

Factors Affecting the Interfacial Polymerization of Polyamide Active Layers for the Formation of Polyamide Composite Membranes

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ABSTRACT: Polyamide (PA) composite membranes were prepared by interfacial polymerization with piperazine, *m*-phenylene diamine, and trimesoyl chloride as monomers and polysulfone ultrafiltration membranes as supports. Factors affecting the performances of the composite membranes by changing the characteristics of the PA active layers were studied. First, the monomer compositions were varied, and organic solvents (benzene and 1,2-dichloroethane) with better solubility for PA than hexane were used for the interfacial polymerization. As chemical additives capable of changing the property of the interface formed between water and organic phases, *n*-propanol and *i*-propanol were used, and

phase-transfer catalysts such as triethyl benzyl ammonium bromide were used to improve the polymerization efficiency of the PA active layers. The characteristics of the PA composite membranes prepared, including their permeation properties and morphology, were carefully studied with various analytical methods, such as field emission scanning microscopy, atomic force microscopy, differential scanning calorimetry, and permeation testing. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2781–2787, 2002

Key words: interfacial polymerization; polyamide; composite membrane; reverse osmosis; polysulfone

INTRODUCTION

Traditional water-treatment membranes include reverse-osmosis (RO), ultrafiltration (UF), and microfiltration membranes. Of these, RO membranes have usually been used for desalting processes; polyamide (PA) composite RO membranes have most often been used.^{1–4} Consisting of a thin, highly crosslinked PA active layer and a microporous support layer, PA composite RO membranes usually show good permselective performance for desalting. However, because of the excessively tight crosslinking and excessively low free volume of the PA active layers prepared from primary diamines and trifunctional acid chlorides such as trimesoyl chloride (TMC), the flux of the PA composite RO membrane is too low under a moderate pressure. Therefore, there have been efforts to make loose RO membranes with better flux and rather low salt rejection to meet the requirements of applications other than desalting, such as the rejection of low molecular organics.

For the preparation of loose RO membranes, several methods have been employed, such as using piperazine (PIP) mixtures with *m*-phenylene diamine (MPD) as a diamine monomer and treating regular PA RO membranes surfaces in acid or base solutions to re-

duce the degree of crosslinking of the PA active layers.^{5,6} Of the methods used to make loose RO membranes by controlling the characteristics of PA active layers, the easiest is changing the compositions of the monomers used for the membrane formation. Mostly, PIP consisting of aliphatic C—C bonds and secondary amines has been used together with MPD for the formation of the membranes because it can provide higher free volumes and larger pore sizes to the PA active layers. The chair shape of PIP in its lowest energy state makes the crosslinked PA molecules more difficult to pack together, providing more free volume to the PA active layers.

Other than changes in the monomer compositions, there could be several other methods for the formation of loose RO PA composite membranes, but not many attempts have been published yet. Therefore, in this study, several other methods, such as changing organic solutions for the interfacial polymerization, using additives, and using phase-transfer catalysts (PTCs), were tried for the fabrication of loose RO PA composite membranes. In particular, as much PIP as possible, instead of MPD, was used because PA prepared from secondary diamine monomers has been known to have better chlorine tolerance.

EXPERIMENTAL

Materials

Polysulfone (PSf) UF membranes with a molecular weight cutoff (MWCO) of about 30,000 g/mol, pur-

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chased from Fluid System Co., were used as microporous supports, and the monomers used for the formation of PA active layers were PIP, MPD, and TMC from Aldrich Co. Triethyl benzyl ammonium bromide (TEBAB), trimethyl benzyl ammonium bromide (TMBAB), and triethyl benzyl ammonium chloride (TEBAC), purchased from Aldrich, were used as PTCs. 1,2-dichloroethane and benzene, bought from Tokyo Kasei, were used as organic solvents for the interfacial polymerization and mixed with hexane from Tokyo Kasei. *i*-Propanol (IPA) and *n*-propanol (NPA) from Tokyo Kasei were used as chemical additives for the interfacial polymerization. Other chemicals used in the experiments were used without further purification.

