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Plasma treatment of polypropylene and polysulfone supports for thin film composite reverse osmosis membrane

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Abstract

Low temperature plasma treatment of membrane supports was carried out to investigate the performance enhancement of thin film composite (TFC) reverse osmosis membrane. Commercial polypropylene (PP) microfiltration membrane (Celgard 2400) and polysulfone (PSf) ultrafiltration membrane prepared by conventional phase inversion method were plasma treated before interfacial polymerization. Hydrophilic monomers such as acrylic acid, acrylonitrile, allylamine, ethylenediamine and *n*-propylamine were used to hydrophilize the support membrane. Hydrophilic plasma treatment of PSf support showed slightly enhanced flux and rejection of TFC membrane when compared to the values of conventional TFC membranes. Plasma treatment remarkably enhanced the performance of membrane with PP support. It enabled PP support to be used for TFC membrane, which was not possible so far due to PP's hydrophobicity. Performance enhancement by plasma treatment of the supports was interpreted in terms of surface chemical composition and contact angle. Plasma treatment of supports enhanced not only the adhesion properties between active layer and support but also the chlorine resistance of the composite membrane.
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Keywords: Thin film composite membrane; Support; Plasma treatment; Polypropylene; Polysulfone

1. Introduction

Thin film composite (TFC) membrane is most popularly used for reverse osmosis (RO) process due to its several advantages over the other membranes. It provides higher water flux and rejection by its enhanced physicochemical properties under lower operating pressure than those obtained with former cellulosic asymmetric membranes. Several preparation methods have been developed for RO composite membrane 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 [1–3].

It is well known that active layer of TFC membrane plays the most important role in terms of performance and durability of the membrane, and many efforts have been dedicated to the enhancement of active layer. Various materials were developed for the active layer of TFC membranes, and aliphatic or aromatic diamines or their derivatives were tested [4,5]. Several research works to enhance the performance of membranes were attempted, e.g., surface modification by H_2O_2 and plasma process to increase its separation performance and chemical resistance [6,7].

However, support for TFC membrane has not been intensively investigated even though it has much influence on the performance of the membrane. Selection of support for polyamide TFC was limited to polysulfone (PSf), due to the fact that it is relatively hydrophilic and can easily be used for soaking in aqueous amine solution for interfacial polymerization. Expanding the selection of support is expected to enhance the performance and other properties of TFC membranes [8–11]. Also, it was reported that while polyamide TFC membrane has salt rejection greater than 99% with excellent heat resistance, it is weak to chlorine or ozone during sterilization resulting in decomposition of membrane and performance decline [12–14].

Plasma process has been widely utilized in preparation or modification of membrane [15–20]. Plasma polymerized layer has better thermal stability and adhesion properties than the layer formed by conventional methods. Low temperature plasma treatment processes have been extensively studied to modify

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the surface of polymeric ultrafiltration and microfiltration membranes for enhancement of permeability, selectivity and fouling resistance [21–25]. However, low temperature plasma processes have not been utilized for preparation of RO composite membrane in spite of its unique and effective characteristics.

In our previous work, RO composite membranes were fabricated by plasma polymerization of hydrophilic monomers on polypropylene (PP) and polysulfone (PSf) supports [11]. Effects of plasma polymerization conditions such as types of monomer, supplied power, monomer flow rate and reaction time were investigated, and comparable performances were attained to those of the commercial ones. This confirmed the possibilities of application of plasma process in fabrication of TFC membrane. PP support, which has not been previously used as support for interfacial polymerization due to its hydrophobicity, was first employed to fabricate TFC membrane.

Performance enhancement of composite membranes can be achieved by the aid of plasma treatment prior to interfacial polymerization in terms of flux and rejection. In addition, plasma process offers many advantages such as increased adhesion properties regardless of material being used including polymer, ceramic and metal. Active layer of composite membrane, which was formed on support by interfacial polymerization, is physically adhered on the support surface. Hybrid process of plasma treatment followed by interfacial polymerization can provide improvement of adhesion property between active layer and support.

In this work, we attempted to modify the conventional PSf and hydrophobic PP supports by plasma treatment with hydrophilic materials prior to interfacial polymerization for polyamide TFC membrane preparation. Plasma treatment is expected to hydrophilize the PP and PSf supports for better soaking with aqueous amine solution during interfacial polymerization. Effects of plasma monomer and plasma treatment time were investigated. Improvements of adhesion property and chlorine resistance of active layer were evaluated in terms of stability of the resulting TFC membrane.

2. Experimental

2.1. Materials

Microporous PP microfiltration membrane (Celgard 2400) was purchased from Hoechst-Celanese Co., which has the thickness of 23–26 μm and elliptical shape pores of 50 nm × 125 nm. Its porosity was reported as 28–40%. PSf ultrafiltration membrane was prepared by the conventional phase inversion method, details of which were described in our previous work [11]. These PP and PSf membranes were then used as the supports for interfacial polymerization in preparation of the TFC membrane.

Meta-phenylenediamine (MPDA) and trimesoylchloride (TMC) for interfacial polymerization were obtained from Fluka Co. as purum grades. The hydrophilic monomers for plasma treatment were selected as acrylic acid (AA), acrylonitrile (AN), allylamine (AM), ethylenediamine (ED) and *n*-propylamine (PA), and purchased as reagent grades from Junsei Chemical Co. Inhibitors contained in monomers were removed by filtering

them through the inhibitor remover (306312, Aldrich Co.) in prepacked column (311332, Aldrich Co.) before use. A piece of FT-30 membrane was extracted from commercial spiral wound module.

2.2. Plasma treatment of supports

Plasma reactor system and experimental details reported in previous work were also employed in this work [11]. Longer plasma reaction time resulted in the formation of coating layer on the support, which was confirmed by SEM image. Shorter plasma reaction time changes only the chemical composition of support without any layer deposition. Modification by plasma treatment is usually confined to the top several 100 angstroms and does not affect the bulk properties of support. Plasma treatment of support was performed at 10 W of power, which was optimized in consideration of support damage by excessive power. Monomer flow rate was adjusted at 0.6 sccm using mass flow controller. Plasma reaction time was optimized depending on types of the support.

