Preparation and Characterization of Polyamide Reverse-Osmosis Membranes with Good Chlorine Tolerance

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ABSTRACT: To prepare reverse-osmosis membranes with good permeation properties and good chlorine tolerance, polyamide (PA) composite membranes were prepared with a conventional interfacial polymerization method. Diamine compounds, including metaphenylene diamine (MPD), 2,6-diaminotoluene (2,6-DAT), 2,4-diaminotoluene, 3,4-diaminotoluene, 2,4-diaminoanisol, 4-chlorometaphenylene diamine, and N,N′-diphenylethyldiamine, were polymerized with trimesoyl chloride (TMC) or isophthaloyl chloride to form PA polymers. The polymers were then tested for chlorine tolerance and hydrophilicity. Among the diamines tested, 2,6-DAT and MPD were used for the formation of thin-film composite (TFC) membranes by their interfacial polymerization with TMC on the surface of microporous polysulfone supports. Their performance and chlorine tolerance were test under various conditions. The TFC membranes prepared from 2,6-DAT and TMC showed better chlorine tolerance than the membrane prepared from MPD and TMC, and the permeation properties of these membranes were comparable to each other. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1245–1252, 2011

Key words: hydrophilic polymers; membranes; polyamides; separation techniques; thin films

INTRODUCTION

Today, a membrane technology using reverse-osmosis (RO) membranes is the leading technology for water treatment and water pollution control.[1] Among the various RO membranes, a thin-film composite (TFC) membrane composed of a thin, dense skin layer formed over a microporous support has been widely used. Particularly, aromatic polyamides (PAs) have been the ones used most widely as a skin (active) layer material of commercial RO membranes. In many cases, metaphenylene diamine (MPD) and trimesoyl chloride (TMC) have been used for the fabrication PA TFC RO membranes with good permselective performances.[2]

The effect of the molecular structure of PAs used for the active skin layer of a TFC RO membrane was investigated by Roh et al.[3] They concluded in their article that the main factors affecting the salt rejection of the PA composite membranes appeared to be the positions of the diamine groups and the number and position of the acyl chloride on the aromatic ring of the monomers used. They also reported that the membranes obtained from amine and acyl chloride showed the typical tradeoff between solute rejection and water flux. Nevertheless, the TFC PA RO membranes reached a relatively high level with regard to the salt rejection and water permeability.

However, there is still a problem with TFC PA RO membranes. It has been pointed out that the aromatic PA of MPD and TMC is very sensitive to chlorine; this results in a low chlorine tolerance. Normally, it has been well accepted that the degradation of PA layers of the membranes mainly includes N-chlorination by the substitution of the hydrogen on the amide nitrogen first, followed by ring chlorination via an intermolecular rearrangement.[4] In other articles, authors have mentioned that the chlorine tolerance of the PA TFC membrane is very sensitive to the pH of the feed solution; particularly, at higher pH's in the presence of chlorine, the chlorine tolerance is very low and is accompanied by bond breaking by the hydrolysis reaction.[5,6]

So, if the performance and chlorine resistance are enhanced together, applications of TFC RO membranes can be broadened. Because of these problems of conventional RO membranes, many researchers have tried to seek an effective way to prevent oxidative membrane degradation.[7–9] Konagaya et al.[7] tried to use piperazine, with a secondary amine, to replace MPD, with a primary amine, in the formation of PA TFC membranes to avoid N—H groups in the PA network, but they got low salt rejection. Some others

have tried many different methods to improve the chlorine tolerance of PA TFC RO membranes; some of them have been successful, but some have not.[8,9] So, still, there is a great need to improve the chlorine tolerance of PA RO membranes.

In this study, we tried to develop a PA TFC RO membrane with several different amines. Different PAs were prepared from various diamines by reactions with isophthaloyl chloride (IPC), and their chlorine tolerance was tested to select a proper amine monomer for the formation of PA TFC RO membranes with good chlorine tolerance. The prepared PA TFC membranes were tested and are discussed in terms of their chlorine tolerance and membrane performance.