Preparation of the PA composite membranes

PA composite membranes were prepared by the conventional interfacial polymerization of PA active layers on microporous PSf supports under different interfacial polymerization conditions such as different monomer compositions, different organic solvent systems, and the presence or absence of PTCs. The typical, simple process used in this study was as follows. A PSf support whose surface was cleansed with a dilute sulfuric acid solution in water (0.01M) was dipped into a 1.0 wt % PIP solution in water, in which 1.0 wt % triethylamine was also dissolved, for about 1 min, with some shaking. The surface of the support was then rolled with a rubber roller for the removal of excess PIP solution that remained on it and was immersed in a 0.05 wt % TMC solution in hexane for 10 s for the interfacial polymerization of PA active layers on the PSf support. Afterward, it was dried in air at room temperature for 2 h, and the PA composite membrane so prepared was kept in distilled water before use.

Characterization

The surface and cross-section morphologies of the PA composite membranes were studied with field emission scanning microscopy (FESEM; XL 30, Philips Co., Eindhoven, The Netherlands) and atomic force microscopy (AFM; NanoScope IIIa, Di Co., Santa Barbara, CA). For the indirect determination of the degree of crosslinking of the PA active layers by the measurement of their glass-transition temperatures (T_g 's), differential scanning calorimetry (DSC; 910, DuPont, Wilmington, DE) was used.

Permeation test

The PA composite membranes were tested with various feed solutions, such as 1000 ppm aqueous solutions of poly(ethylene glycol) (PEG) 200 and NaCl, to

determine their permeation performances with a general RO test setup. Backpressure regulators controlled the operating pressure, which ranged from 100 to 400 psi. Other test conditions were the same as those previously reported.⁷ The flux was measured by the weighing of the permeate that penetrated through the membrane per unit of time, and the solute rejection was calculated from the concentrations of the feed solution and permeate with the following equation:

$$\text{Rejection} = 100 \times (C_f - C_p) / C_f$$

where C_f and C_p are the concentrations of the feed solution and permeate, respectively. They were measured with a high-performance liquid chromatograph (501, Waters, Milford, MA) that was attached to an R401 differential refractometer used as a detector.

RESULTS AND DISCUSSION

Effect of the monomer compositions

The active layer structure of PA composite membranes has been known to be an important factor in determining their permeation characteristics. In particular, the MWCO and permeation rate are dependent on the physical and chemical structure of the active layer. The pore size and free volume of the PA active layer, the most important parameters determining the flux and rejection of the membranes, can be determined first hand by the monomer compositions employed to form the active layer. For general PA composite membranes, PIP, MPD, and TMC are among the most frequently used monomer combinations.

Figure 1 shows the permeation properties of the PA composite membranes, which were obtained from tests with a 1000 ppm PEG 200 solution in water as a feed solution. The PA composite membranes were prepared from different compositions of PIP/MPD mixtures, along with TMC. The PIP/MPD composition ratio was changed from 9/1 to 7/3 (w/w). With increasing PIP in the monomer composition, the flux increased, but the rejection decreased. When the PIP/MPD ratio was 8/2, the flux and rejection at 200 psi of the membrane were 2.2 m³/m² day and 90%, respectively, with the membrane becoming a typical nanofiltration (NF) membrane. With a further increase in PIP, the flux increased to 2.4 m³/m² day (at 200 psi), but the rejection decreased to 78%.

This result represents the dependence of the permeation characteristics of PA composite membranes on the characteristics of the monomers used. More flexible monomers, consisting of aliphatic alkyl chains instead of aromatic chains, such as PIP are more favorable for the formation of bigger pore sizes or free volumes in the PA active layers, increasing the per-

