Fabrication of reverse osmosis membrane via low temperature plasma polymerization

Hyun Il Kim, Sung Soo Kim*

Division of Environmental and Chemical Engineering, Kyung Hee University, Center for Advanced Functional Polymers, Yongin, Kyunggido 449-701, South Korea

Abstract

Composite membranes for reverse osmosis were fabricated by low temperature plasma polymerization process. Microporous polysulfone and polypropylene membranes were used as the support for the composite membranes. Various hydrophilic monomers were employed in the plasma polymerization process to form the hydrophilic active layers on the support. Each combination of monomer and support membrane showed its own characteristics. Polysulfone and polypropylene membranes treated with allylamine showed the comparable performances to those of the commercial ones. As plasma polymerization time increased, more plasma polymer was deposited on the support to result in the flux decline and rejection increase. Input power had influence on the plasma polymer deposition rate at low power range especially for monomer-deficient system. Sample got damaged at excess power to reduce the performances in every case. Proper combination of polymerization time and power can secure the economic aspects of the process. At too low monomer flow rate, plasma polymer was not formed enough to cover the surface of the microporous membrane to result in high flux with poor rejection. In the optimum monomer flow rate range highly cross-linked coating layer was formed. When the monomer flow rate exceeded the optimum range, energy transferred to monomer molecule was decreased to result in less cross-linked and unstable layer formation despite the increase of deposition. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Plasma polymerized membrane; Reverse osmosis; Composite membrane

1. Introduction

The reverse osmosis (RO) process has been developed for the water purification processes such as desalination, ultra pure water preparation, and wastewater treatment [1–3]. Several techniques for RO membrane preparation have been developed by employing many materials. Thin film composite (TFC) membrane consisting of dense top layer and porous support is the most popular RO membrane

* Corresponding author. Tel.: +82-31-201-2591;
fax: +82-31-202-1946.
E-mail address: sungkim@khu.ac.kr (S.S. Kim).

these days due to its several advantages over the other RO membranes such as asymmetric membranes [4–7]. It has provided better flux and separation of organics by its enhanced physico-chemical properties under lower operating pressure than those obtained with cellulosic asymmetric membranes [8–14].

There have been developed several methods for preparation of RO composite membranes including lamination, dipping, plasma polymerization and interfacial polymerization. Among those methods, interfacial polymerization is most widely used and polyamide composite membranes are commercially produced by this method. While polyamide TFC membrane has salt rejection greater than 99% with

excellent heat resistance, it is weak to chlorine or ozone during sterilization to result in decomposition and performance decline [15]. Plasma created by glow discharge causes a radical polymerization reaction. Plasma polymerization is an atomic polymerization propagated by combination of atoms or resolved molecules and the resolution pattern strongly depends on polymerization conditions. Chemical structure of plasma polymer is more affected by plasma polymerization conditions than the monomer structure. Plasma polymer deposited on solid surface has very high degree of cross-linking, which is much related with energy supplied to unit monomer. Polymer thin film can be formed by plasma polymerization for most of the organic and silicon-containing gas. Plasma polymerization between monomer molecules and support can form a layer of 0.01 μm of thickness with high degree of cross-linking and pinhole free uniformity. Plasma polymerization only affects the surface to have influences on permeability and selectivity of membrane [16]. Thus, formed layer has better thermal stability, adhesion property and chlorine resistance than the layers formed by other methods. Plasma polymerization provides still unique characteristics compared to those of other polymerization in many applications [17–20].

There have been several attempts to make composite membranes for reverse osmosis by plasma polymerization. Yasuda fabricated the composite membranes by plasma polymerization of nitrogen-containing monomers on the polysulfone support [21]. Hollhan et al. prepared the composite membranes by using the mixed gas of allylamine and argon, which had water flux of 0.225 l/m^2 h bar and salt rejection of 90.8%. It showed better water flux than the cellulose acetate asymmetric membranes with similar rejection [22]. Bell et al. prepared symmetric cellulose nitrate-based RO composite membrane by plasma polymerization using allylamine as a monomer which showed water flux of 0.212 l/m^2 h bar and salt rejection of 99.1% [23,24]. Nitrogen-containing monomer and alkyl metal with an inert carrier gas were plasma polymerized on the porous support by Yoshihiro [25]. Sano and Tsutsui prepared the polyacrylonitrile (PAN)-based RO composite membranes via plasma polymerization using allylamine as a monomer, which had been commercialized by Sumitomo Co. in the name of Solrox [26,27]. Solrox

membrane attained the water flux of 0.39 l/m^2 h bar and salt rejection of 98.3% at 48 bar operating pressure. Even though they produced the various types of this series, their performance still needed to be improved.

In this work we intended to enhance the performance of the plasma polymerized membrane by improving the apparatus and optimizing the plasma polymerization conditions. So far, polysulfone support has been commonly used as a support for composite membrane, but polypropylene support has not been used despite its better physico-chemical properties than other supports. We tried to examine the feasibility of the polypropylene membrane as a support for composite membrane. We also investigate the plasma polymerization process as a method to improve durability and chlorine resistance of the membrane.