2.3. Interfacial polymerization

Interfacial polymerization process was conducted as described in patent for FT-30 TFC membrane [3]. MPDA in aqueous phase was reacted with TMC in *n*-hexane phase at interface according to the reaction scheme as described in Fig. 1. Untreated and plasma treated PSf and PP membranes were tested as supports for interfacial polymerization and they were compared with each other to examine the effects of the plasma treatment. Initially the supports were soaked in 0.5 wt.% MPDA aqueous solution for 5 min, and the excess solution was removed
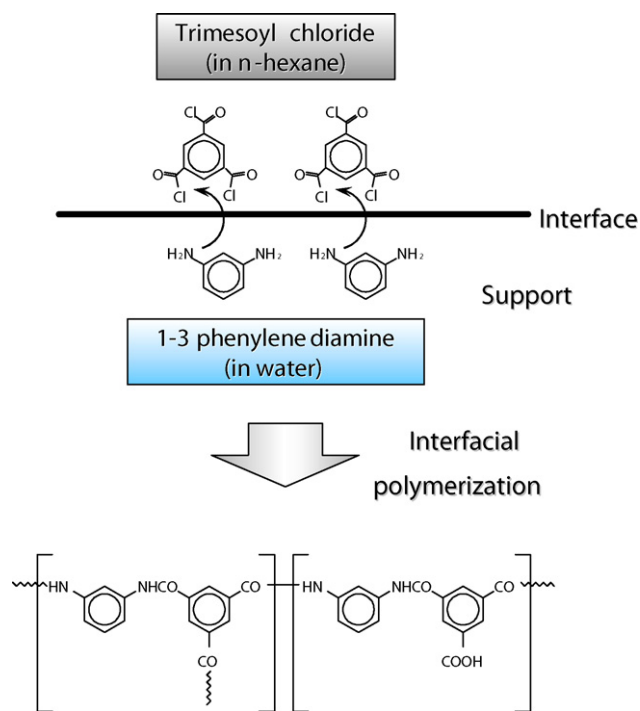

Fig. 1. A schematic reaction mechanism of interfacial polymerization.

by pressing the film with a soft rubber roller. Then it was exposed to 0.5 wt.% TMC solution in *n*-hexane for 5 min. Since water phase and *n*-hexane are immiscible, monomer in each phase was polymerized at the interface to produce very thin active layer of TFC membrane.

2.4. Characterization of membranes

Conventional reverse osmosis test apparatus for flat membrane was assembled with effective membrane surface area of 13.85 cm². NaCl solution of 2000 mmol/mol (ppm) was circulated at a rate of 240 ml/min and operating pressure was maintained at 30 bar. Feed reservoir was temperature controlled at 25 °C by using constant temperature circulator. Morphologies of surface and cross-section of the membrane were analyzed by using a scanning electron microscope (SEM, Leica, Stereoscan 440). Surface chemical composition was characterized by XPS (ESCA 2000, VG MicroTech.). Static contact angle was measured by the sessile drop method with a contact angle goniometer (Phoenix 300, SEO Co.) equipped with video capturing system. About 1 μl of single water drop was formed on the leveled surface of the membrane for contact angle measurement.

Adhesion property between support and active layer was examined by back flush test. Membrane was placed in the test cell with upside down, and permeation operation was conducted for 20 min under a specified pressure up to 10 bar. Since the active layer is placed at the bottom in back flush test mode, every membrane tested showed much greater flux and lower rejection than those in normal mode. After back flush test the membrane was placed in the cell in the normal mode, and flux and rejection of the membrane were measured. Performances of membrane with plasma treated support after back flush test were compared with those of the membrane with untreated support. For evaluation of chlorine resistance of the membrane, membrane active layer surface was contacted with NaOCl solution of 1000 mmol/mol (ppm) for 2 h and membrane performance variation was examined before and after the contact with NaOCl solution.