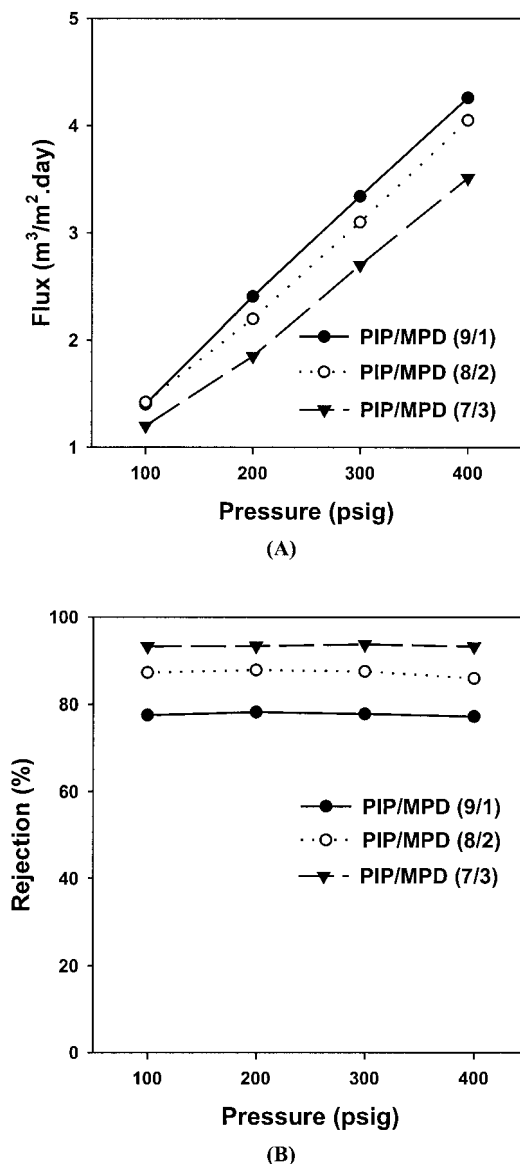


Figure 1 Permeation properties of PA composite membranes as a function of the operating pressure at room temperature: (A) flux and (B) rejection. The amine monomer compositions used (PIP/MPD w/w) to form the membranes were 9/1, 8/2, and 7/3. The feed solution was a 1000 ppm PEG 200 solution in water.

meability and MWCO of the composite membranes. Compared with MPD, which is composed of an aromatic ring structure, PIP, with aliphatic C—C bonds, is more flexible, and its chair structure at its lowest energy state is more difficult to pack tightly, imparting a high free volume to the PA active layers.

Effect of the organic solutions

For general interfacial polymerization, the characteristics of the organic solution employed are among the most important factors affecting the molecular weight of the polymers. The organic solution contains organic

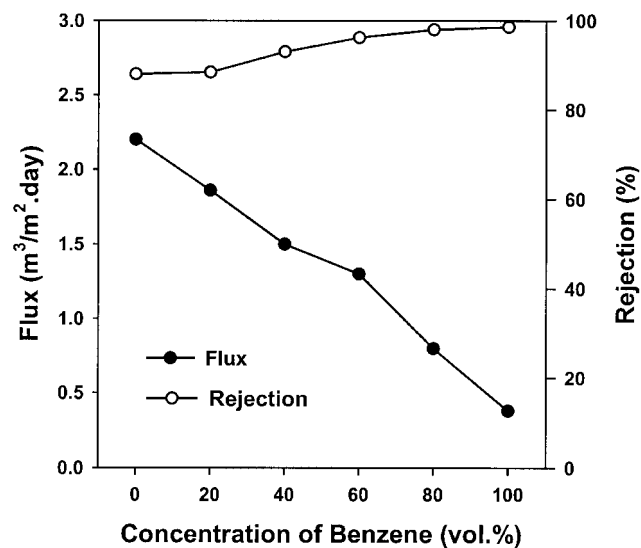
soluble monomers and forms an interface with the water phase, in which water-soluble monomers are dissolved. In general, the polymerization site of the interfacial polymerization is not just on the interface but is slightly shifted into the organic phase.⁸ Therefore, the solubility of the polymers being polymerized into the organic solution is important, especially for the molecular weight of the polymers. The more soluble they are, the higher their molecular weight is. This is because in a poor solvent the polymer can easily be precipitated, with the reaction site buried in the polymer coagulants, prohibiting further polymerization.

With this kind of knowledge, it is possible to speculate that changing the organic solvent from hexane to others with better solubility for PA could affect the performance of the PA composite membranes. The characteristics of the PA active layer, such as the degree of crosslinking and thickness, would be affected. It is expected that a good solvent will improve the polymerization efficiency for the formation of the PA active layer, increasing its degree of crosslinking and thickness.