EXPERIMENTAL

Materials

Polysulfone (PSf) ultrafiltration membranes, whose composition was 17/83 PSf/NMP wt %, prepared from a PSf solution in N-methylpyrrolidone (NMP) by the conventional non-solvent-induced phase-inversion method, were used as microporous supports. PA active layers were prepared from seven different kinds of diamine compounds and IPC or TMC. MPD, 3,4-diaminotoluene (3,4-DAT), TMC, and IPC were purchased from Aldrich Co. (Milwaukee, WI). The other diamines were purchased from Tokyo Chemical Industry Co. Sodium chloride (NaCl), bought from Junsei Co., was used as a solute of the feed solution. Membrane chlorine tolerance experiments were performed with a sodium hypochlorite solution from Aldrich Co. Other chemicals used in these experiments were used without further purification.

Preparation of the PAs

An aqueous diamine solution (100 mL, 0.01 mol) was slowly dropped into 100 mL of an IPC (0.0.1 mol) dichloroethane solution. The mixture was stirred at room temperature for 30 min. The mixture was then poured into ethanol to precipitate the product. It was filtered, washed with ethanol, and dried in vacuo.

Preparation of the membranes

PA TFC membranes were prepared by the conventional interfacial polymerization of PA active layers on microporous PSf supports. An NMP solution of PSf with a composition of 17/83 PSf/NMP wt % was cast on the polyester nonwoven fabric with a doctor's knife and solidified in the water used as a nonsolvent by the phase inversion for the formation of a microporous PSf support. For the preparation of

PA TFC membranes from diamine [MPD or 2,6-diaminotoluene (2,6-DAT)] and TMC, the PSf support was immersed in an aqueous mixture solution of diamine (3.0 wt %), sodium lauryl sulfate (0.15 wt %), triethylamine (3.0 wt %), camphorsulfonic acid (6.0 wt %), and isopropyl alcohol (IPA) (5.0 wt %) for 1 min. Excess diamine solution was removed from the surface layer of the support. The support was then immersed into a 0.2 wt % TMC solution in a hydrocarbon solvent (Isol-C, Isol-E, Isol-G, or Isol-H, SK Energy Co., Daejeon, Korea) for 10 s for the interfacial polymerization, after which it was dried at 120°C for 3 min. The prepared PA TFC membrane was then dried for characterization.

Characterization

The physical and chemical properties of the PAs prepared by the interfacial polymerization of different diamines with IPC were characterized with Fourier transfer infrared (FTIR) spectroscopy–attenuated total reflection (MAGNA-IR560, Nicolet, Waltham, MA), gel permeation chromatography (GPC; PL-GPC220, SEC Instruments, Church Stretton, UK), and differential scanning calorimetry (DSC; DSC Q1000, TA Instruments, New Castle, DE). The hydrophilicity of the PA polymers was also observed with a contact-angle analyzer (SEO300A, SEO Co., Suwon, Korea).

For the characterization of the PA TFC membranes, especially for the study of the morphologies of the membranes, field emission scanning electron microscopy (FESEM; JSM-6700F, JEOL, Tokyo, Japan) was used. The chlorine tolerance and separation performance of the membranes were test with the permeation test setup, which is explained in the following section.

Permeation test

For the test of the performance and chlorine tolerance of the PA TFC membranes, a 1000-ppm aqueous NaCl solution and a 2000-ppm aqueous solution containing 2000 ppm NaOCl were used as feed solutions, respectively. The membranes were exposed to NaOCl for the whole time during the performance test for 20 h. The conventional RO test setup was used for this experiment, with backpressure regulators to control the operating pressure, which ranged from 100 to 600 psi. All tests were conducted at 25°C. We measured the flux by weighing the permeate that penetrated through the membrane per unit time, and solute rejection was calculated from the concentrations of the feed solution and permeate with the following equation:

$$\text{Rejection} = 100 \times (C_f - C_p)/C_f$$
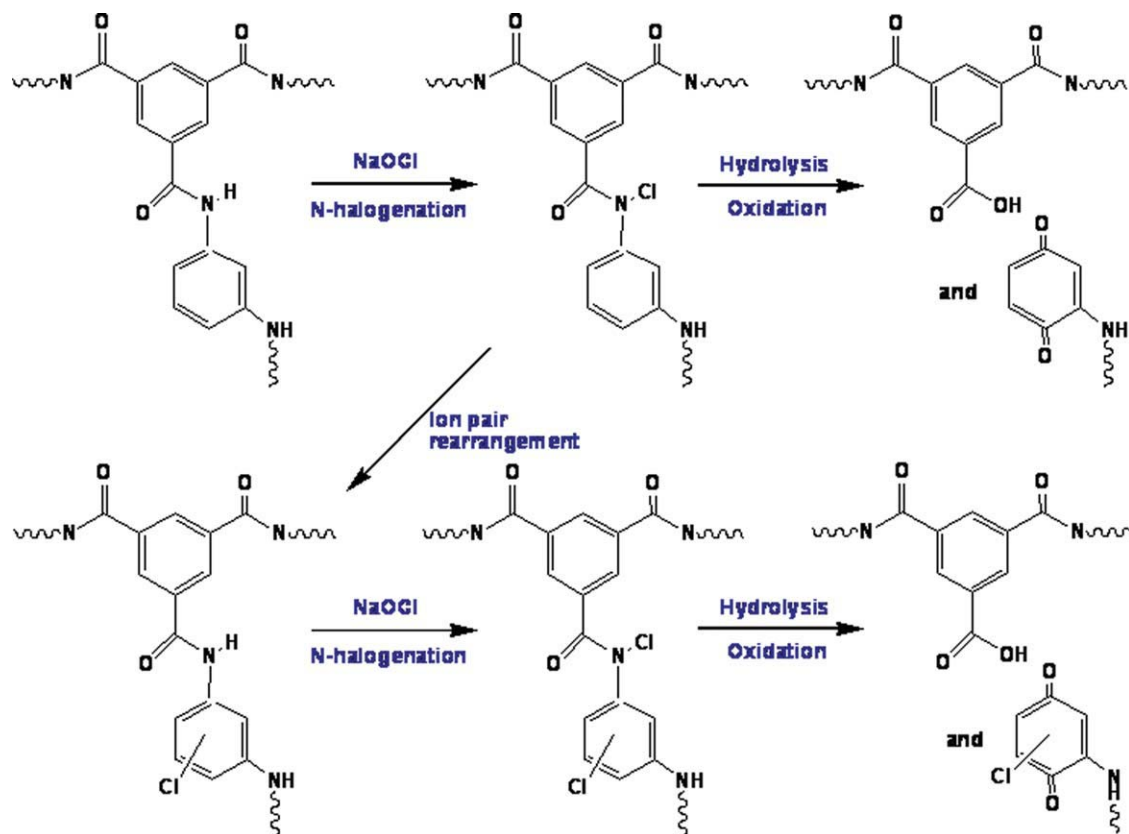
Figure 1 Mechanism of the oxidative degradation of the crosslinked PA network by NaOCl.[4] [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

where C_f and C_p are the concentrations of the feed solution and permeate, respectively. C_f and C_p were measured with high-performance liquid chromatography (model Waters 501, equipped with a differential refractometer R401 as a detector, Milford, MA).

RESULTS AND DISCUSSION

Preparation of PAs by interfacial polymerization

PA TFC membranes are usually prepared by the interfacial polymerization of MPD with TMC on the surface of a microporous support. They have been known to have a high flux and high rejection for the water treatment, including seawater desalination. However, the chlorine tolerance of PAs prepared from MPD and TMC is not satisfactory for enduring the harsh conditions of sea water desalination because of its degradation by strong oxidants, such as NaOCl. As shown in Figure 1, the crosslinked chemical bonds of PA have been known to be degraded by NaOCl.[4]

To prepare a RO membrane with better chlorine tolerance, in this study, some diimines other than MPD were used. Among them were derivatives of MPD with electron-donating or electron-withdrawing groups attached to it, such as 2,6-DAT, 2,4-diaminotoluene (2,4-DAT), 3,4-DAT, and 4-chlorometa-

phenylene diamine (4-CMPD), and others, such as 2,4-diaminoanisol (2,4-DAA). The reason that we selected such diamines was to see how the substituent of the phenyl ring of MPD affected the chlorine tolerance of the resulting PAs. Before we used them for the formation of RO membranes, they were polymerized with IPC by interfacial polymerization, and then, they were characterized in terms of the chemical structure of the polymers, molecular weight, chlorine tolerance, and hydrophilicity, to determine which one was good for the formation of a RO membrane with good chlorine tolerance.