3. Results

3.1. TFC membrane with untreated supports

Untreated PP and PSf supports were used for preparation of polyamide TFC membranes and their performances were compared with those of the commercial FT-30 membrane tested in our laboratory. As shown in Table 1, PSf supported composite membrane, which had been prepared by intrinsically the same method as FT-30 membrane, showed the equivalent performance to that of FT-30 membranes. However, PP supported membrane showed too low rejection value to be used for reverse osmosis process. Since PP support is hydrophobic, MPDA aqueous
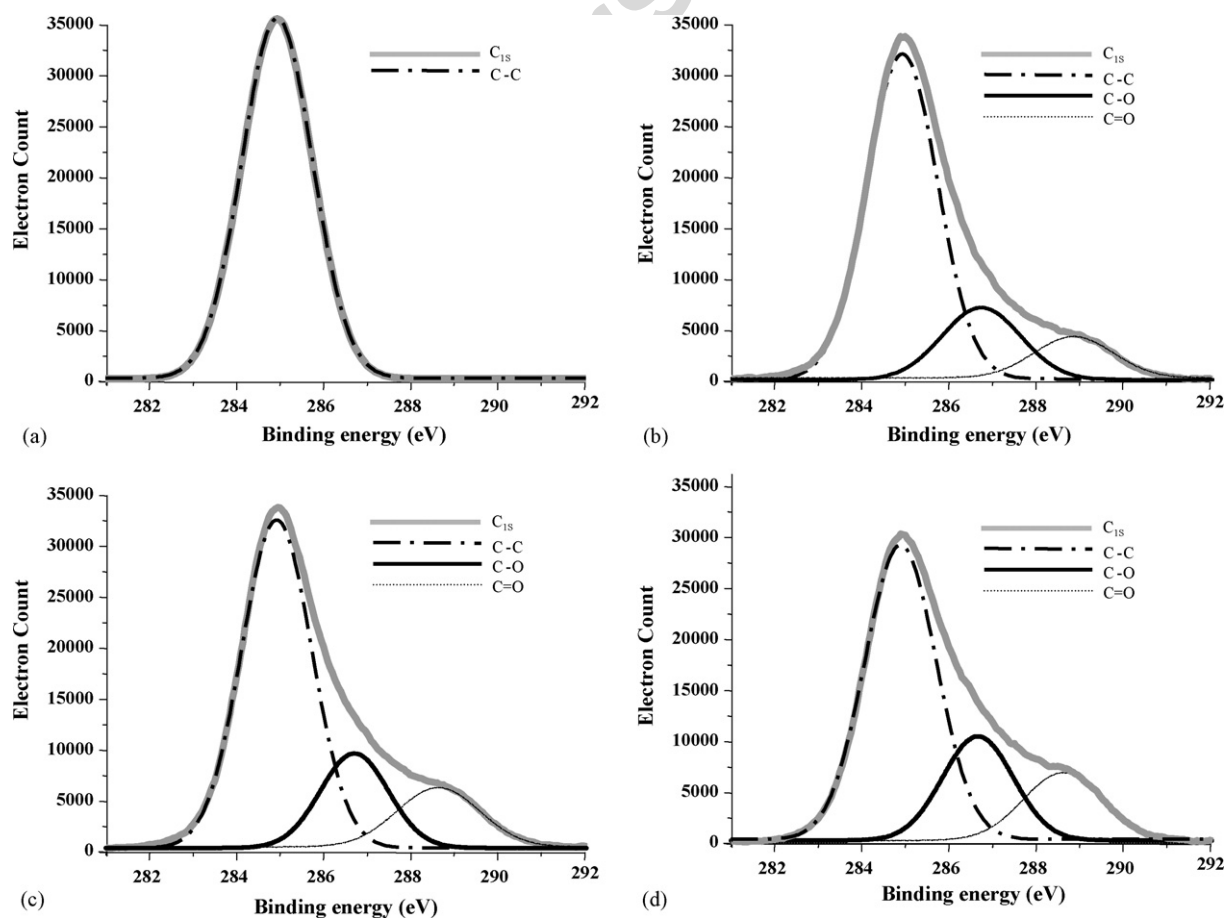

Fig. 2. C$_{1s}$ XPS core-level spectra change of PP support plasma treated with acrylic acid: (a) untreated, (b) 10 min treated, (c) 30 min treated and (d) 60 min treated.
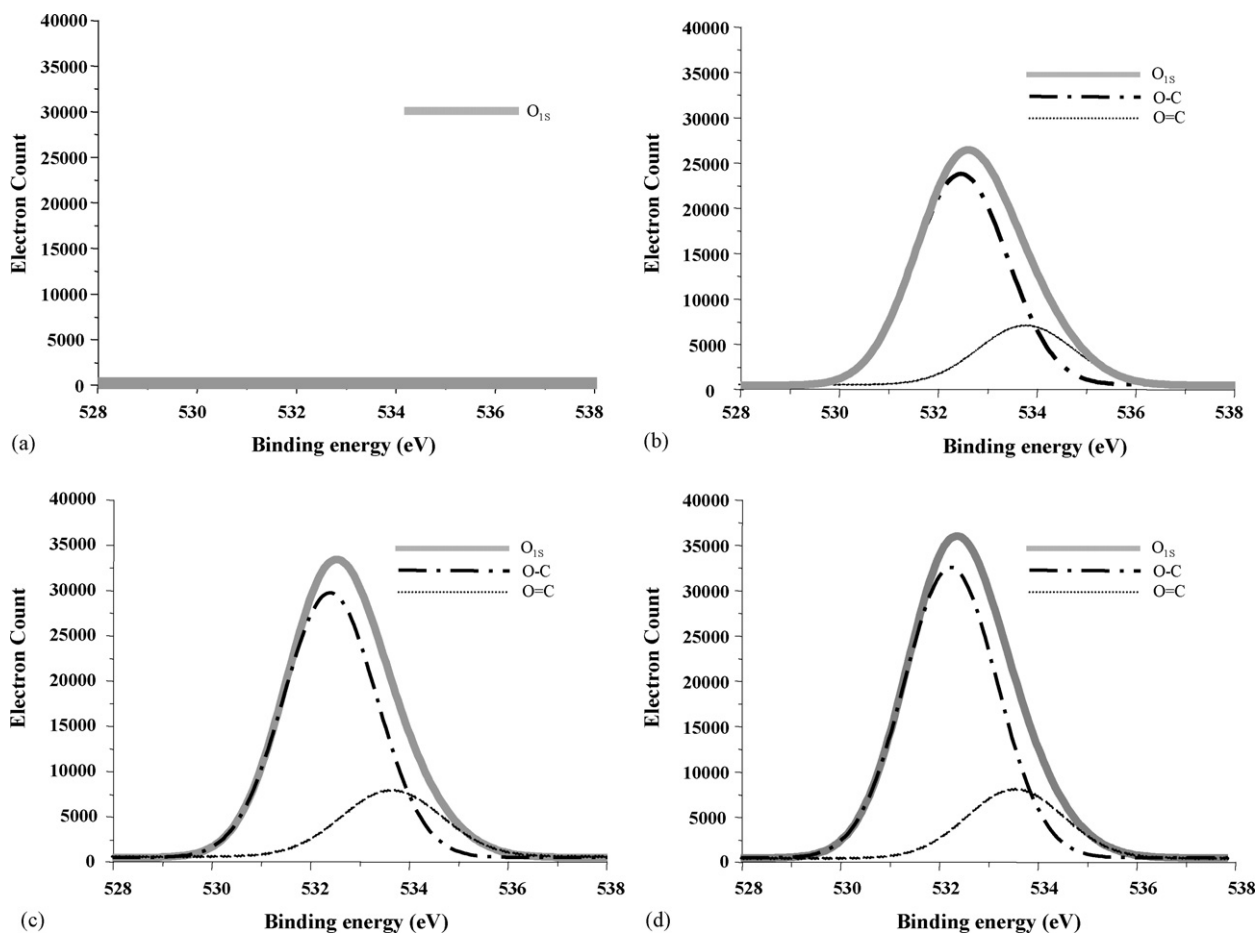
Fig. 3. O_{1s} XPS core-level spectra change of PP support plasma treated with acrylic acid: (a) untreated, (b) 10 min treated, (c) 30 min treated and (d) 60 min treated.