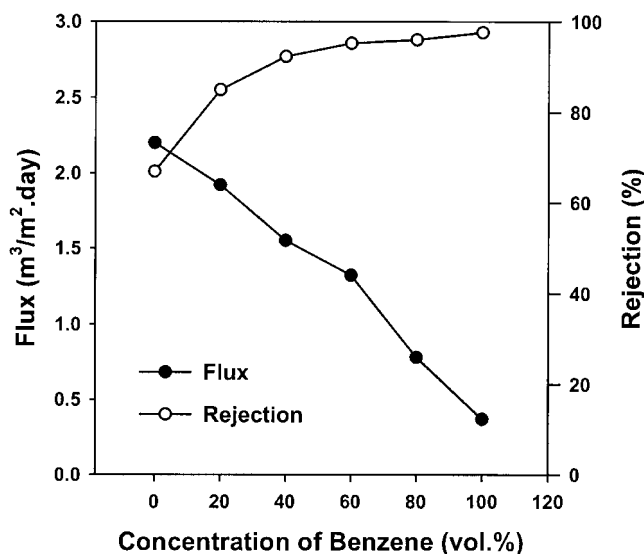
Therefore, three different organic solvents were used in this study: hexane, benzene, and 1,2-dichloroethane. Hexane is a typical organic solvent most often used for the formation of PA composite membranes by interfacial polymerization because it does not hurt the support structure during interfacial polymerization. The other two organic solvents, benzene and 1,2-dichloroethane, have better solubility toward PA polymers. In this study, benzene and 1,2-dichloroethane were used as cosolvents and mixed with hexane for the interfacial polymerization. PIP/MPD mixtures were dissolved in the solution mixtures. The ratios of benzene or 1,2-dichloroethane to hexane were controlled to avoid the destruction of the microporous structure of the PSf supports.

Figures 2 and 3 show the permeation properties of the PA composite membranes prepared as a function of the concentration of benzene or 1,2-dichloroethane in benzene/hexane or 1,2-dichloroethane/hexane mixtures. The monomers used were PIP/MPD (8/2 w/w) mixtures and TMC. The feed solutions used were 1000 ppm PEG 200 solutions and 1000 ppm NaCl solutions. The operating pressure was 200 psi. When benzene was used for the interfacial polymerization, with an increasing concentration of benzene, the flux decreased gradually and became $0.4 \text{ m}^3/\text{m}^2 \text{ day}$ as the concentration of benzene reached 100%. However, the rejection of both PEG 200 and NaCl increased, approaching almost 99%.

We have found that it is possible to make PA composite membranes that have very different permeation performances, ranging from NF to RO, by only changing the organic solvents. With the same monomer composition, the characteristics of the active layers of



(A)



(B)

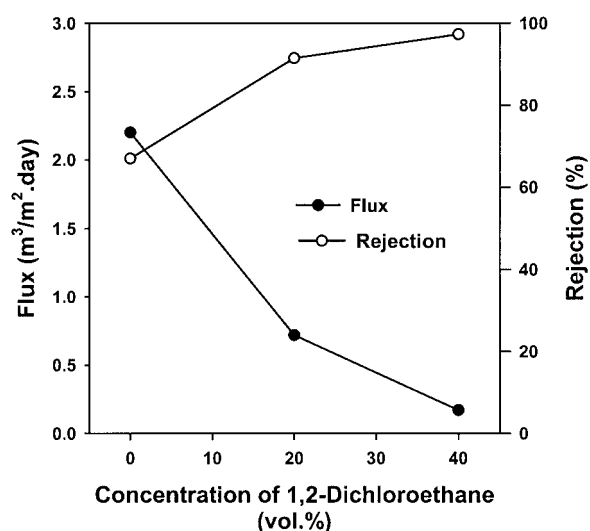
Figure 2 Rejection and flux of the PA composite membranes as a function of the concentration of benzene (vol %) in the benzene/hexane mixtures used. The feed solutions were (A) 1000 ppm PEG 200 and (B) NaCl solutions in water.