2. Experimental

2.1. Materials

Microporous polypropylene (PP) and polysulfone (PSf) membranes were used as support membranes for plasma polymerization. Celgard 2400® PP microfiltration membrane was purchased from Hoechst-Celanese Co., and PSf ultrafiltration membranes were prepared by the conventional solvent casting method. Dope solution was composed of PSf (Udel P-1700, Amoco Co.), *n*-methyl-2-pyrrolidone (NMP, Aldrich Co., HPLC grade) as solvent, and polyvinylpyrrolidone (PVP, GAF Chemical Co., K-15) as an additive at the composition of PSf:PVP:NMP = 18:15:67. Distilled water was used as a nonsolvent. Figs. 1 and 2 show scanning electron microscope (SEM) images of PP and PSf support used in this study. PP support has microfibril structure formed by stretching with high porosity above 70%. PSf support was asymmetric structure, which consist of sponge structure at top layer and finger-like structure at bottom. It was typical shape prepared by wet phase inversion process. The hydrophilic monomers for plasma polymerization were selected as acrylic acid, acrylonitrile, allylamine, ethylenediamine, *n*-propylamine, and methylmethacrylate (MMA). They were purchased from Junsei Chemical and used with no further purification.
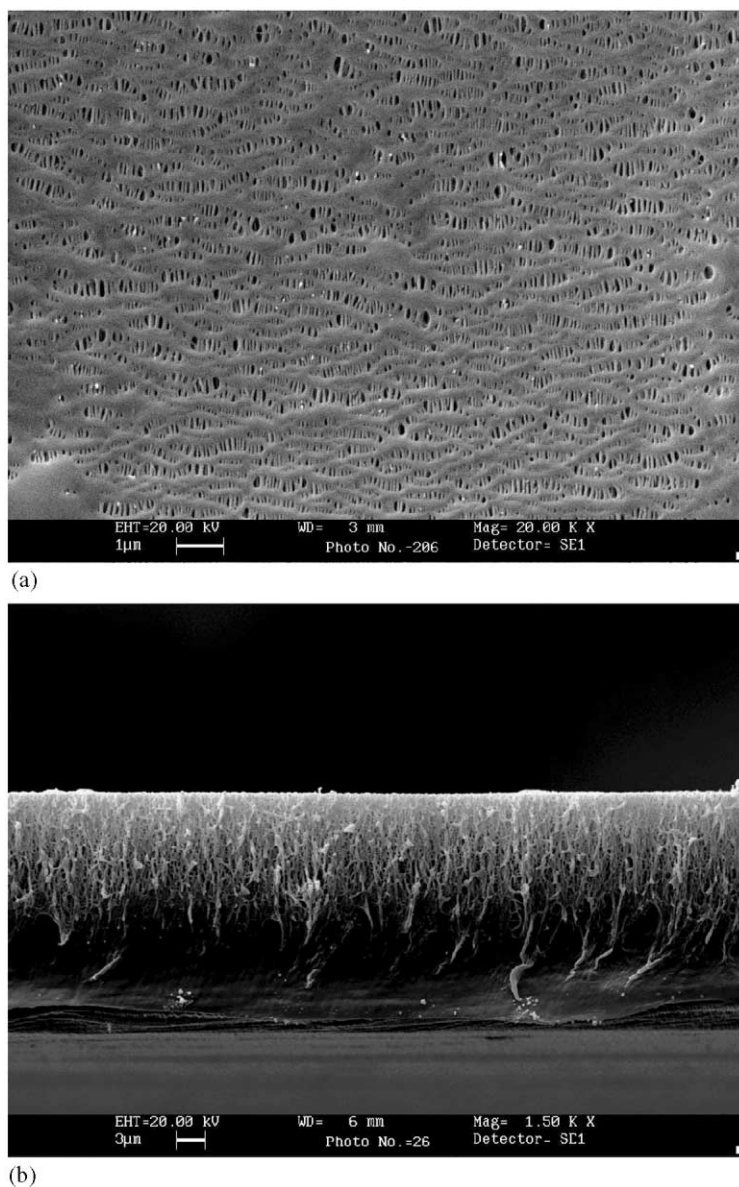
(a)

(b)

Fig. 1. Scanning electron micrographs of untreated PP membrane: (a) surface; (b) cross-section.

2.2. Plasma reactor

A schematic diagram of plasma reactor is shown in Fig. 3. Tubular type Pyrex reactor with a pair of copper electrodes with 10 cm apart was assembled. The rf generator (model RFX-600, advanced energy) which operated at frequency of 13.56 MHz and matching network (Model ATX-600 advanced energy) were used to convert the complex impedance of plasma to 50 Ω resistance. A rotary vacuum pump (E2M8, Edwards) was used to evacuate the reactor for the proper glow discharge.
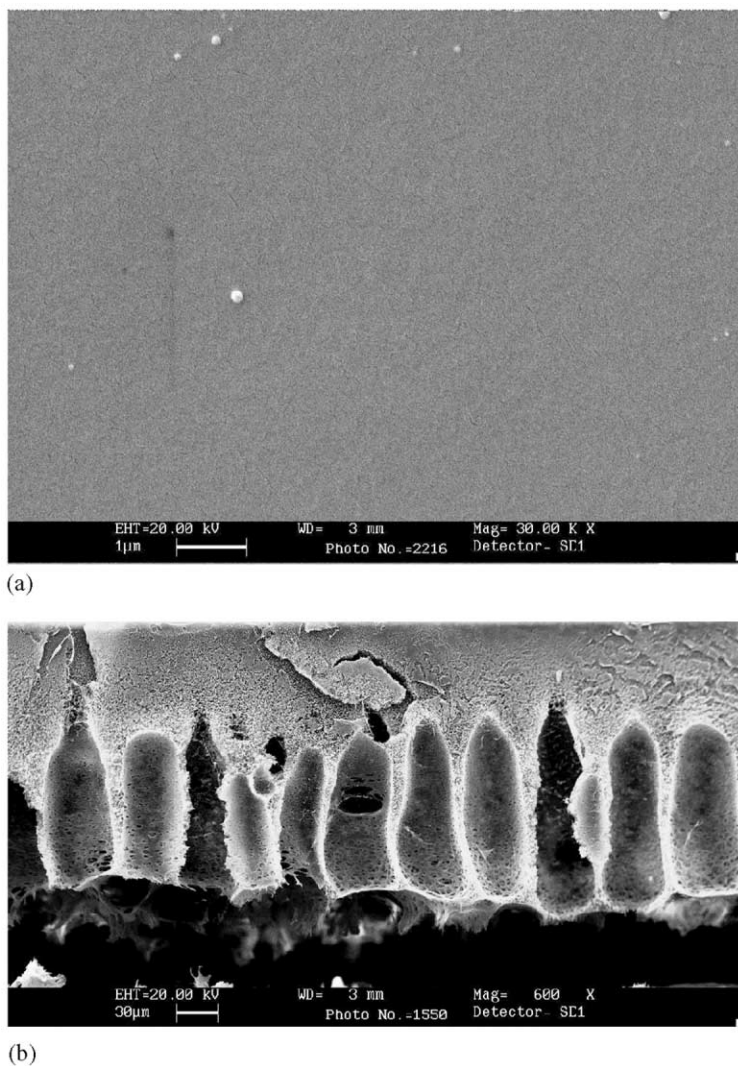
Fig. 2. Scanning electron micrographs of untreated PSf membrane: (a) surface; (b) cross-section.