Figure 2 shows the FTIR spectra of the PAs prepared from the corresponding diamines with IPC. As shown, every spectra showed a strong ketone (C=O) peak at 1700 cm^{-1} and N—H peaks of the amide linkage at 1660 and 3300 cm^{-1}. We found a slight difference between the spectra because the only difference in the polymers was the side group attached to the phenylene diamine group of the polymer.

Characterization of the PAs

The physical properties of the PAs prepared were then characterized with GPC and DSC to determine their molecular weights and glass-transition temperatures (T_g's). Table I shows the initial molecular
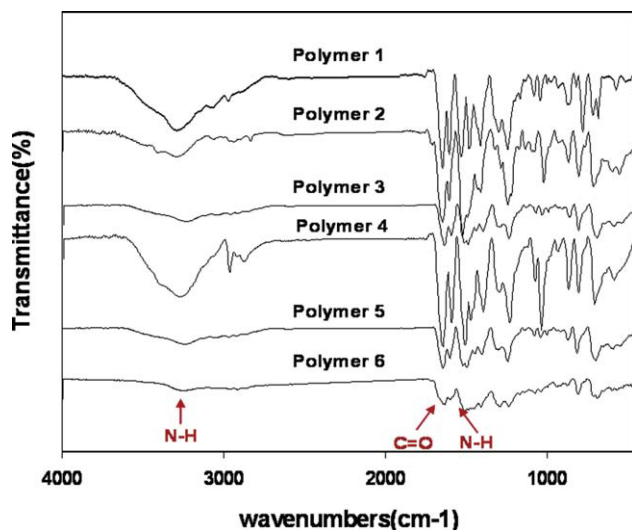
Figure 2 FTIR spectra of PAs prepared from different diamines: (1) MPD, (2) 2,4-DAA, (3) 2,4-DAT, (4) 4-CMPD, (5) 2,6-DAT, and (6) 3,4-DAT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

weight, T_g, and degradation ratio of each polymer. As shown, the molecular weight of the PAs prepared by the interfacial polymerization with 1,2-dichloroethane as an organic solvent ranged from 24,000 to 47,000 g/mol, depending on the diamine monomer used. The lowest molecular weight (24,000 g/mol) was obtained with 2,4-DAA, and the highest molecular weight (47,000 g/mol) was obtained with 4-CMPD, but there seemed to be no close relationship between the molecular weight and chemical structure of the polymer prepared, but the effect of the solubility in the dichloroethane (polymerization organic media) of the PA being prepared has to be accounted, because usually higher molecular weight can be obtained by the interfacial polymerization when the polymers being prepared have a good solubility in the organic solvent.

The T_g values of the polymers measured with DSC ranged from 110 to 185°C and reflected the chemical structures of the polymers: T_g of the PA prepared from MPD was only 110°C. However, for

the polymers prepared from 2,4-DAA, 2,4-DAT, 2,6-DAT, 3,4-DAT, and 4-CMPD, which had side groups such as —OCH₃, —CH₃, and —Cl, T_g increased substantially up to 185°C because of the side groups attached to the phenyl ring, which could have caused steric hindrance to the rotation of the polymer backbone and resulted in the rigidity of the polymer main chain. It is very well known that a short side group attached directly to the main chain of a polymer restricts the rotation of the polymer main chain and increases T_g of the polymer. However, there was not much difference among the T_g values of the polymers with side groups because the side groups were not very different in size.

The chlorine tolerance of the PAs was tested by measurement of the change of their molecular weights before and after treatment with NaOCl. As explained in the Experimental section, some of the polymers were kept in an aqueous solution of 1.0 wt % NaOCl at room temperature for 48 h to let them react with NaOCl. After that, they were filtered, washed with an excess amount of distilled water, and dried *in vacuo* before we measured the molecular weight of each polymer using GPC. From the molecular weights before and after treatment with NaOCl, the degradation ratio was defined as follows:

$$\text{Degradation ratio} = (M_{wi} - M_{wa}) \times 100/M_{wi}\,(\%)$$

where M_{wi} and M_{wa} represent the molecular weights of the polymer before and after treatment with NaOCl, respectively.