PA composite membranes can be varied to give three different types of membranes: NF, loose RO, and RO membranes. In particular, when the concentration of benzene was 40%, a loose RO membrane with a fairly good permeation performance (1.5 m³/m² day of flux and over 90% of rejections) was obtained.

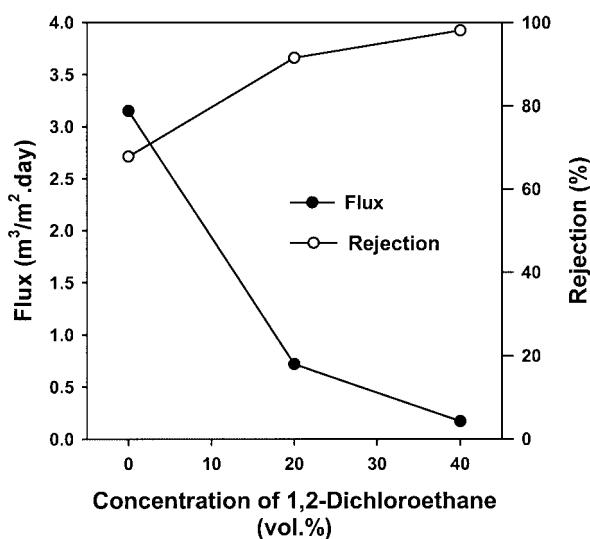
We also have found that using benzene as a cosolvent is a good way of controlling the permeation properties of the PA composite membranes without changing the monomer compositions. This method seemed especially good for making loose RO PA composite membranes with better chemical stability. With a small amount of benzene, it was possible to make a

loose RO membrane out of a PIP/MPD (8/2 w/w) composition. Using such a low amount of MPD, a primary amine, is good for better chlorine tolerance because it is very well known that a secondary amine monomer is better than a primary amine for chlorine tolerance in PA composite membranes.^{9,10}

When 1,2-dichloroethane, a better solvent for PA polymers than benzene, was used, the tendency of the permeation properties of the PA composite membranes was the same, but the flux decline was very serious, even at low contents of 1,2-dichloroethane, as shown in Figure 3. When its concentration was 20%, the flux became about 0.7 m³/m² day (NaCl rejection ~ 90%).



(A)



(B)

Figure 3 Rejection and flux of the PA composite membranes as a function of the concentration of 1,2-dichloroethane (vol %) in the 1,2-dichloroethane/hexane mixtures used. The feed solutions were (A) 1000 ppm PEG 200 and (B) NaCl solutions in water.

