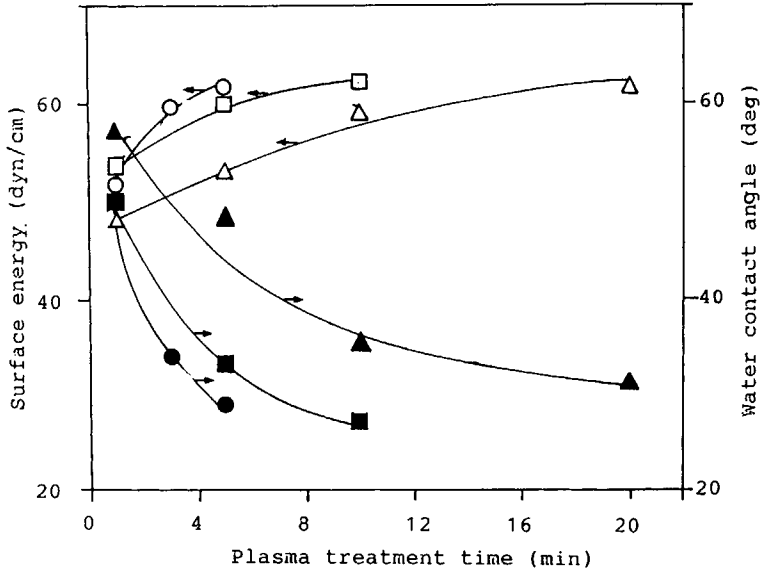


Fig. 4. Effect of oxygen plasma treatment time on surface energy and water contact angle. Plasma condition: (Δ) 40 W; (\square) 80 W; (\circ) 100 W.

treatment time in a reactor with oxygen. It also shows that the surface energy increases with increasing plasma treatment time and supply power. The surface energies of argon and nitrogen plasma-treated membranes are increased to 56.3 and 55.9 dyn/cm, respectively, under a 100-W power supply with 20-min plasma treatment time. As shown in Figure 3(c), the membrane surface etched by plasma treatment was not as serious as by formic acid annealing.

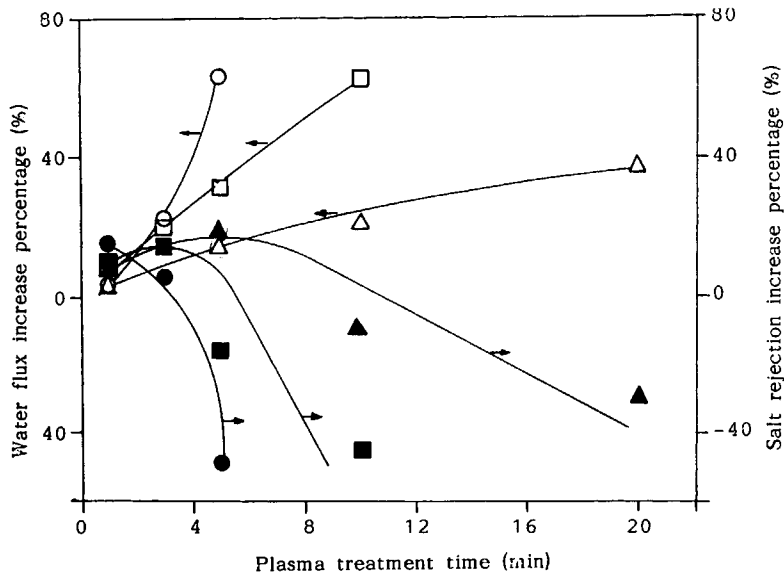


Fig. 5. Effect of oxygen plasma treatment time on water flux and salt rejection of nylon 4 membrane. Plasma condition: (Δ) 40 W; (\square) 80 W; (\circ) 100 W.

TABLE I
Effect of Various Gases Plasma Treatment on Unannealing Nylon 4
Membrane Performance (80 W, 3 min, 0.2 m kg/cm²)

Plasma-treated gases	WF × 10 ⁵ (g/cm ² s)	SR (%)
Untreated	2.69 ± 0.03	66.7 ± 0.92
O ₂	3.61 ± 0.23	73.1 ± 0.50
N ₂	3.28 ± 0.06	69.7 ± 2.25
Ar	3.31 ± 0.04	68.9 ± 3.04

The pure water permeability, water flux, and salt rejection of pure nylon 4 membranes with 70°C–40 min heat treatment are 3.05×10^{-5} g/cm² s, 2.69×10^{-5} g/cm² s, and 66.7%, respectively. Figure 5 shows the effect of power supply and oxygen plasma treatment time on RO properties of nylon 4 membranes. The water flux increases remarkably and the salt rejection decreases when the plasma supply power of 100 W is used. For 40- and 80-W supply power, the salt rejection increases gradually and passes through a maximum for a short time treatment and then decreases rapidly for a longer time. This could be explained by the fact that the surface energy rapidly increasing for short plasma treatment time plays an important role and the etching effect plays a major role for longer plasma treatment time.