2.3. Preparation of membranes

Plasma polymerization formed the active layers on the PP and PSf supports to make TFC membranes. Support was placed in the reactor before it was evacuated. When the pressure inside the reactor reached to below 20 mTorr, the monomer vapor was introduced into the reactor by adjusting the microvalve to maintain the steady state at 40 mTorr. The rf power supply was switched on to initiate the glow discharge for the plasma polymerization.

The best first-order approach to dealing with plasma polymerization conditions is to use the composite parameter, (W/FM), proposed by H. Yasuda, where W is the discharge power, and F and M are the volume flow rate and molecular weight of monomer, respectively [18]. Because each parameter affects the structure and physico-chemical properties of plasma polymer interdependently, it needs to be optimized. In this work effects of discharge power, monomer flow rate, plasma polymerization time and kind of monomers were investigated.
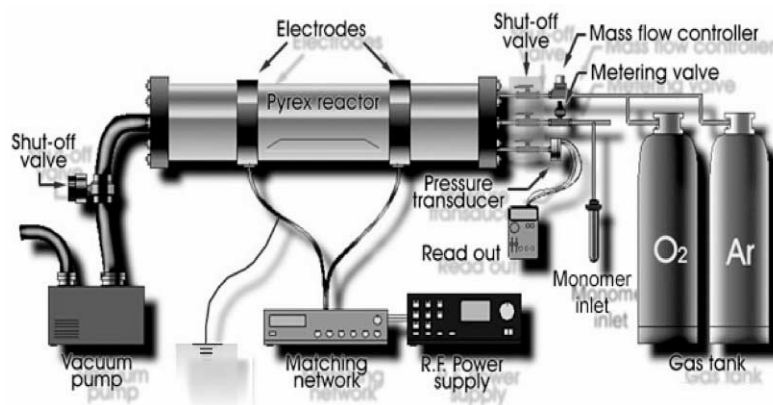
Fig. 3. A schematic diagram of the plasma reactor.

2.4. Characterization of membranes

Conventional reverse osmosis apparatus for flat membrane was assembled with effective surface area of 13.85 cm^2. About 2000 ppm NaCl solution was recirculated at a rate of 240 ml/min, and operating pressure was maintained at 30 bar. Chlorine resistance of the membrane was examined by comparing the performances of the original membrane with those of the membrane after contacting with 1000 ppm NaOCl solution for 2 h.

Morphological analyses of membrane surface and cross-section were performed by using a scanning electron microscope (SEM, Lica, Stereoscan 440). Chemical analysis of the surface was performed by FTIR–ATR (System 2000, Perkin-Elmer) at an incidence angle of 45°. Thermal stability of membrane was measured by using a thermo-gravimetric analyzer (Perkin-Elmer, TGA 7).

3. Results

3.1. Effect of a kind of monomer

Various hydrophilic monomers were plasma polymerized on the support to make the hydrophilic active layers. Same operating conditions were applied by maintaining (*W/FM*)*t* as 1.72×10^{10} J min/kg for each monomer molecule to receive the same energy. Reverse osmosis performances of each membrane were compared in Fig. 4. Untreated PP and PSf support membranes were not able to remove salt because they are microporous membranes. After they were plasma coated, micropores at the surface were blocked by plasma polymer and they could reject the salt to some extent. Since PP membrane is hydrophobic, it has very low water flux and has not been popularly used for water permeation process in spite of its outstanding physico-chemical properties. Plasma polymerization of PP membrane with hydrophilic monomers modified the surface of the membrane more hydrophilic to achieve the appreciable flux and salt rejection. It can afford the possibilities that PP membranes can be used as RO membranes with better properties such as physical strength and durability than those of the other reverse osmosis membranes so far.

Plasma polymerization with ethylenediamine showed no rejection telling that it was not properly plasma polymerized on the supports. Membranes treated with acrylonitrile and MMA have much reduced flux without attaining appreciable rejection. *N*-propylamine and acrylic acid made the membranes with lower rejection and greater flux than RO membranes. Membranes treated with allylamine plasma showed the salt rejection greater than 90% with comparable flux to those of commercial membranes. In this work we have attained the better performances than those of the previous works reported [21–27]. Improvement of apparatus such as tubular reactor with external electrode and matching network helped make uniform polymerization on the surface, which
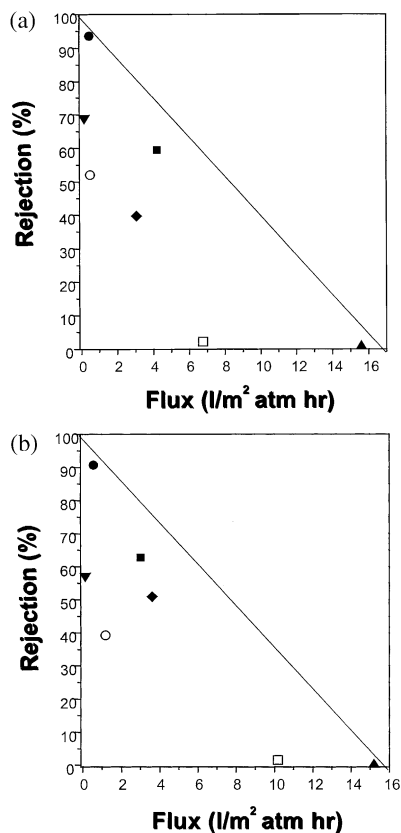
Fig. 4. Performances of plasma treated membranes with various monomers: (untreated ($\blacktriangle$); acrylic acid ($\blacksquare$); allylamine ($\bullet$); MMA($\bigcirc$); acrylonitrile ($\blacktriangledown$); n-propylamine ($\blacklozenge$); ethyldiamine ($\square$); $(W/FM)t = 1.72 \times 10^{10}$ J min/kg). (a) PP support; (b) PSf support.
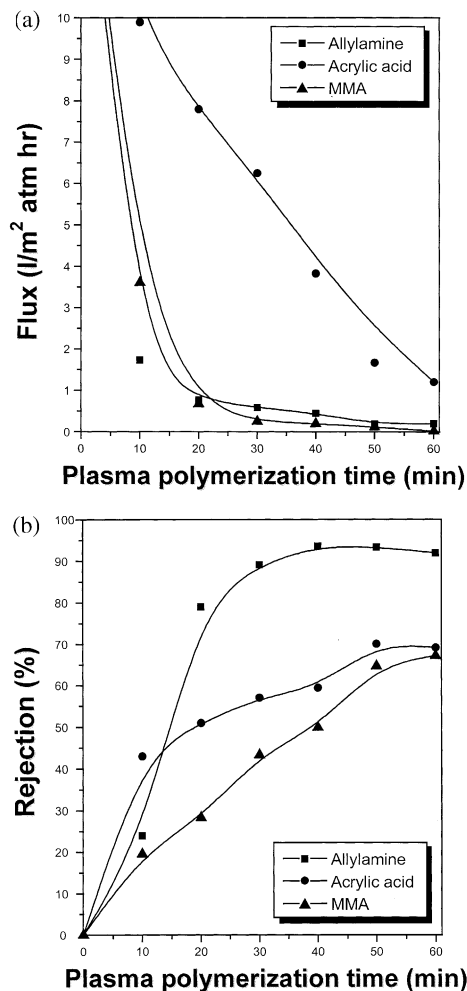