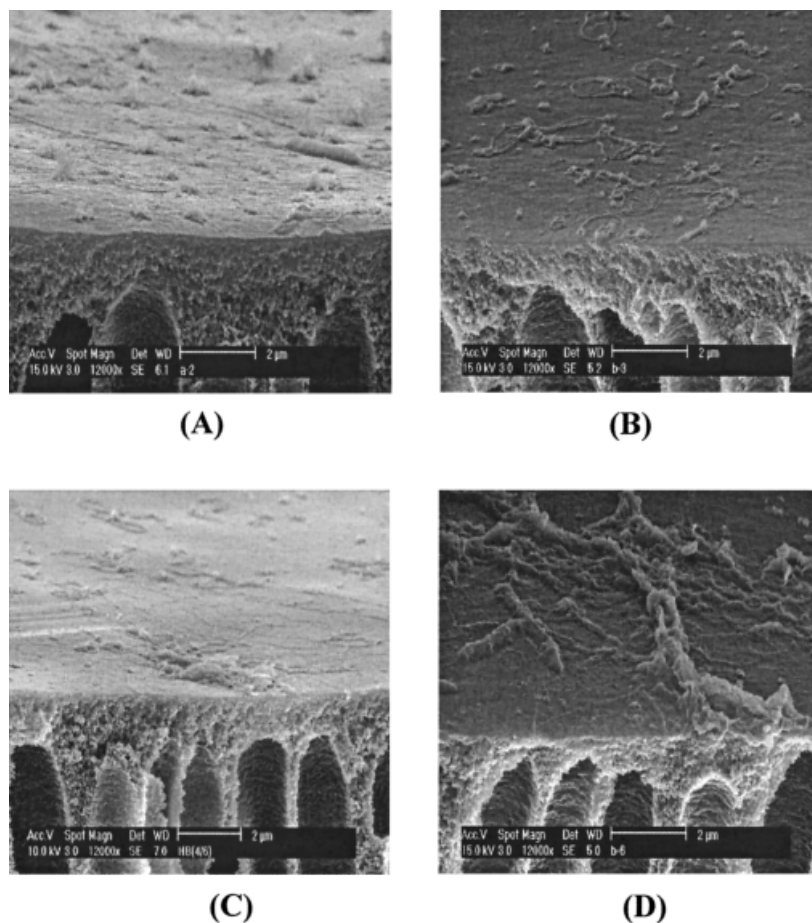


Figure 4 FESEM photographs of the PA composite membranes prepared with different benzene/hexane (v/v) ratios: (A) 0/10, (B) 4/6, (C) 6/4, and (D) 10/0.

To determine the differences in the morphologies of the PA active layers according to the different organic solutions, we took FESEM photographs of the PA composite membranes, as shown in Figure 4. As the content of the benzene in the benzene/hexane mixture solutions increased, the thickness of the active layer seemed to increase. In particular, for a 100% benzene solution, the increase in thickness seemed distinctive. This kind of result is reasonable because, with the increasing solubility of the polymer in the interfacial polymerization, the molecular weight of the polymers being polymerized is increased. This increase in the thickness of the active layer proves the improved efficiency of the interfacial polymerization through the replacement of organic solutions with solutions having better solubility. From these results, it can be suggested that the variation in the permeation performance of the PA composite membranes as a function of the content of benzene in the organic solution mixtures is partially attributable to the increased thickness and the increased crosslinking degree of their active layers.

In this study, we also tried to analyze the variation of the degree of crosslinking of the active layers pre-

pared under different conditions, using DSC. However, it turned out to be impossible to determine their T_g 's. Their degree of crosslinking was too high to show their T_g 's below their degradation temperatures. From these experiments, we found that the degree of crosslinking of PA active layers of the composite membranes prepared in this study was high enough not to show their T_g 's below their degradation points.

Effect of the additives

In interfacial polymerization, the characteristics of the interface are important because the polymerization site is in the organic phase near the interface. Therefore, as the interface is sharp, the polymerization site will be a narrow, regular region near the interface. However, for a diffused interface, the place at which polymerization occurs should be rather diffused, too, because the monomer dissolved in the water phase has to move through the diffused interface into the organic phase for the polymerization. The diffused region in which polymerization happens would be expected to give a polymer layer with a rather rough surface morphology. In other words, during the for-

mation of PA composite membranes, when the interface is sharp, the morphology of the PA active layer being formed will be smooth, but when the interface is diffused, it will be rather rough, giving more surface area.

In this study, alcohol solutions such as NPA and IPA were employed to make diffused interfaces in the interfacial polymerization. Alcohol solutions that would be mixed easily with both water and hexane solutions were expected to diffuse the interface effectively. Figure 5 exhibits the permeation properties of the PA composite membranes prepared with NPA as a function of the NPA content in water/NPA mixtures. The monomers used for the formation of the membranes were PIP/MPD (8/2 w/w) and TMC. The feed solution and operating temperature were a 1000 ppm PEG 200 solution in water and room temperature, respectively.

As shown in Figure 5, until a 20 vol % NPA content, the flux increased with almost constant rejection, but as the NPA content increased further, the flux increased drastically with a large decrease in the rejection. A similar result was also obtained when IPA was used. From these results, it can be speculated that the small amount of alcohol mixed with water changed the miscibility of water with hexane, making it slightly more miscible and making the interface that formed between the water and hexane layers diffuse. The diffused interface can be attributed to the formation of the rough surface of the PA active layers of the PA composite membranes.