Table I shows that the water flux increases of membranes with argon and nitrogen plasma treatment are not as much as that of the membranes with oxygen plasma treatment. It is well known that the polar groups are always incorporated onto plasma-treated polymer surfaces regardless of gas types. Argon plasma treatment is a physical sputtering, which is essentially a momentum-exchange process. Argon plasma can ionize other molecules or sputter materials but is not consumed in chemical reaction. Nitrogen plasma treatment is a chemical reactive process that causes no oxidation but hydrophilic groups incorporate onto the surface of substrate. The strong etching effect of oxygen plasma treatment is due to its oxidation of materials' surfaces. Table II indicates that the water flux of the plasma-treated membrane with annealing is highly improved comparing to that of membrane without annealing. The best performance of 4.86×10^{-5} mL/cm² s of water flux with 74.2% of salt rejection can be obtained in the conditions of plasma treatment for 80 W, 3 min in a reactor with oxygen, on 4-h annealing nylon 4 membrane.

TABLE II
Effect of Annealing and Unannealing before Plasma Treatment on
Nylon 4 Membrane Performances

Plasma treatment conditions	WF × 10 ⁵ (g/cm ² s)		SR (%)	
	Unannealing	Annealing ^a	Unannealing	Annealing ^a
40 W, 5 min in O ₂	3.18 ± 0.04	4.72 ± 0.41	75.3 ± 0.58	67.8 ± 1.69
80 W, 3 min in O ₂	3.61 ± 0.23	4.86 ± 0.17	73.1 ± 0.50	74.2 ± 1.69
100 W, 3 min in O ₂	3.60 ± 0.19	5.10 ± 0.28	66.7 ± 1.09	69.7 ± 1.81

^aAnnealing with 25% formic acid aqueous solution at 25°C for 4 h.

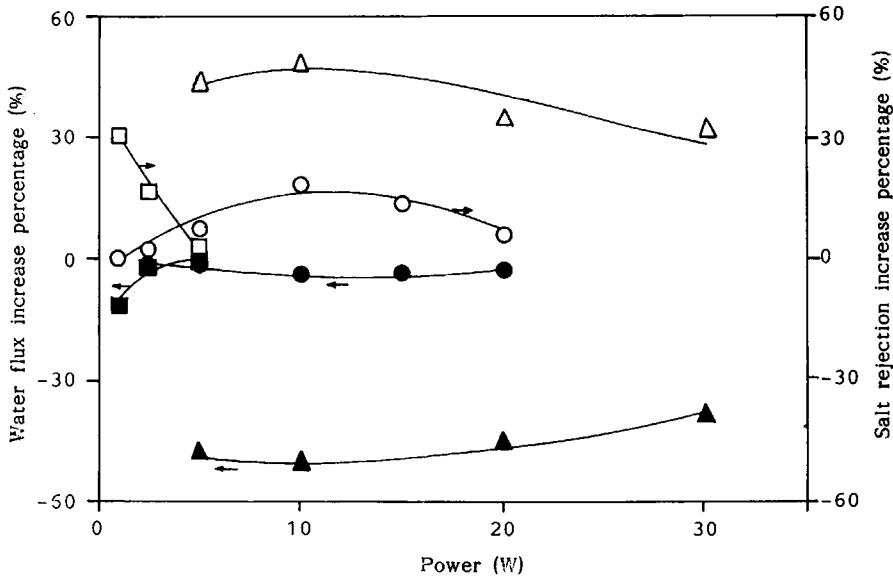


Fig. 6. Effect of VP, HEMA, and AA plasma deposition supply power on water flux and salt rejection. Plasma deposition condition: 1 h, 0.04 m kg/cm² for VP (□) and HEMA (○); 30 min, 0.04 m kg/cm² for AA (Δ).

TABLE III
Performances of VP, HEMA, and AA Plasma-Deposited
Unannealing Nylon 4 Membranes

Monomer used in plasma deposited membranes	WF × 10 ⁵ (g/cm ² s)	SR (%)
Undeposited	2.69 ± 0.03	66.7 ± 0.92
VP ^a	2.05 ± 0.25	80.4 ± 7.56
HEMA ^b	2.64 ± 0.05	74.9 ± 1.40
AA ^c	1.48 ± 0.10	93.9 ± 1.09

^a Plasma deposition condition, 1 W, 1 h, 0.04 m kg/cm².