solution was not well presoaked into PP support, and interfacial polymerization afterwards was not properly performed. Although PP has better physicochemical properties than other support materials used, it has not been used as support for RO composite membrane for this reason. Therefore, surface modification of PP support by plasma treatment was attempted in this work to hydrophilize the surface for better interfacial polymerization. Surface modification was also performed for PSf support in order to further improve the performance and properties of conventional polyamide TFC membrane.

3.2. XPS analyses of plasma treated supports

Chemical composition variation of plasma treated PP and PSf supports with acrylic acid was investigated by XPS analyses. Changes in the C_{1s} spectra of PP support were observed

Table 1
Performance of composite membranes prepared by interfacial polymerization with untreated supports

Membrane	Water flux (l/m^2 atm h)	Rejection (%)
Commercial FT-30	0.5	98.0
PSf supported	0.7	92.3
PP supported	4.3	11.4

as plasma treatment time increased as shown in Fig. 2. Original PP support has a single peak at 285.0 eV corresponding to C–C group [26–28]. It was significantly decreased with plasma treatment time, while two additional peaks 286.5 and 289 eV were found to grow, which correspond to C–O group and C=O group, respectively [26–28]. O_{1s} spectra change was examined as shown in Fig. 3. Original PP support has no O_{1s} spectrum as expected. As plasma treatment time increased, peaks at 531.8 and 533.3 eV were found to grow, which correspond to O–C and O=C groups, respectively [27,28]. The results in Figs. 2 and 3 confirmed that plasma treatment of PP support with acrylic acid modified the surface chemical composition.

C_{1s} spectra of original PSf has peaks at 285.0 and 286.5 eV, which correspond to C–C and C–O groups, respectively, as shown in Fig. 4. As plasma treatment time increased, peak at 285 eV remained nearly constant while peak at 286.5 slightly increased. New peak at 289.0 eV, which is assigned to C=O bond, was formed and showed maximum increase around 30 min. The narrow scan of O_{1s} region showed the presence of two kinds of oxygen in the untreated PSf support, which are attributed to O–C at 531.8 eV and O=S at 533.3 eV as shown in Fig. 5. O–C peak at 531.8 eV increased by acrylic acid plasma treatment as C–O peak at 286.5 eV increased in Fig. 4. O=C group is also expected to be formed by plasma treatment in PSf support. Unfortunately, O=C bond has binding energy at 533.3 eV, which has exactly the
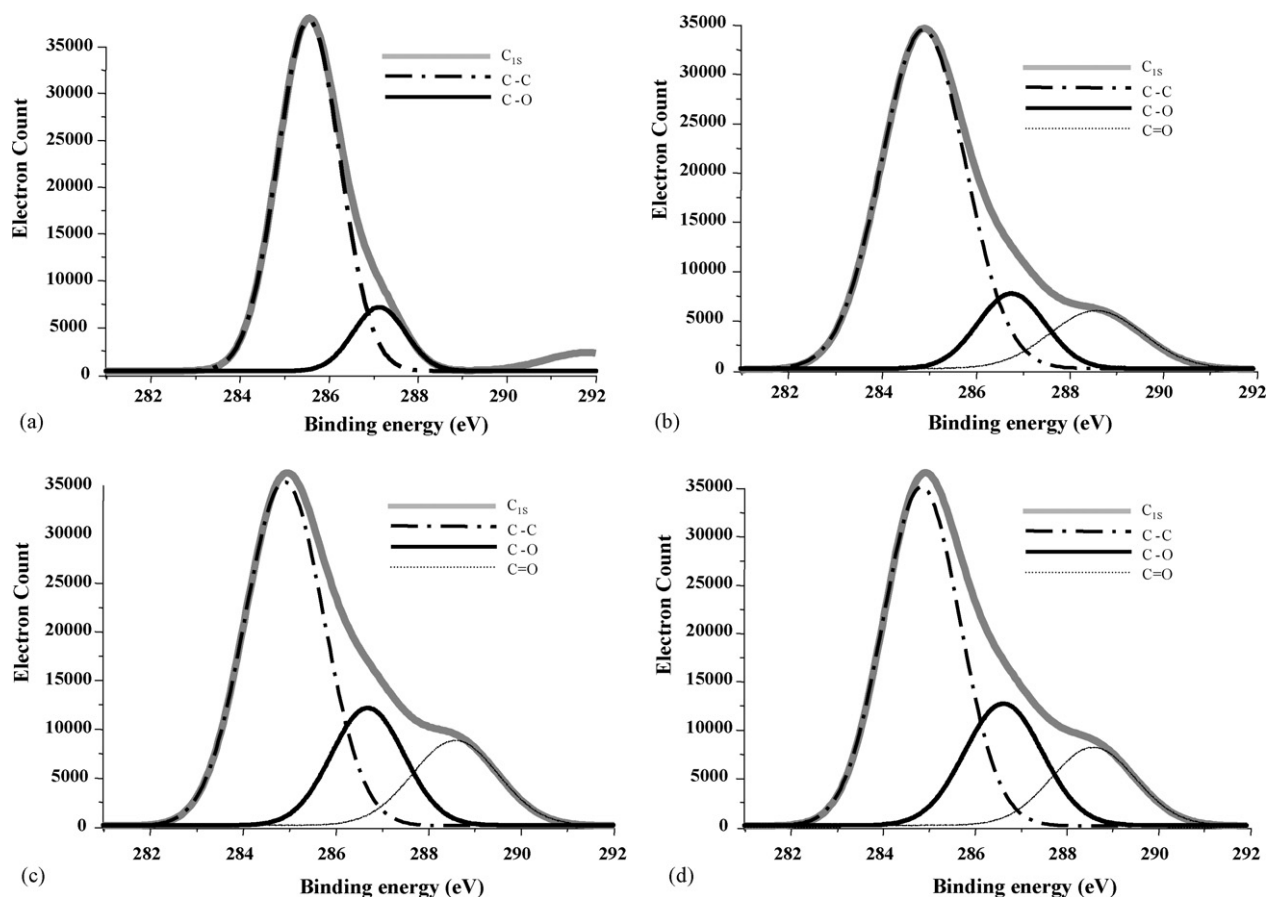
Fig. 4. C_{1s} XPS core-level spectra change of PSf support plasma treated with acrylic acid: (a) untreated, (b) 10 min treated, (c) 30 min treated and (d) 60 min treated.