Fig. 5. Effect of plasma polymerization time on performance of PP support membrane (supplied power: 10 W; monomer flow rate: 0.8 sccm): (a) flux; (b) rejection.

contributed to enhance the performances. Trends of performance change by plasma polymerization are nearly same for both PP and PSf supports. Performances of plasma treated membrane were more dependent on the kind of monomer than the kind of support. Allylamine, acrylic acid and MMA were selected representing each group of compound to be used in the experiments in examining the operating conditions.

3.2. Effects of plasma polymerization time

Effects of plasma polymerization time were examined for three monomers with fixed conditions of discharge power of 10 W and monomer flow rate of

0.8 sccm. As shown in Fig. 5, increase of polymerization time resulted in flux decrease and rejection increase by more deposition of plasma polymer on the surface of the PP support. Micropores were disappeared after 30 min polymerization to make dense membrane with active layer of plasma polymer as shown in Fig. 6. Performance change of PSf membrane was in the similar trend to that of PP membrane (Fig. 7), which is telling that active layer formed by plasma polymer is more important than the supports. For both supports, allylamine showed the better performances than the other two monomers. MMA was
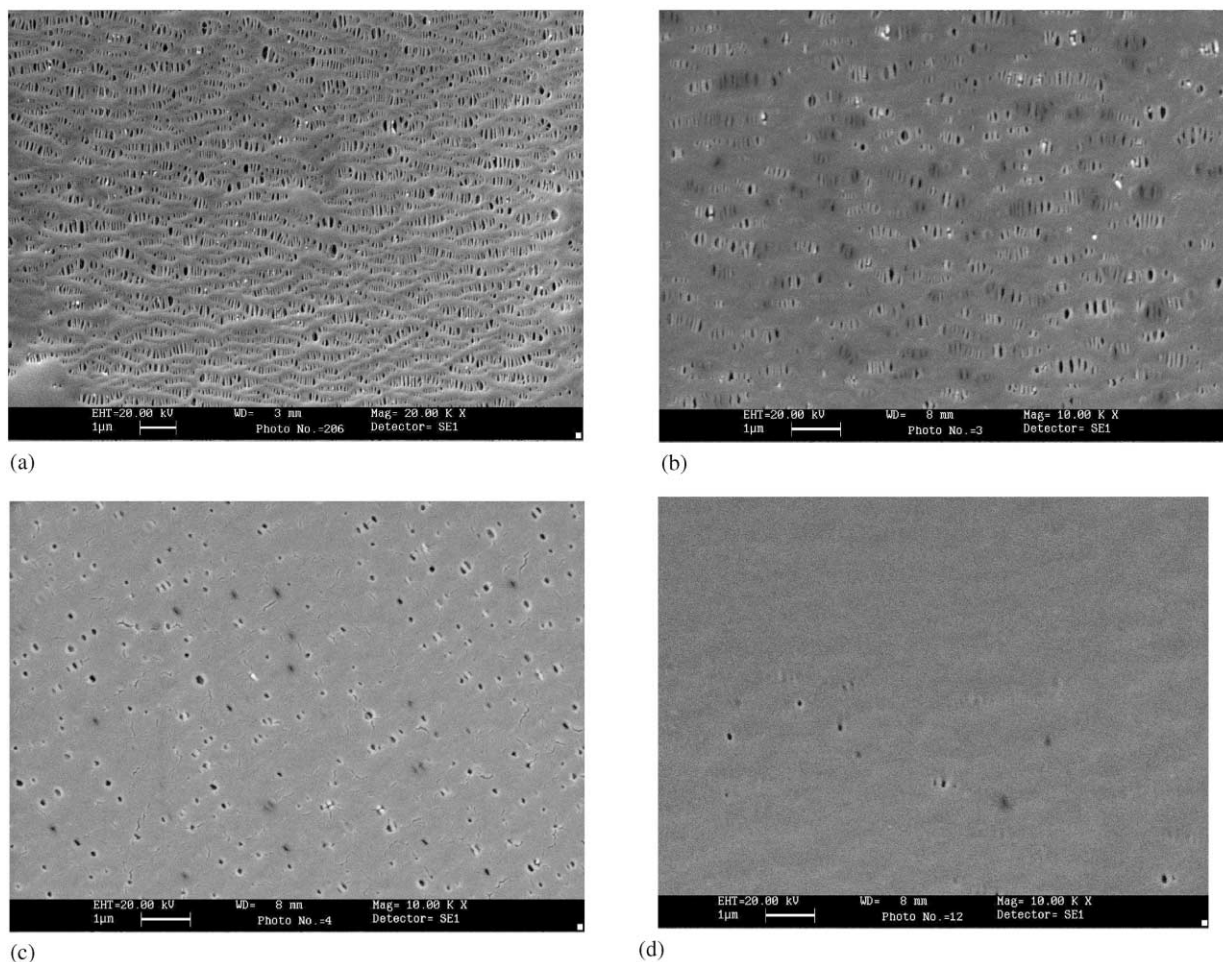
Fig. 6. Surface images of PP membranes plasma treated with acrylic acid for different polymerization time (supplied power: 10 W; monomer flow rate: 0.8 sccm): (a) untreated; (b) 10 min; (c) 20 min; (d) 30 min.

not as effectively plasma coated as allylamine and acrylic acid for PP support. Any appreciable change at the surface of the PSf membrane was not observed by SEM because it has already dense surface before plasma polymerization. PP membrane treated with allylamine for 30 min or more showed the fairly good performances.