The degradation ratio showed quite a large difference among the polymers. For MPD, it was about 0.19%, and for 4-CMPD, the chlorinated MPD, it was about 0.68%; this indicated that the electron-

TABLE I
Properties of PAs Prepared from Different Diamine Monomers and IPC

Amine	Initial $M_w \times 10^4$	T_g (°C)	PA degradation ratio
MPD	3.2	110	0.19
2,4-DAA	2.4	174	0.34
2,4-DAT	3.4	175	0.13
2,6-DAT	2.9	185	0.0007
3,4-DAT	2.8	–	0.53
4-CMPD	4.7	170	0.68

M_w = weight-average molecular weight.

TABLE II
Water Contact Angles of PAs Prepared from Different Diamine Monomers and IPC

| Amine	Contact angle (°)	Image
MPD (26.83°)	25.13 25.88 29.50	
2,4-DAA (32.88°)	32.19 33.80 32.65	
2,4-DAT (30.97°)	31.03 30.82 31.08	
4-CMPD (43.64°)	43.57 44.03 43.34	
2,6-DAT (27.56°)	28.27 26.02 28.39	
3,4-DAT (39.4°)	38.72 38.27 41.21	
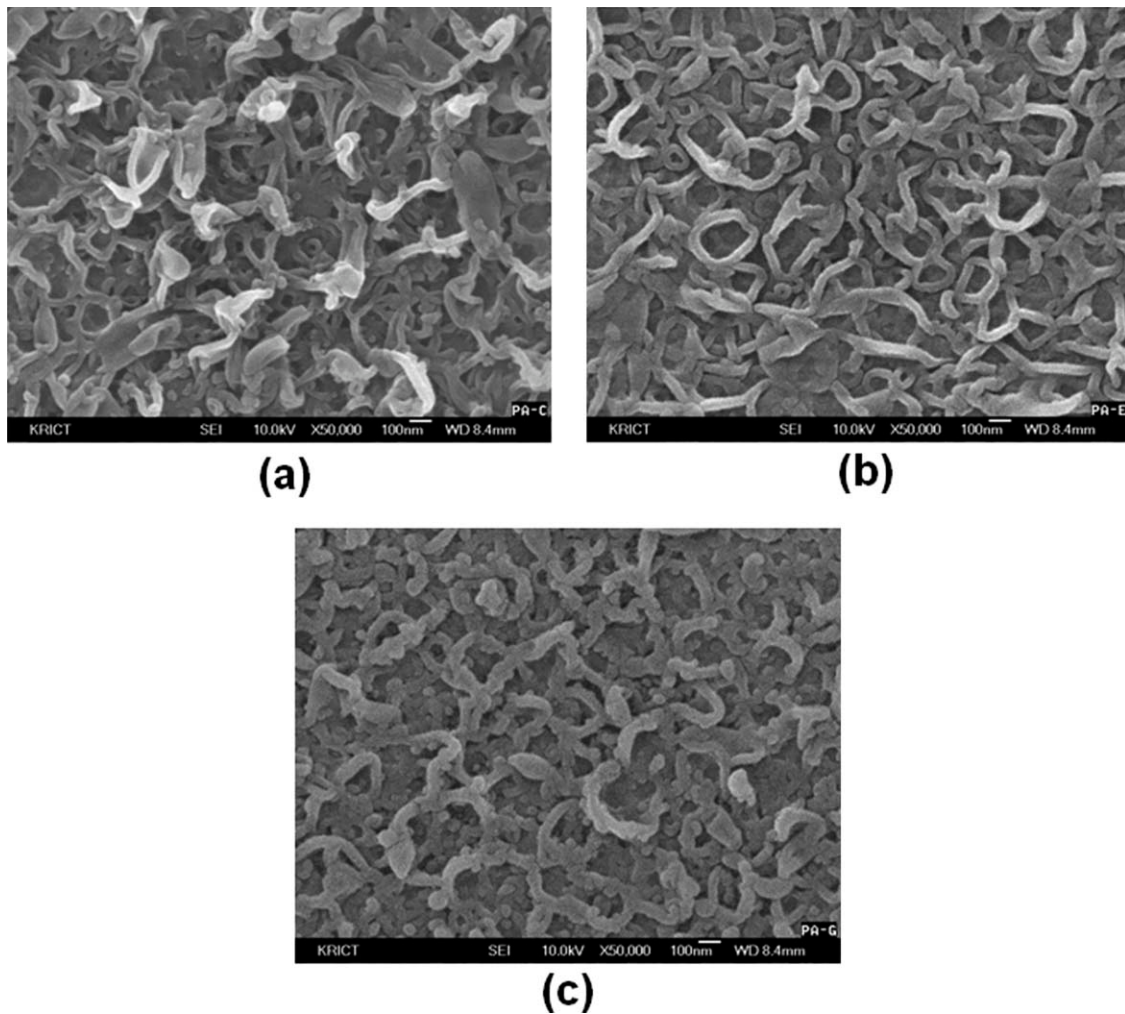
Figure 3 FESEM photographs of the surfaces of PA TFC RO membranes prepared from MPD and TMC with different organic solvents: (a) Isol-C, (b) Isol-E, and (c) Isol-G.