same binding energy of O=S [27,28]. Therefore, it is impossible to distinguish O=C from O=S peak at 533.3 eV. Peak at 533.3 eV slightly decreased with plasma treatment time, but it cannot be explained in detail with present data obtained.

Fig. 6 shows the [O]/[C] ratio, (C_{1s} area of C=O and C–O)/(C_{1s} area of C–C), of plasma treated PP and PSf membrane. The [O]/[C] ratio of PP membrane increased with plasma treatment time. Even though the rate of increase somewhat decreased after 10 min, notable increase is still obtained with increasing reaction time after 10 min. The oxygen-containing groups originated from acrylic acid are incorporated into the PP support surface by plasma reaction, and these newly formed polar groups enhanced the hydrophilicity of support. For PSf support [O]/[C] ratio remarkably increased for first 10 min and remained nearly constant afterwards. Therefore, optimum plasma treatment time is recommended for PSf support.

3.3. TFC membrane with plasma treated supports

Fig. 7 shows the performances TFC membranes using plasma treated PP and PSf supports with acrylic acid. Plasma treatment of PP support with acrylic acid enhanced the performance of the composite membrane. With the increase of plasma treatment time, rejection was continuously increased and flux was much reduced. These performance results are very comparable to those of the composite membranes prepared by conventional interfacial polymerization. PP support is too much hydrophobic

to be soaked with MPDA aqueous solution, thus took longer time to be well hydrophilized by plasma treatment than PSf support.

Longer plasma treatment time for PP support also resulted in the deposition layer formation. However, PP support used in this work belongs to microfiltration range, and it has much greater pore size than that of PSf support which is in ultrafiltration range. Fifty minutes of plasma treatment covered the micropores of the PP support to be used as a support for interfacial polymerization, and it showed the comparable performance to those of PSf supported one. Composite membrane with untreated PP support showed uneven surface due to the poor interfacial polymerization, whereas plasma treated one showed nodular structured dense surface which enhanced the performance as shown in Fig. 8. As mentioned above for Fig. 6, the [O]/[C] ratio of PP membrane increased as plasma treatment time increased, and it indicated that more polar components were produced on the PP support surface to help interfacial polymerization.

Water flux as well as rejection was slightly enhanced by the plasma treatment of PSf support when compared with the untreated PSf support. The membrane using plasma treated PSf support has ridge-and-valley surface structure slightly modified from that of untreated support as shown in Fig. 9, which might contribute to the performance enhancement. It showed the best performance at 10 min of treatment time for both rejection and flux. Therefore, plasma treatment with optimum time overcame the trade-off trend, which usually occurs in membrane per-
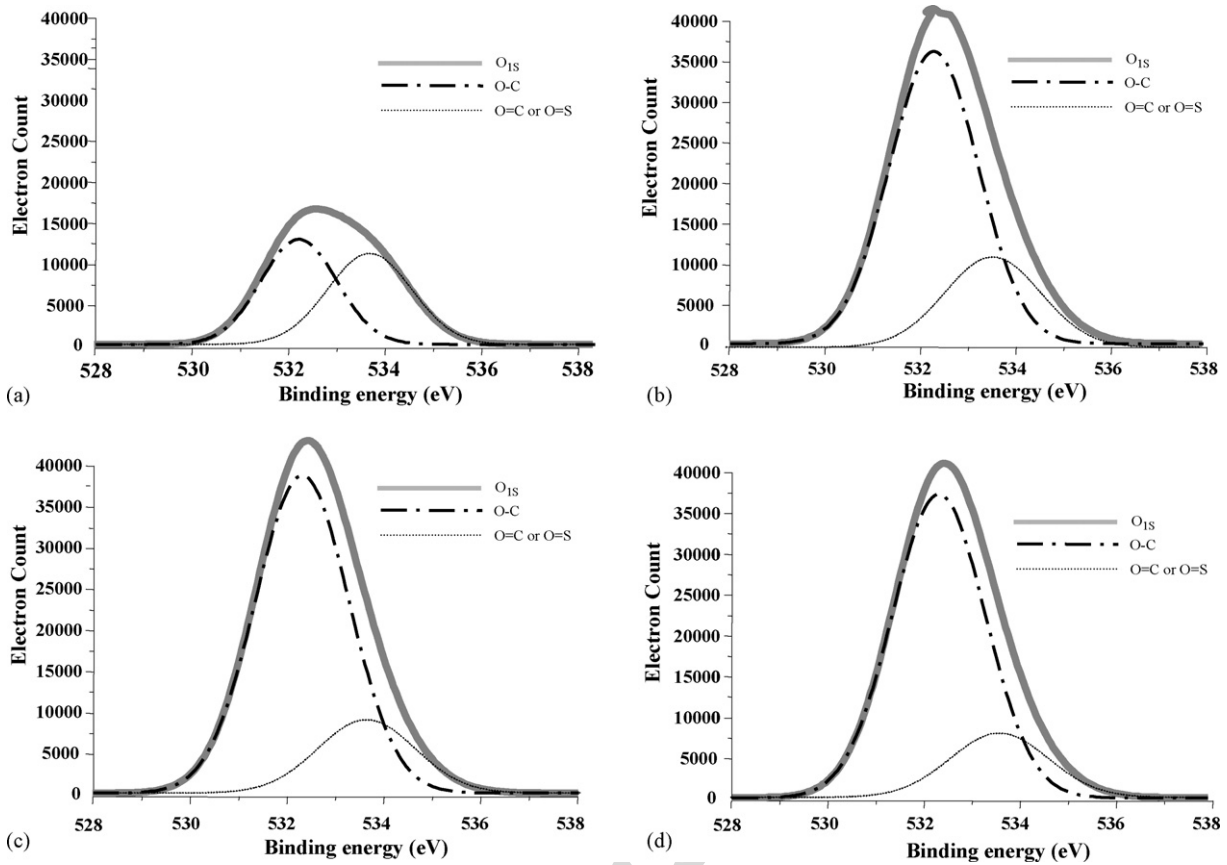
Fig. 5. O_{1s} XPS core-level spectra change of PSf support plasma treated with acrylic acid: (a) untreated, (b) 10 min treated, (c) 30 min treated and (d) 60 min treated.