Active layer formation at the surface was confirmed by FTIR–ATR spectra for PP and PSf supports treated with acrylic acid are shown in Fig. 8. The characteristic peak for carbonyl stretching at $1720 \, \text{cm}^{-1}$ was observed to reveal the acrylic acid layer formation on the surface. With increase of plasma polymeriza-

tion time more acrylic acid layer was formed, which was represented by the increase of carbonyl stretching peak. C=C aromatic double bond peak of PSf membrane declined with increase of polymerization time at $1580 \, \text{cm}^{-1}$ by plasma polymer deposition on membrane surface.

In terms of the economic aspects of the process, plasma polymerization time needs to be minimized. In this work it was attempted to reduce the plasma polymerization time while maintaining the same $(W/FM)t$ value at $2.09 \times 10^{10} \, \text{J min/kg}$ by increasing the power. As shown in Fig. 9(a), PP membrane treated with acrylic acid showed performance
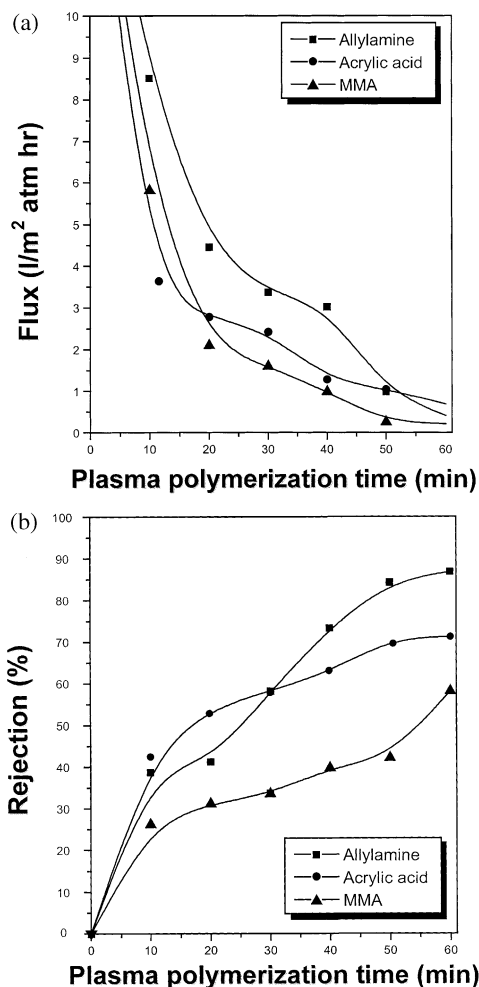
Fig. 7. Effect of plasma polymerization time on performance of PSf support membrane (supplied power: 10 W; monomer flow rate: 0.8 sccm): (a) flux; (b) rejection.

Fig. 8. FTIR–ATR spectra of PP and PSf support treated with acrylic acid plasma for various polymerization time (supplied power: 10 W; monomer flow rate: 0.8 sccm; (1) untreated; (2) 10 min; (3) 40 min; (4) 90 min). (a) PP support; (b) PSf support.

deterioration at high power and short polymerization time. PP support might get damaged by high power. PSf membrane showed quite satisfactory results as shown in Fig. 9(b). When it was plasma treated with acrylic acid it could retain the performance until the polymerization time was reduced to 6 min. PSf membranes seemed to be less damaged by plasma polymerization than PP membrane. PP membrane is semicrystalline and was expected to be more stable than amorphous PSf membrane. However, PP membrane was less resistant to plasma polym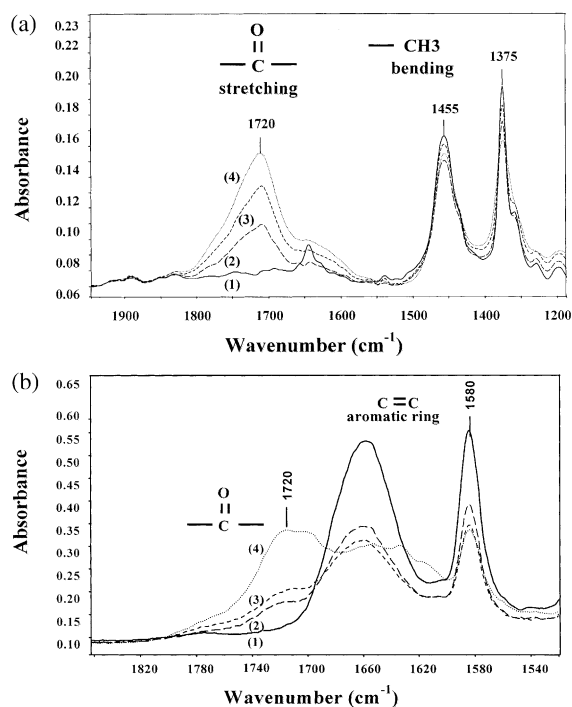erization than PSf membrane. PP support membrane has greater pore size and was more porous than PSf support membrane. Damage by plasma polymerization might more depend on the microporous structure of the membrane than the material properties. Similar trends were observed for the membranes treated with allylamine.

3.3. Effect of power

Electric power input to a plasma polymerization system was varied from 10 to 50 W at constant molar flow rate (0.8 sccm) and polymerization time (30 min). Figs. 10 and 11 show the performance variations of PP and PSf composite membranes treated with allylamine, acrylic acid, and MMA by applying different electric power. Increase of power at constant monomer flow rate supplied more energy to monomer and support membrane. Power less than 10 W was too weak to treat the support membrane properly to result in very poor reverse osmosis performances. It was reported
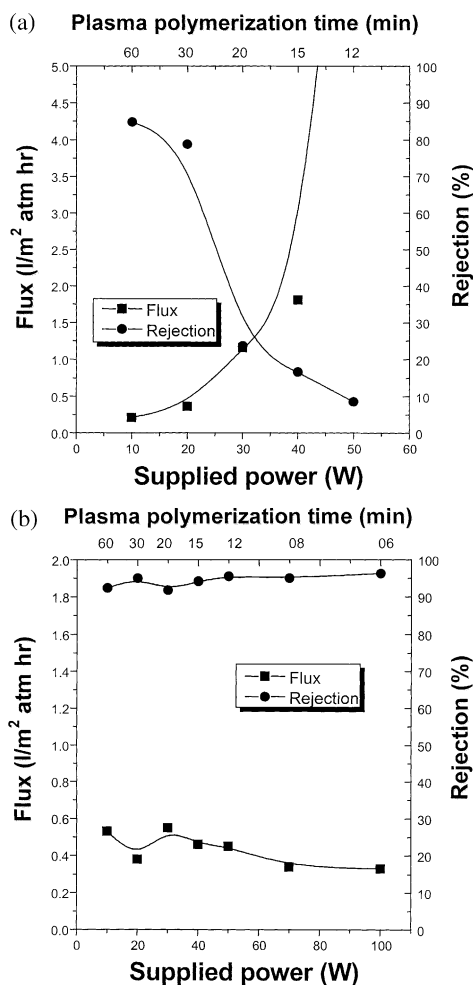
Fig. 9. Effects of polymerization time and power on performance of plasma treated membranes with acrylic acid: (a) PP support; (b) PSf support.