^b Plasma deposition condition, 10 W, 1 h, 0.04 m kg/cm².

^c Plasma deposition condition, 10 W, 30 min, 0.04 m kg/cm².

TABLE IV
Effect of Monomers Deposited on Water Contact Angle and Surface Energy

Monomer used in plasma deposited membranes	Water contact angle	Surface energy
Undeposited	75	43.1
VP ^a	32	61.0
HEMA ^b	65	44.9
AA ^c	54	51.2

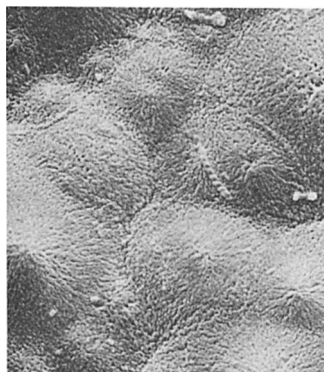
^a Plasma deposition condition, 1 W, 1 h, 0.04 m kg/cm².

^b Plasma deposition condition, 10 W, 1 h, 0.04 m kg/cm².

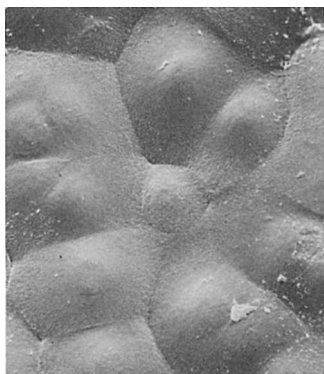
^c Plasma deposition condition, 10 W, 30 min, 0.04 m kg/cm².

Effect of Monomer Plasma Deposition

Figure 6 shows that the salt rejection of nylon 4 membrane increases and reaches a maximum and then decreases as the supply power increases for depositing HEMA onto nylon 4 membrane at a constant depositing time of 60 min. The water flux is almost kept the same as non-plasma-treated membrane.



(b)



(c)

Fig. 7. SEM ($\times 3500$) of monomers plasma deposition: (a) HEMA; (b) VP; (c) AA.

For constant depositing time of 60 min, the HEMA plasma depositing is essentially a polymer formation process for supply power less than 10 W and appreciably affected by ablation process for higher supply power. Similar results were reported by Yusuda²¹ and John et al.²² The supply power is limited to 2 W for depositing VP onto the membrane due to the serious ablation effect. As shown in Table III, the salt rejections are increased and the water fluxes are decreased compared to those of the original nylon 4 membranes for VP, HEMA, and AA monomer-deposited nylon 4 membranes. Table IV shows that the water contact angles are decreased and surface energies are increased by depositing monomers onto unannealing nylon 4 membranes. The polymers of VP and AA by chemical polymerization are soluble in water, but by plasma polymerization they are not soluble in water due to crosslinking. This explains why the surface energies and hence the water fluxes of monomers deposited membranes are not higher. The hydrophilicity of HEMA is also decreased due to crosslinking caused by plasma polymerization. The SEM study of Figure 7 shows that, among the three deposited membranes, the surface structure of poly(HEMA) is the loosest and highest voids due to its longest molecular side chain and hence largest free volume of polymer. This causes the highest water fluxes and the lowest salt rejection of HEMA-deposited membranes. The surface of poly(AA) deposited membrane is smooth, tight, and with much less voids. The surface structure makes the water flux of AA-deposited membranes lower and PAA with charge makes the salt rejection higher.

Effect of Substrates

Though the salt rejection is improved, the water flux is still low for the monomer-deposited nonetched nylon 4 membranes. In order to improve the water flux of deposited membranes, three methods are considered: (1) nylon 4 membranes are treated with formic acid annealing; (2) nylon 4 membranes are treated with oxygen plasma etching; (3) nylon 4 membranes are treated with annealing followed with oxygen plasma etching.

TABLE V
Effect of Substrates on Performances of Plasma-Deposited membrane

Monomer used in deposited membranes	Substrates used					
	With annealing ^a		With O ₂ plasma etching ^b		With annealing and O ₂ plasma etching	
	WF × 10 ⁵ (g/cm ² s)	SR (%)	WF × 10 ⁵ (g/cm ² s)	SR (%)	WF × 10 ⁵ (g/cm ² s)	SR (%)
VP ^c	4.12 ± 0.12	78.8 ± 1.54	3.05 ± 0.12	87.4 ± 3.65	4.85 ± 0.24	84.2 ± 1.94
HEMA ^d	4.42 ± 0.21	74.5 ± 1.56	3.25 ± 0.34	78.7 ± 2.24	4.97 ± 0.40	76.4 ± 2.75
AA ^e	3.36 ± 0.55	87.3 ± 3.8	2.08 ± 0.15	95.0 ± 2.81	3.64 ± 0.29	90.9 ± 3.29

^aAnnealing condition, 25% formic acid aqueous solution at 25°C.