formance control. However, when plasma treatment time was longer than 10 min, deposition layer was formed as previously revealed in our published paper [11]. Thus formed layer blocked the ultrafiltration scale micropores of PSf support, which had adverse effects in soaking with MPDA aqueous solution. Poorly soaked support caused poor interfacial polymerization with TMC resulting in performance decrease. As shown in Fig. 6, [O]/[C] ratio of PSf membrane reached the nearly constant value after 10 min of plasma treatment time indicating that

polar component on the membrane surface remained constant. For these reasons, the optimum performance was obtained when the plasma treatment time was 10 min for PSf support.

3.4. Effects of monomers

Several hydrophilic monomers were used for plasma treatment of the supports. PP support was plasma treated for 50 min and PSf for 10 min. The other plasma treatment conditions were
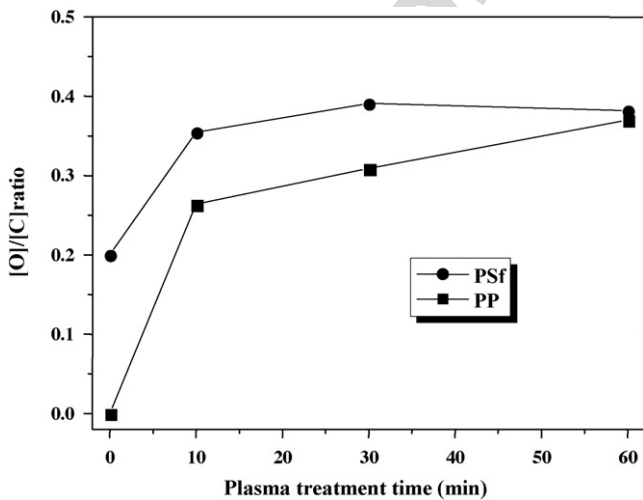

Fig. 6. [O]/[C] ratio change with acrylic acid plasma treatment.
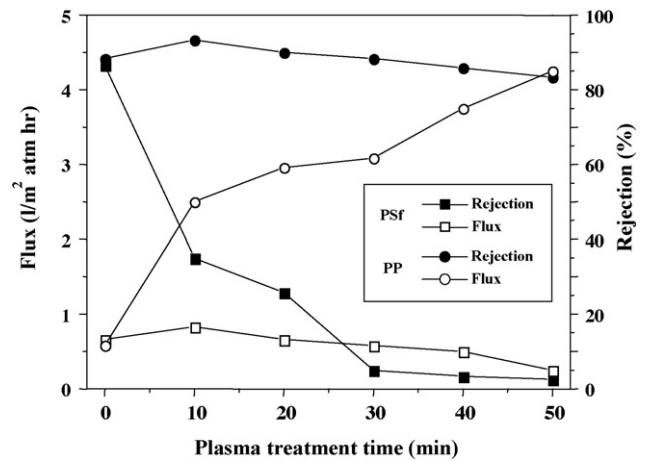

Fig. 7. Performance change of composite membranes with plasma treated supports with acrylic acid.
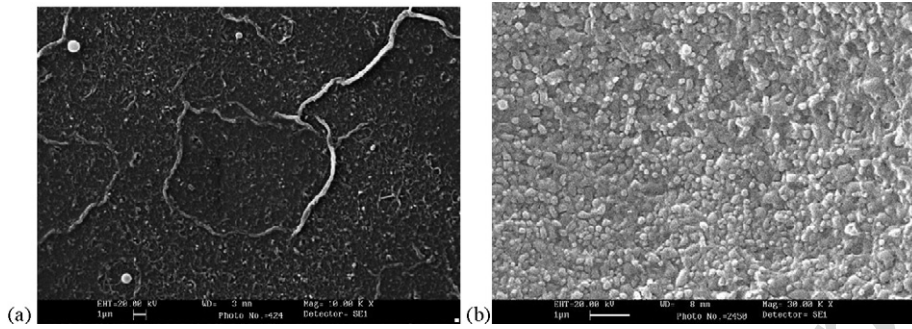
Fig. 8. Surface images of TFC membranes with PP support: (a) untreated support and (b) plasma treated support with acrylic acid for 50 min.
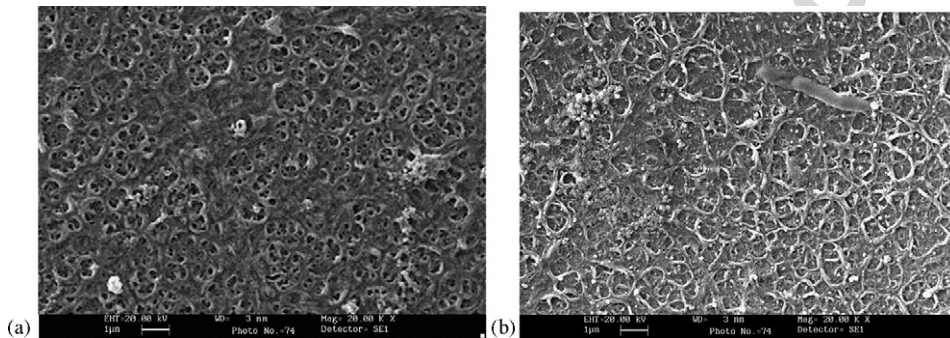