withdrawing group attached to the phenyl ring of MPD was not favorable for chlorine tolerance. On the other hand, for the diamines with electron-donating groups such as —CH$_3$ and —OCH$_3$, at different positions of MPD, it was less than that of MPD. Notably, 2,6-DAT showed a very low value, 0.0007%.
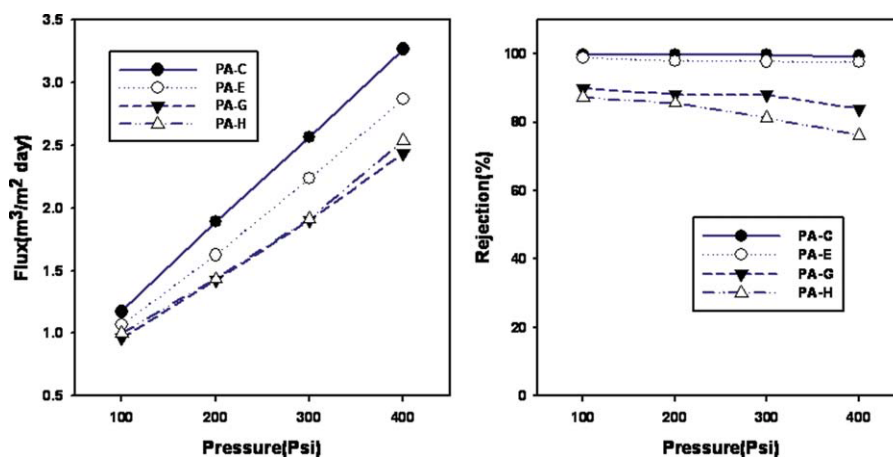
Figure 4 Permeation properties of PA TFC RO membranes prepared from MPD and TMC with different organic solvents: (PA-C) Isol-C, (PA-E) Isol-E, (PA-G) Isol-G, and (PA-H) Isol-H. The feed solution was a 1000-ppm NaCl aqueous solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
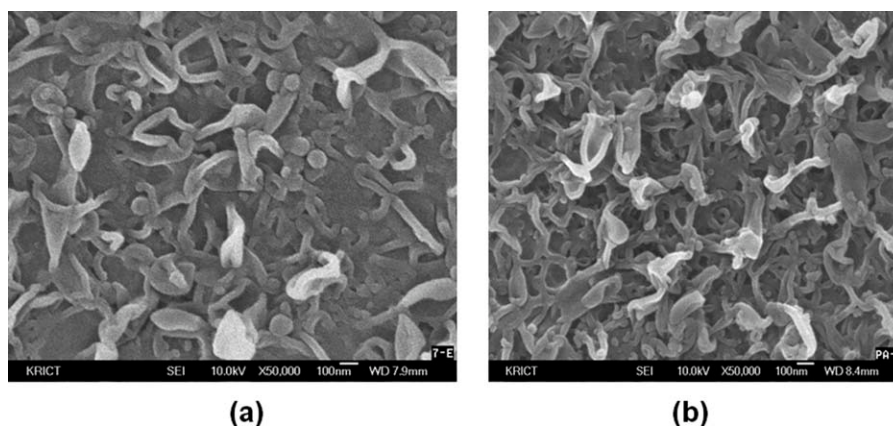
Figure 5 FESEM photographs of the surfaces of PA TFC RO membranes prepared from (a) 2,6-DAT and (b) MPD (diamine monomers) and TMC (acylchloride monomer).

From this result, we concluded that the MPD derivative with electron-donating groups, although it depended on the position of the substituent to the phenyl ring of MPD, was favorable for chlorine tolerance. Among them, 2,6-DAT was found to be the best.