^bPlasma treatment condition, O₂, 80 W, 3 min, 0.2 m kg/cm².

^cPlasma deposition condition, 1 W, 1 h, 0.04 m kg/cm².

^dPlasma deposition condition, 10 W, 1 h, 0.04 m kg/cm².

^ePlasma deposition condition, 10 W, 30 min, 0.04 m kg/cm².

The performances of monomer plasma deposited onto substrates with different methods of treatment are listed in Table V. Both the water fluxes and salt rejections of deposited membranes are increased by using etched membrane substrates and depositing monomers, respectively. The method with annealing followed with oxygen plasma etching is the most promising. The salt rejection of 90.9% with water flux of 3.64×10^{-5} g/cm² s of the deposited membrane is obtained in the conditions of depositing AA monomer onto the substrate membrane previously treated with chemical annealing followed with oxygen plasma etching. The higher water fluxes and a little bit lower salt rejection of VP and HEMA deposited membranes are 4.85×10^{-5} , 4.79×10^{-5} g/cm² s, and 84.2, 76.4%, respectively, with the same conditions as the AA-deposited membranes mentioned.

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References

1. R. Y. M. Huang, U. Y. Kim, J. M. Dickson, D. R. Lloyd, and C. Y. Peng, *J. Appl. Polym. Sci.*, **26**, 1135 (1981).
2. R. Y. M. Huang, U. Y. Kim, J. M. Dickson, D. R. Lloyd, and C. Y. Peng, *J. Appl. Polym. Sci.*, **26**, 1907 (1981).
3. J. Y. Lai, T. C. Chang, Z. J. Wu, and T. S. Hsieh, *J. Appl. Polym. Sci.*, **32**, 4709 (1986).
4. A. Jong, T. C. Chang, and J. Y. Lai, *J. Appl. Polym. Sci.*, **36**, 87 (1988).
5. H. Yasuda and H. C. Marsh, *J. Polym. Sci.*, **15**, 991 (1977).
6. H. Yasuda, H. C. Marsh, E. S. Brandt, and C. N. Reilley, *J. Appl. Polym. Sci.*, **20**, 2205 (1976).
7. A. K. Sharma, F. Millich, and E. W. Hellmuth, *J. Appl. Polym. Sci.*, **26**, 2205 (1981).
8. T. Shimomura, M. Hirakawa, I. Murase, M. Sasaki, and T. Sano, *J. Appl. Polym. Sci. Appl. Polym. Symp.*, **38**, 173 (1984).
9. I. H. Coopes and K. J. Gifkins, *J. Macromol. Sci. Chem.*, **A17**(2), 217 (1982).
10. H. Yasuda and M. Gazicki, *Biomaterials*, **3**, 68 (1982).
11. Yasmeen Haque and Buddy D. Ratner, *J. Appl. Polym. Sci.*, **32**, 4369 (1986).
12. H. Yasuda and C. E. Lamaze, *J. Appl. Polym. Sci.*, **17**, 1519, 1533 (1973).
13. J. R. Hollahan and T. Wydeven, *Science*, **179**, 500 (1973).
14. J. Y. Lai and C. C. Chou, *J. Appl. Polym. Sci.*, **37**, 1465 (1989).
15. D. H. Kaeble and J. Moacanin, *Polymer*, **18**, 475 (1977).
16. Y. Haruvy and L. A. Rajbenbach, *J. Appl. Polym. Sci.*, **32**, 4649 (1986).
17. Y. Haruvy, L. A. Rajbenbach, and J. Jagur-Grodzinski, *J. Appl. Polym. Sci.*, **33**, 389 (1987).
18. V. K. Kriable, and K. A. Holst, *J. Am. Chem. Soc.*, **60**, 2976 (1938).
19. K. Hoshino, *Chem. Soc. Jpn. Bull.*, **19**, 156 (1944).
20. C. W. Yao, R. P. Burford, A. G. Fane, C. J. D. Fell, and R. M. McDonogh, *J. Appl. Polym. Sci.*, **34**, 2399 (1987).
21. H. Yasuda, *Plasma Polymerization*, Academic, Orlando, FL, 1985, Chap. 7.
22. John R. Hollahan and T. Wydeven, *J. Appl. Polym. Sci.*, **21**, 923 (1977).

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