Fig. 10. Effect of power on performance of plasma treated PP support membranes (polymerization time: 30 min; monomer flow rate: 0.8 sccm): (a) flux; (b) rejection.

that increase of power initially increased the polymer deposition rate but begins to deviate from linear dependence [19]. Membranes treated with allylamine and acrylic acid showed abrupt changes of flux and rejection at low power range, whereas those treated with MMA showed the gradual change. MMA was less effective in plasma polymerization than the other two monomers, since it was less volatile than the others to be introduced into the reactor. Yasuda stated that, the deposition rate has linear dependence on power input for monomer-deficient system, where sufficient discharge is available to activate the monomers and
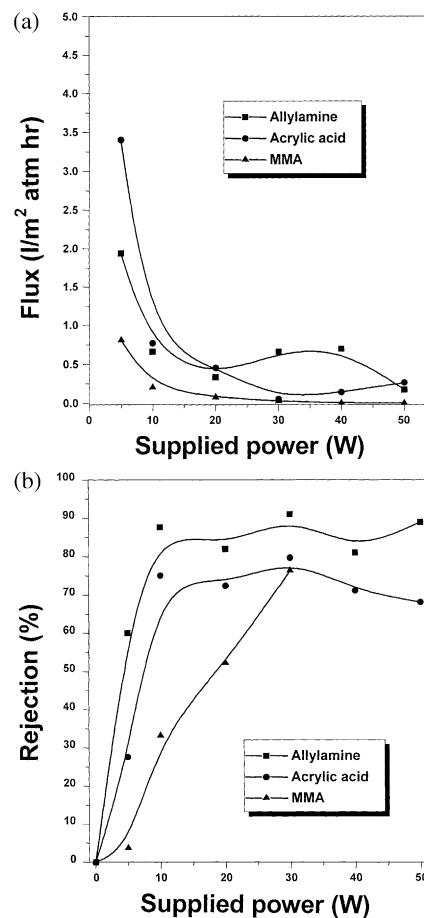
support [19]. MMA system was a monomer-deficient system and showed the gradual changes of performance with power. For every case, the support membrane got damaged at excess power input greater than 50 W to cause the failure of the membrane. Therefore, it should be optimized in terms of performances as well as operating cost.

3.4. Effect of monomer flow rate

Effects of monomer flow rate were investigated in terms of performance and stability of composite membrane. PP and PSf support membranes were plasma treated with allylamine and acrylic acid at fixed sup-
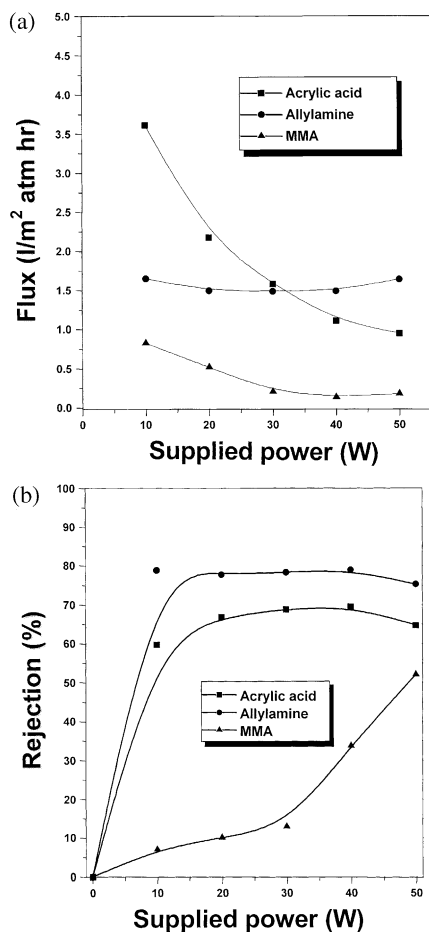
Fig. 11. Effect of power on performance of plasma treated PSf support membranes (polymerization time: 30 min; monomer flow rate: 0.8 sccm): (a) flux; (b) rejection.

Fig. 12. Effect of monomer flow rate on performance of plasma treated PP membranes (polymerization time: 60 min; supplied power: 10 W): (a) acrylic acid; (b) allylamine.

plied power (10 W) and polymerization time (60 min) for monomer flow rate range of 0.1–1.8 sccm. Figs. 12 and 13 showed that every case has similar trend of performance variation to each other. There existed optimum monomer flow rate for flux and rejection in every case. At too low monomer flow rate plasma polymer was not formed enough to make the active layer on the support membrane. It failed to cover the surface of the microporous membrane to result in the great flux with poor rejection. In the optimum monomer flow rate range, energy transferred to monomer is sufficient to form highly cross-linked coating layer. When the monomer flow rate exceeded the optimum range, performances of the membranes got deteriorated again,
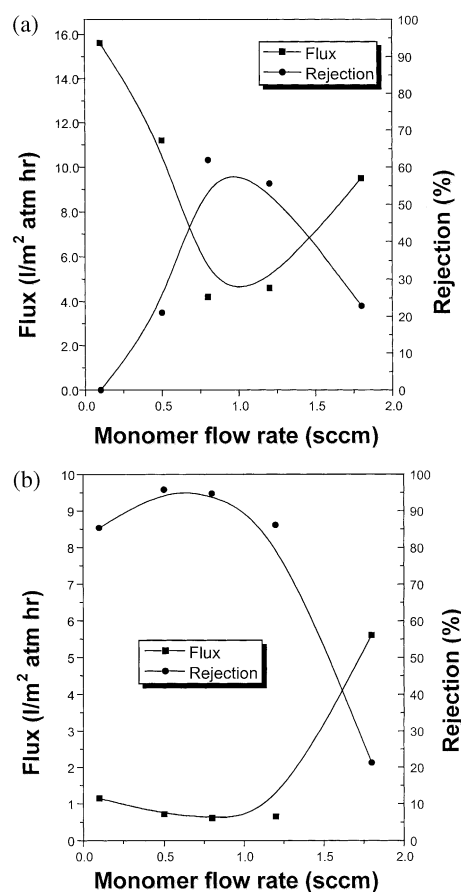
which should be much related with the stability of plasma-coated active layer of composite membrane.