Contact-angle measurement

To be used as a coating material of an RO membrane, it is better for the coating material to be hydrophilic because a membrane with a hydrophilic surface is better for a higher flux. Generally, to determine the hydrophilicity of a material, the contact angle with water must be measured. So, in this study, the water contact angles of the PAs, explained previously, were measured, and the results are shown in Table II.

As shown, all of the PAs prepared from derivatives of MPD showed higher contact angles; this

indicated that their hydrophilicity was less than that of the polymer from MPD. However, one thing good was that the contact angle of the PA of 2,6-DAT was very close to that of the PA of MPD.

From this result, 2,6-DAT was found to be proper for the formation of a PA TFC RO membrane with good chlorine tolerance.

Preparation of the PA TFC RO membranes

To prepare the PA TFC RO membranes, the conventional interfacial polymerization technique was used. To optimize the interfacial polymerization conditions for the formation of membranes with high performance, different organic solvents (Isol-C, Isol-E, Isol-G, and Isol-H) were tested. The Isol series of solvents was a mixture of alkane solvents (e.g., *n*-hexane), whose carbon numbers ranged from 6 to 35. So, different Isol solvents had different compositions, but their
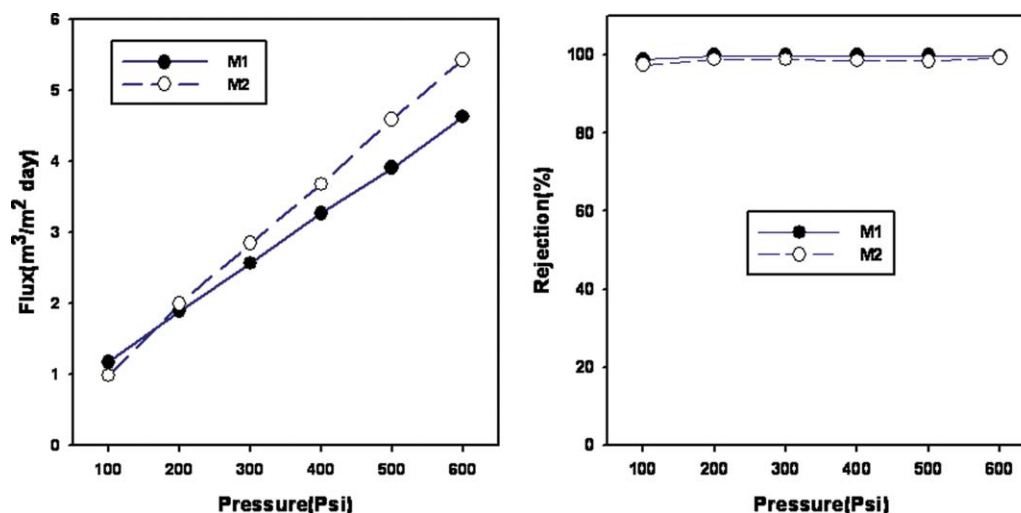
Figure 6 Permeation properties of PA TFC RO membranes prepared from 2,6-DAT or MPD (diamine monomers) and TMC (acylchloride monomer): (M1) MPD and (M2) 2,6-DAT. The feed solution was a 1000-ppm NaCl aqueous solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
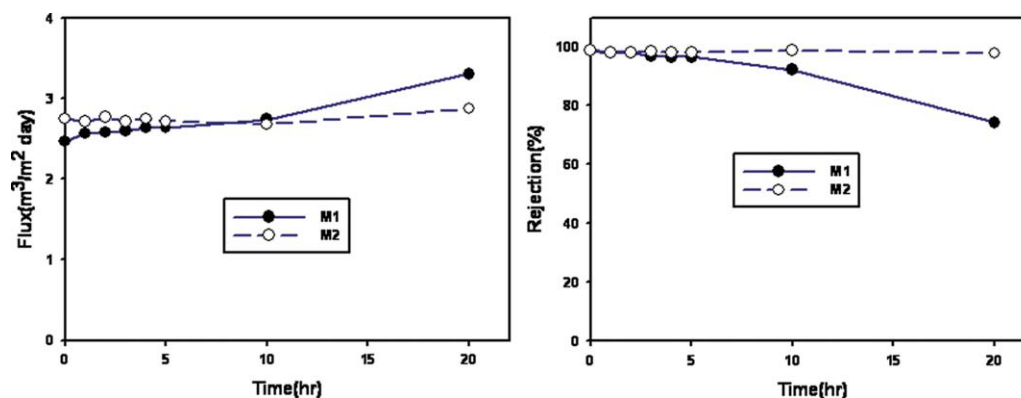
Figure 7 Chlorine tolerance of membranes prepared from diamines and TMC: (M1) MPD and (M2) 2,6-DAT. The behaviors of the flux and rejection with respect to the operation time are shown with a 2000-ppm NaCl aqueous solution containing 2000 ppm NaOCl. This experiment was carried out under an operating pressure of 400 psi at room temperature for 20 h; after 10 h of continuous operation, the operation was stopped for another 10 h while the membrane soaked in the feed solution in the cell. After that, the flux and rejection were measured again. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