AFM pictures of the surfaces of the PA composite membranes prepared with or without NPA for the

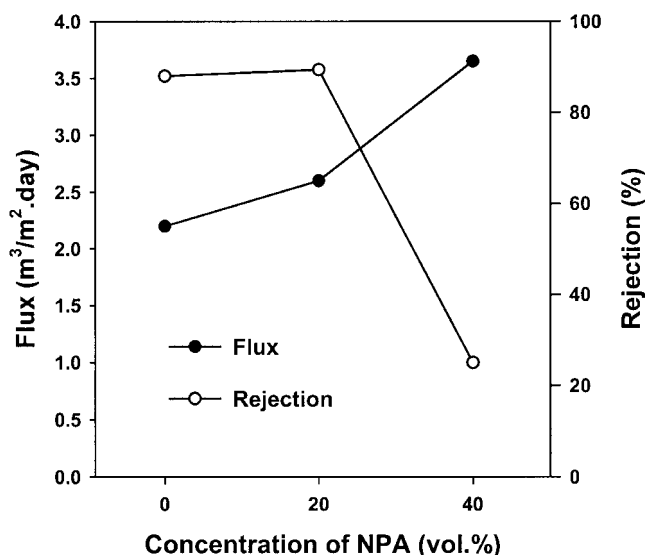


Figure 5 Permeation properties of the PA composite membranes as a function of the compositions of the NPA/water (v/v) mixtures used. The feed solution was a 1000 ppm PEG 200 solution in water, and the operating temperature was room temperature.

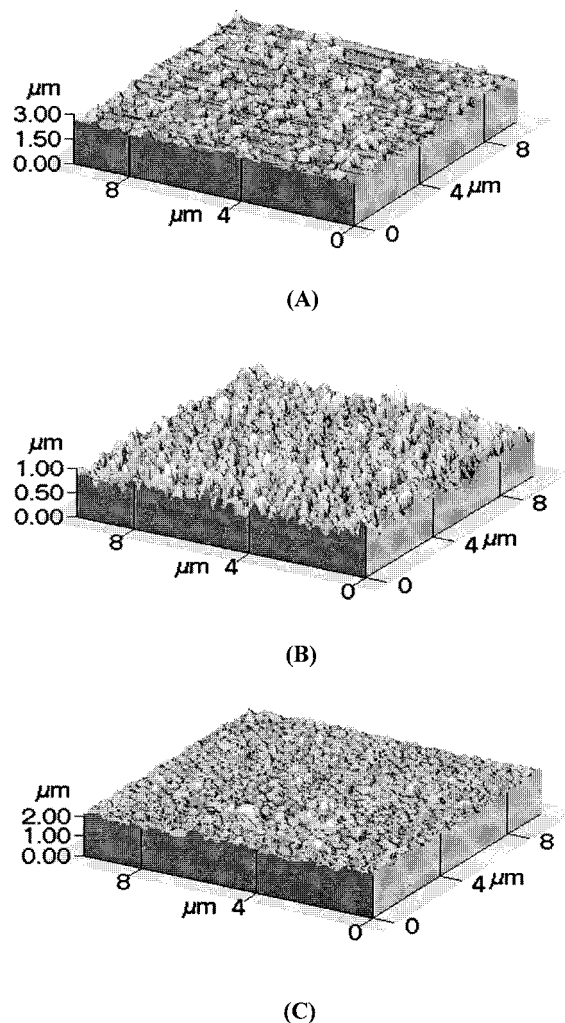


Figure 6 AFM photographs of the PA composite membranes prepared under different conditions: (A) without NPA or PTC, (B) with 20 vol % NPA, and (C) with 0.2 wt % PTC.

interfacial polymerization are shown in Figure 6. With 20% NPA, the surface of the PA composite membrane became quite rough in comparison with the surface of the PA composite membrane prepared without NPA, confirming previous speculation.

However, as the alcohol content exceeded 20%, the flux increased drastically, but the rejection decreased to a large extent; this indicates that a highly diffused interface is not favorable for the formation of PA active layers with a proper degree of crosslinking. In other words, as the interface layer was diffused too much, the path through which monomers in the water phase had to pass for the polymerization was so long that monomer transfer from the water layer to the organic layer became more difficult or sluggish, making the polymerization of the PA layers unfavorable.