Stability of the active layer is much related with the plasma polymerization conditions, especially, the monomer flow rate. Increase of monomer flow rate resulted in the decrease of the energy transferred to monomer molecule and support membrane. Therefore, excess monomer flow rate inhibited the plasma polymerization and the active layer formed at high monomer flow rate should be unstable due to the low degree of cross-linking. Stability of the active layer was characterized by thermo-gravimetric analysis. TGA thermograms of each membrane at various monomer flow rates are shown in Fig. 14. Plasma treated membrane surface has cross-linked
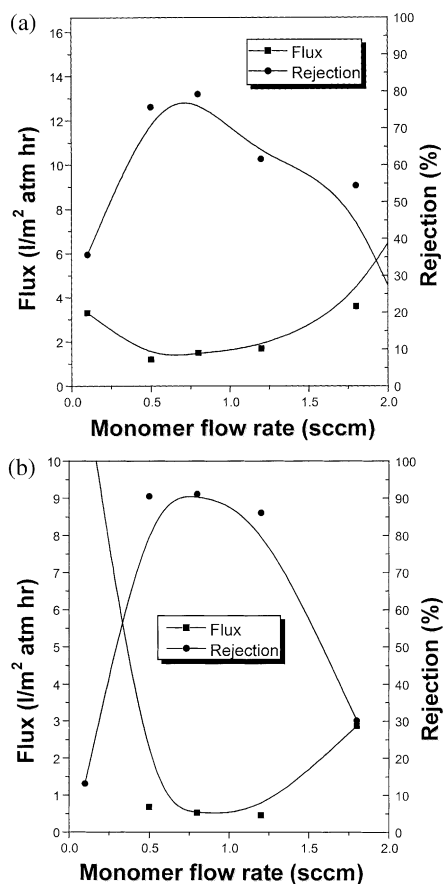
Fig. 13. Effect of monomer flow rate on performance of plasma treated PSf membranes (polymerization time: 60 min; supplied power: 10 W): (a) acrylic acid; (b) allylamine.
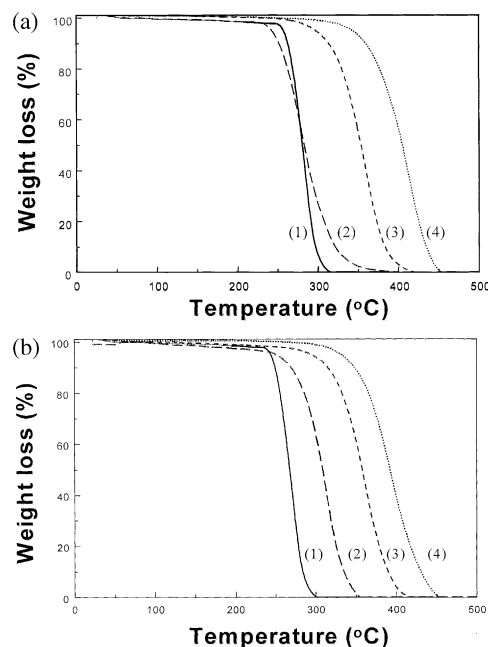

Fig. 14. TGA thermograms of plasma treated PP support for various monomer flow rates: (1) untreated; (2) 1.8 sccm; (3) 0.8 sccm; (4) 0.1 sccm (scanning rate=20°C/min; supplied power: 10 W; polymerization time: 60 min). (a) Acrylic acid; (b) allylamine.

plasma polymer, which is formed by recombination of molecule and atoms from monomer and support. Since cross-linked polymer has better thermal resistance than uncrosslinked one, plasma treated membranes had better thermal resistance and higher decomposition temperature than untreated ones. PSf-based membrane shows same trends. Increase of monomer flow rate increased the amount of deposition on the membrane surface. However, it was observed that increase of monomer flow rate reduced the decomposition temperature. As mentioned above increase of monomer flow rate caused insufficient plasma polymerization to form less stable layers. Optimum monomer flow rate can make the highly cross-linked stable layer of composite membrane.

3.5. Chlorine resistance

Chlorine resistance has been an important issue in RO membrane developments. Chlorine resistance of plasma polymerized composite membranes were compared with those prepared by interfacial polymerization as used for FT-30 membrane. As shown in Table 1, the salt rejection was reduced to 65.0% while the water flux was increased by 2.5 times for interfacial polymerized membrane after NaOCl treatment. Plasma polymerized composite membrane using PP support were also deteriorated after NaOCl treatment. However, PSf support maintained its original performance after NaOCl treatment even though same monomers were plasma polymerized. The chlorine resistance were much improved by plasma polymerization when compared with interfacial polymerization for the same support. More highly cross-linked coating layer was formed by the plasma polymerization and adhesion between plasma polymer and support played an important role in chlorine resistance.

Table 1
Comparison of chlorine resistances of composite membranes prepared by plasma polymerization with that of interfacial polymerized[a]

Membranes			Before NaOCl treatment		After NaOCl treatment	
			Flux (l/m^2 atm h)	Rejection (%)	Flux (l/m^2 atm h)	Rejection (%)
Interfacial polymerization	PSf support	PSf support	0.5	94.0	1.3	65.0
Plasma polymerization	PSf support	AA	0.5	84.0	0.5	85.9
Plasma polymerization	PSf support	AM	0.8	94.0	0.8	93.2
Plasma polymerization	PP support	AA	0.3	81.3	0.7	61.4
Plasma polymerization	PP support	AM	0.4	85.4	1.0	38.2

[a] Plasma polymerization conditions: power = 20 W, polymerization time = 360 min, monomer = acrylic acid (AA) and allylamine(AM), monomer flow rate = 0.8 sccm; NaOCl treatment: concentration = 1000 ppm, time = 2 h.