exact compositions were not known. Figure 3 shows the FESEM pictures of the surface morphology of the membranes prepared from MPD and TMC with different organic solvents. Most of them showed a ridge-and-valley structure, but when Isol-C was used as the organic solvent, the surface morphology was the most favorable for the membrane to have the highest flux and rejection, as shown in Figure 3. The permeation properties of the membranes represented in Figure 4 also confirmed this fact. When Isol-C was used, the highest flux (2.0 m^3 m^{-2} day^{-1} at 200 psi) and highest rejection of NaCl (>99.5%) was obtained when the 1000-ppm aqueous solution of NaCl was used as a feed solution. From this result, the right conditions for the formation of a PA TFC RO membrane with 2,6-DAT as a monomer were obtained.

Figures 5 and 6 show the surface morphology and permeation properties of the membrane from 2,6-DAT, respectively. As shown in Figure 5, the surface morphology of the membrane from 2,6-DAT was quite similar to that of the membrane of MPD. Also, the permeation properties of the membrane of 2,6-DAT were found from Figure 6 to be even better than that of the membrane of MPD, with a higher flux and similar rejection; this indicated that 2,6-DAT was a another good monomer for the formation of a PA TFC RO membrane with good performance. For the 1000-ppm aqueous solution of NaCl, the flux was as high as 5.5 m^3 m^{-2} day^{-1} (at 600 psi), and the rejection was about over 99.5%

Chlorine tolerance of the 2,6-DAT membrane

To confirm the chlorine tolerance of the membrane prepared from 2,6-DAT, it was tested with a feed solution of 2000 ppm aqueous NaCl containing 2000 ppm NaOCl for about 20 h at room temperature. Figure 7 shows the behavior of the flux and rejection

of the membranes prepared from different monomers under different conditions according to the operating time at 400 psi of operation pressure. During this test, for up to 10 h, it was operated continuously. After 10 h, the operation for the permeation test was stopped for 10 h, and the membrane was left in the membrane cell to soak in the feed solution of 2000 ppm NaOCl. After that, the operation was restarted, and the flux and rejection were measured. By doing this, we tested the chlorine tolerance of the membranes and compared them with each other.

As shown, the rejection of the membranes from MPD decreased drastically after 10 h of soaking in the NaOCl solution, but the membrane from 2,6-DAT did not show such a large decrease in rejection under the same conditions. From these results, we found that the PA TFC RO membrane prepared from 2,6-DAT and TMC was a good RO membrane with a high chlorine tolerance and high performance as well.

CONCLUSIONS

A PA TFC RO membrane with good chlorine tolerance was prepared by the conventional interfacial polymerization of 2,6-DAT with TMC on the surface of a microporous PSf membrane. When 2,6-DAT was used, the chlorine tolerance of the resulting membrane was better than that of the membrane prepared from MPD as an amine monomer. The PA prepared from the derivatives of MPD with electron-donating group such as —CH_3 and OCH_3 attached to the phenyl ring of MPD usually showed better chlorine tolerance on the basis of the results from the degradation ratio measurement of the PAs. However, when an MPD derivative with an electron-withdrawing group such as —Cl was used, the resulting membrane showed poorer chlorine

tolerance, with the oxidative degradation accelerated by NaOCl. The RO membrane prepared from 2,6-DAT had a very similar desalination performance to that of MPD and showed an even better flux.

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