Effect of the PTCs

Consulting the results obtained from the formation of PA composite membranes with NPA as an additive,

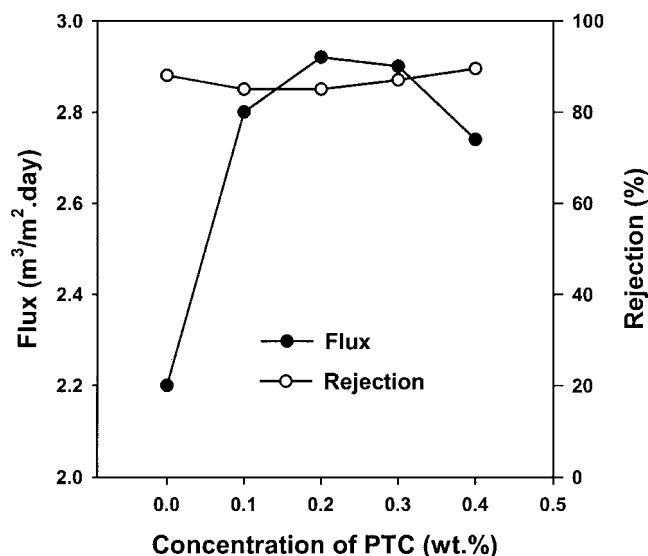


Figure 7 Flux and rejection of the PA composite membranes as a function of the concentration of PTC used. The feed solution and operating temperature were a 1000 ppm PEG 200 solution in water and room temperature, respectively.

we considered it a good idea to use PTCs to improve the polymerization efficiency and increase the surface area. In general, PTCs have been known to improve the polymerization efficiency in interfacial polymerization by helping the monomer in the water phase move into the organic layer.⁸ Improved polymerization efficiency in the formation of PA active layers of composite membranes has the potential to increase the surface area without reducing the degree of crosslinking of the PA active layers.

In this study, three salt compounds (TEBAB, TMBAB, and TEAC) were used as PTCs. Figure 7 shows the permeation properties of the PA composite membranes prepared with TEBAB as a function of the concentration of TEBAB. The monomers used for the formation of these membranes were PIP/MPD (8/2 w/w) and TMC. As shown in Figure 7, with an increasing concentration of PTC, the flux of the membrane increased drastically up to 0.2 wt % PTC and then slightly decreased with a further increase in the concentration of PTC. There was about a 40% increase in the flux when 0.2 wt % PTC was used. However, the rejection of the membranes depended slightly on the PTC content, decreasing slightly and then increasing with increasing PTC content. The rejection almost remained at about 90%. However, when TMBAB and TEAC were used, there was no effect on the perfor-

mance of the PA composite membranes; this indicates that they were not the proper catalysts for this study.

On the basis of these results, we have found that the use of PTCs for the interfacial polymerization of PA is favorable for improving the surface area of the PA active layers without reducing the degree of crosslinking, when we consider the surface morphology of the PA composite membranes, as shown in Figure 6.

CONCLUSIONS

The PA composite membranes prepared by the interfacial polymerization of PIP/MPD (8/2 w/w) and TMC on microporous PSf supports, with hexane as an organic solution, were typical NF composite membranes with a 200 g/mol MWCO and 2.5 m³/m² day of flux at 200 psi. However, changing the hexane solution into benzene/hexane or 1,2-dichloroethane/hexane mixture solutions, with benzene and 1,2-dichloroethane being better solvents for PA than hexane, improved salt rejection substantially, making possible a loose RO membrane with the same monomer composition as the NF membrane. When 40 vol % benzene was used, a PA composite membrane with loose RO performance (1.5 m³/m² day of flux and 90% NaCl rejection at 200 psi) was obtained. A small amount of an alcohol solution such as IPA or NPA was effective in increasing the surface area of the PA composite membranes but reduced the rejection. PTCs such as TEBAB were effective at increasing the flux of PA composite membranes by increasing the surface area. The increase in the surface area was attributed to the improved polymerization efficiency for the formation of the PA active layers.

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