Fig. 9. Surface images of TFC membranes with PSf support: (a) untreated support and (b) plasma treated support with acrylic acid for 10 min.

kept the same for all samples; plasma power = 10 W, monomer flow rate = 0.6 sccm. The performance of PP support membrane was remarkably enhanced by plasma treatment with most of the hydrophilic monomers as shown in Fig. 10. Especially, AA and AM increased the rejection up to 90%, quite comparable to that of FT-30 membrane. For PSf support AA and AM enhanced the rejection quite close to that of FT-30 membrane, and they showed much greater flux than that of FT-30 membrane as shown in Fig. 11.

Water contact angles of PP and PSf support after plasma treatment with several monomers are summarized in Table 2. Hydrophilicity of PP and PSf membrane increased by various plasma treatments resulted in decrease of contact angle. AA and AM monomers were found to be more effective in enhancing the wettability for both PP and PSf membranes than other monomers.

The dependency of contact angle on rejection (%) of composite membranes is shown in Fig. 12. General trend was found to be that the support with lower contact angle showed higher rejection. It also has been attempted to make correlation between the water flux and contact angle of support but the data points were too scattered to be plotted. However, results showed the general trend that the flux increased with decrease of the contact angle of
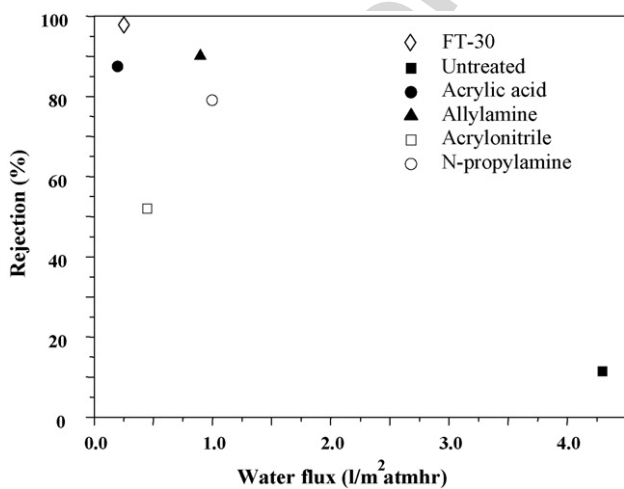

Fig. 10. Performance of composite membranes with PP support plasma treated with various monomers for 50 min.
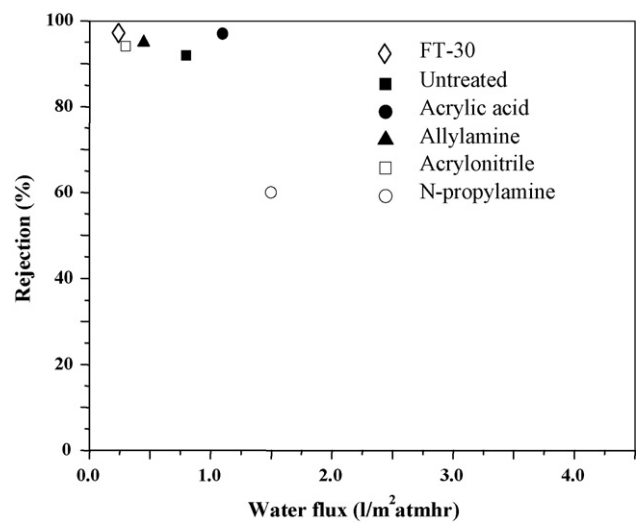

Fig. 11. Performance of composite membranes with PSf support plasma treated with various monomers for 10 min.

Table 2
Water contact angle variation of PP and PSf supports after plasma treatment

	PP support (°)	PSf support (°)
Untreated	108	63
Treated with AA	48	38
Treated with AM	38	24
Treated with AN	57	42
Treated with PA	52	50

Plasma treatment time = 50 min for PP and 10 min for PSf.
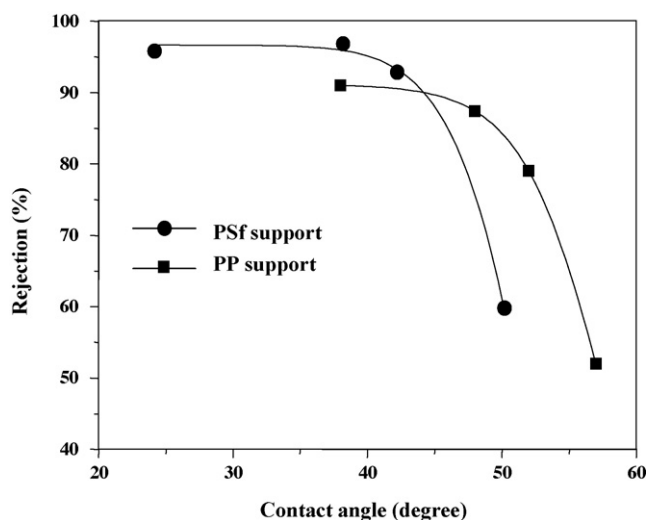

Fig. 12. Effect of contact angle on rejection of composite membranes: (a) PP support (treatment time: 50 min) and (b) PSf support (treatment time: 10 min).

the support. This indicates that hydrophilic surface modification of supports by plasma treatment helped the formation of active layer by interfacial polymerization.