4. Conclusion

PP and PSf supported RO composite membranes were prepared by plasma polymerization of hydrophilic monomers to show the appreciable performances. It could also afford the possibilities of application of plasma process to composite membrane fabrication. Various monomers such as acrylic acid, allylamine, MMA, and acrylonitrile were tested. Each combination of monomer and support membrane showed the different performances depending on its physico-chemical properties, even though identical fabrication conditions were applied to every sample. Longer reaction time brought about more plasma polymer deposition on membrane surface to decrease the flux and increase the salt rejection. Input power initially enhanced the performances at low power range by increasing the plasma polymer deposition rate. At excess power, the sample got damaged to reduce the performances in every case. Power should be optimized both in terms of performances and energy consumption. Too low monomer flow rate could not perform the enough plasma polymerization to fully cover the surface of the microporous membranes. At optimum conditions highly cross-linked coating layer with excellent performances and stability was formed. Excess monomer flow rate reduced the energy transferred to a monomer molecule to cause unstable active layer formation with less cross-linking, which was confirmed by TGA analyses. Improvement of apparatus and optimization of parameters enabled to make uniform polymerization on the support, which contributed to enhance the performances better than those of the previous works. The chlorine resistance of plasma polymerized composite membrane on PSf support was superior to those of the interfacial polymerized membranes due to its highly cross-linked coating layer with better adhesion.

References

[1] G. Belfort, Synthetic Membrane Processes, Academic Press, New York, 1984.
[2] K. Spiegler, A. Laird, Principle of Desalination, Academic Press, New York, 1980.
[3] B.S. Parekh, Reverse Osmosis Technology, Marcel Dekker Inc., New York, 1988.
[4] J.E. Cadotte, Reverse Osmosis Membrane, US Patent no. 4,259,183, 1981.
[5] K. Ikeda, S. Yamamoto, H. Ito, Sulfonated Polysulfone Composite Semipermeable Membranes and Process for Producing the Same, US Patent no. 4,818,387, 1989.
[6] S. Sourirajan, Reverse Osmosis, Academic Press, New York, 1970.
[7] S. Sourirajan, T. Matsuura, Reverse Osmosis/Ultrafiltration Process Principles, National Research Council, Canada, 1985.
[8] A. Prakash Rao, N.V. Desai, R. Rangarajan, Interfacially synthesized thin film composite RO membrane for seawater desalination, J. Membr. Sci. 124 (1997) 263–272.
[9] M. Hirose, H. Ito, Y. Kamiyama, Effect of skin layer surface structures on the flux behavior of RO membranes, J. Membr. Sci. 121 (1996) 209–215.
[10] M. Hirose, H. Ito, Y. Kamiyama, The relationship between polymer molecular structure of RO membrane skin layers and their RO performances, J. Membr. Sci. 123 (1997) 151–156.
[11] W.S. Winston Ho, K.K. Sirkar, Membrane Handbook, Chapman & Hall, USA, 1992.

[12] K. Lang, T. Matsuura, G. Chowdhury, S. Sourirajan, Preparation and testing of polyvinyl alcohol composite membranes for reverse osmosis, Can. J. Chem. Eng. 73 (1995) 686–692.

[13] K. Lang, S. Sourirajan, T. Matsuura, G. Chowdhury, A study on the preparation of polyvinyl alcohol thin-film composite membranes and reverse osmosis testing, Desalination 104 (1996) 185–196.

[14] A.E. Childress, M. Elimelech, Effect of chemistry on the surface charge of polymeric reverse osmosis and nanofiltration membranes, J. Membr. Sci. 119 (1996) 253–268.

[15] R. Singh, Polyamide polymer solution behavior under chlorination conditions, J. Membr. Sci. 88 (1994) 285–287.

[16] H. Yasuda, Plasma Polymerization, Academic Press, London, 1985.

[17] C. Jönsson, A.-S. Jönsson, Influence of the membrane material on the adsorptive fouling of ultrafiltration membranes, J. Membr. Sci. 108 (1995) 79–87.

[18] P.W. Kramer, Y.S. Yeh, H. Yasuda, Low temperature plasma for the preparation of separation membranes, J. Membr. Sci. 46 (1989) 1–28.

[19] J.R. Hollahan, T. Wydeven, Some experimental parameters affecting performance of composite reverse osmosis membrane produced by plasma polymerization, J. Appl. Polym. Sci. 21 (1977) 923–935.

[20] A. Doucouré, C. Guizard, J. Durand, R. Berjoan, L. Cot, Plasma polymerization of fluorinated monomers on mesoporous silica membranes and application to gas permeation, J. Membr. Sci. 117 (1996) 143–150.

[21] H. Yasuda, Composite reverse osmosis membranes prepared by plasma polymerization, in: S. Sourirajan (Ed.), Reverse Osmosis and Synthetic Membranes, Ottawa, Canada, 1977, pp. 263–294.

[22] J.R. Hollahan, T. Wydeven, Synthesis of reverse osmosis membranaes by plasma polymerization of allylamine, Science 179 (1973) 500–501.

[23] D. Peric, A.T. Bell, M. Shen, Reverse osmosis characteristics of composite membranes prepared by plasma polymerization of allylamine: Effects of deposition conditions, J. Appl. Ploym. Sci. 21 (1977) 2661–2673.

[24] P.V. Hinman, A.T. Bell, M. Shen, Composite reverse osmosis membranes prepared by plasma polymrization of allylamine, J. Appl. Ploym. Sci. 23 (1979) 3651–3656.

[25] H. Yoshihiro, Membrane for Reverse Osmosis and Method of Making the Same, US patent no. 4,347,139, 1982.

[26] T. Shimomura, M. Hirakawa, I. Murase, M. Sasaki, T. Sano, Preparation of polyacrylonitrile reverse osmosis membrane by plasma treatment, J. Appl. Ploym. Sci.: Appl. Polym. Symp. 38 (1984) 173–183.

[27] N. Tsutsui, S. Takao, I. Murase, Process for producing polyacrylonitrile reverse osmotic membranes, US patent 4,283,359, 1981.