3.5. Effects of plasma treatment on stability of TFC membrane

Back flush treatment was designed for determination of adhesion property between active layer and support of TFC membrane. Changes in water flux and rejection were examined after back flush treatment. If the adhesion strength of active layer is weak, the water flux will be increased due to delamination of active layer from support during the back flush
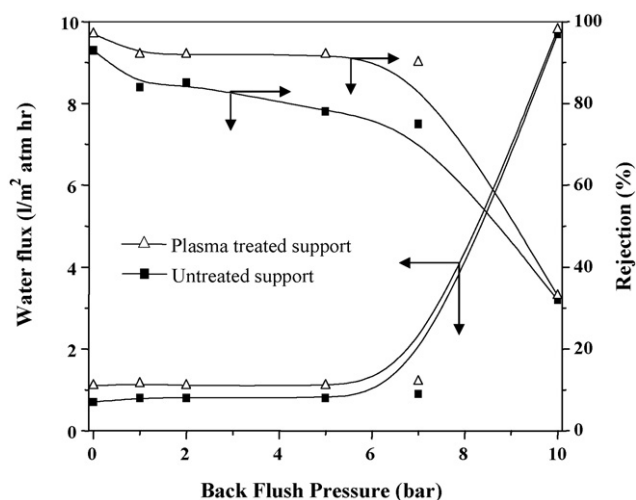

Fig. 13. Performance of composite membrane with PSf support after back flush treatment for 20 min.

treatment. As shown in Fig. 13, the rejection of the membrane with untreated PSf support dropped more rapidly than that with plasma treated PSf support. Rejection was maintained until 7 bar for plasma treated PSf support. This demonstrated that composite membrane using plasma treated support possesses better adhesion strength than that of membrane with untreated support.

Fig. 14 shows the surface images of composite membrane after back flush treatment. Active layer of membrane with untreated PSf support was delaminated at 100 μm scale by back flush treatment while that with plasma treated PSf support was quite maintained. This result corresponds with the performance results in Fig. 13. Enhancement of adhesion property by plasma treatment of support might be due to the formation of chemical bonding between active layer and support.

The chlorine resistance of composite membrane was examined by contacting the active layer surface with NaOCl solution at specified conditions. As summarized in Table 3, plasma treated PP and PSf supports produced more chlorine resistant membrane than untreated support. It may not be meaningful to compare the performances of PP support cases before and after contacting with NaOCl solution, since the untreated PP support showed too great flux and too low rejection to be used for
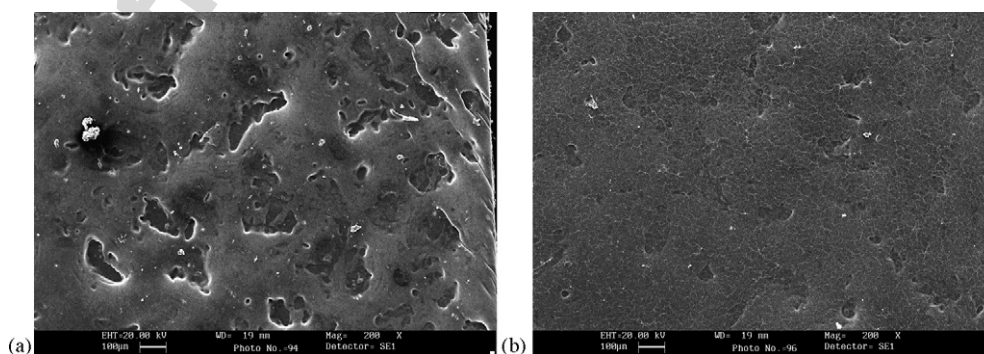

Fig. 14. Surface images of composite membrane with PSf support after back flush treatment: (a) untreated support and (b) plasma treated support with acrylic acid for10 min (back flush pressure: 5 bar, back flush time: 20 min).

Table 3
Comparison of the chlorine resistance of composite membranes

Membranes	Before NaOCl treatment		After NaOCl treatment	
	Water flux (l/m^2 atm h)	Rejection (%)	Water flux (l/m^2 atm h)	Rejection (%)
PP				
Untreated	4.3	11.4	4.4	10.9
Plasma treated	0.2	87.4	0.9	77.9
PSf				
Untreated	0.7	93.0	1.3	65.0
Plasma treated	1.1	97.0	1.1	96.4

Plasma treatment time = 50 min for PP and 10 min for PSf 1000 mmol/mol (ppm) NaOCl solution for 2 h.

reverse osmosis regardless of contacting with NaOCl solution. Plasma treated PP showed reduction of rejection by only 10% and increase of flux after chlorine resistance test. Untreated PSf support had flux increase by two-folds while the salt rejection decreased from 93% to 65%. But, the membrane with plasma treated PSf support retained its initial water flux and rejection after contacting with NaOCl solution. Therefore, it was confirmed that chlorine resistance could be improved by plasma treatment.

4. Conclusion

Plasma treatment of PSf support enhanced the rejection as well as the flux of conventional TFC membrane. Plasma treatment of PP support improved the performance of TFC membrane, and it enabled the use of PP as support which has not been used so far due to its hydrophobicity. AA and AM showed the best performance among the several monomers tested and results were discussed in terms of surface chemical composition and surface properties of support. Furthermore, plasma treatment of membrane supports assisted in better interfacial polymerization to enhance the adhesion properties between active layer and support. Chlorine resistance of the composite membrane was also improved notably by plasma treatment of support inducing chemical bonding between active layers and support.

Acknowledgement

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