Preparation and Characterization of Nanofiltration Composite Membranes Using Polyacrylonitrile (PAN). II. Preparation and Characterization of Polyamide Composite Membranes

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ABSTRACT: Polyamide (PA) composite membranes in which PA active layers were interconnected with support layers via the formation of ionic bonds were prepared by the interfacial polymerization of piperazine (PIP) with trimesoyl chloride (TMC) on the surfaces of microporous polyacrylonitrile (PAN) supports containing carboxylic acid groups. Formation of the ionic bonds through an acid-base reaction between —NH group of PIP and —COOH of the support was studied using FTIR-ATR spectroscopy. Variation of the surface morphologies of the composite membranes that was induced by the presence of the ionic bonds was observed with a FESEM and an AFM. Permeation tests with various feed solutions such as PEG 600, Na_2SO_4, $MgSO_4$, $MgCl_2$, and NaCl solutions were carried out to see how the characteristics of the PAN supports affected on the flux and rejection of the corresponding PA composite membranes. Chemical stabilities of the composite membranes with the ionic bonds were studied and compared with that of a conventional PA composite membrane, using alcohol solutions. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2729–2736, 2001

Key words: PA composite membranes; nanofiltration; polyamide; polyacrylonitrile

INTRODUCTION

Polyamide (PA) composite membranes have been widely used for nanofiltration (NF) due to their high permeation performances. Most of them have been generally prepared by forming thin PA active layers on microporous supports prepared from engineering plastic polymers such as polysulfone (PSf) and polyetherimide (PEI).[1–5] The supports prepared from such polymers usually have very good mechanical and chemical proper-

ties but do not have on their surfaces any functional groups that can form chemical bonds with the PA layers. Consequently, there is no such strong interaction as covalent or ionic bond between the active and the support layers for the conventional PA composite membranes.

Generally, the conventional PA composite membranes have been known to be stable in most applications. However, their chemical stability should be reconsidered to extend their applications into harsh conditions such as the solutions that contain chemicals enable to swell the support layer seriously. It will cause the active layer to be detached from the support layer and the membrane will be then in an undesirable condition.

To cope with this kind of problems, the introduction of strong interaction between active and support layers was considered in this study. One of the good strong interactions would be definitely covalent or ionic bond. In this study, PAN was used as a support material, because the —CN groups of PAN on the surface of the support can be converted into —COOH groups by simple treatment with a NaOH solution at ambient temperature.[6,7] The —COOH groups produced will be useful for the formation of ionic and covalent bonds with amine compounds. The ionic bond formation between the two layers will act positively for the flux as well as for the chemical stability of the PA composite membrane.

For the realization of such kind of PA composite membranes, the PAN supports were treated with a 2-M NaOH solution before interfacial polymerization of PA active layers. In this article, the details of the characteristics of the PA composite membranes containing ionic bonds such as the chemical structures of the active layers, surface morphologies, permeation performances, and physical stabilities are described.

EXPERIMENTAL

Materials

PAN (M_W = 168,000 dalton), generously supplied by the Hanil Synthetic Fiber Co. (South Korea), was used for the formation of microporous supports. Sodium hydroxide, purchased from the Showa Chemical Co., and hydrochloric acid from the Junsei Chemical Co. were used for the modification of the PAN supports. Piperazine (PIP) and trimesoyl chloride (TMC) purchased from Tokyo Kasei Co. (TCI) were used as monomers of PA active layers. Triethylamine (TEA), bought from Tokyo Kasei (TCI), was used as a catalyst of the interfacial polymerization of PA. Poly(ethylene glycol), with molecular weight of 600 g/mol (PEG 600), Na$_2$SO$_4$, MgSO$_4$, MgCl$_2$, and NaCl, bought from the Junsei Co., were used as the solutes of feed solutions. Other chemicals were also used as purchased.

Preparation of PA Composite Membranes

PA composite membranes were prepared by the conventional interfacial polymerization of PA active layers on the surface of microporous PAN supports. The PAN supports were prepared as explained in the previous article,[7] using PAN/NMP solutions with various compositions (10/90, 15/85, and 20/80 in wt %). The PAN supports thus prepared were modified with a 2-M NaOH solution for 1 h at 40°C to form —COOH groups on their surfaces.[7]

The details of the formation of the PA composite membranes are as follows: after coating the support with an 1 wt % PIP solution in water containing 1 wt % of TEA, the excess amount of the PIP solution remained on its surface was removed and it was then immersed into a 0.05 wt % TMC solution in hexane for 10 s for the interfacial polymerization, after which it was dried in air at room temperature for 1 day. The PA composite membranes so prepared were kept in distilled water until its use.

Characterization

The morphologies of the PA composite membranes were observed with a FESEM (XL30, Philips Co., USA) and an AFM (NanoScope IIIa, DI Co., USA). The chemical structures of the active layers of the PA composite membranes prepared were studied, using a FTIR-ATR (MAGNA-IR 560, Nicolet, USA) spectroscopy.

Permeation Test

The PA composite membranes were tested with various feed solutions such as 1000 ppm aqueous solutions of PEG 600, Na$_2$SO$_4$, MgSO$_4$, MgCl$_2$, and NaCl to determine their permeation performances, using a general NF test setup.[7] The operating pressure, ranging from 100 to 400 psi, was controlled by using back-pressure regulators. Other test conditions were as same as the previous report.[7] A flux was measured by weighing the permeate penetrated through the membrane per unit time and a solute rejection was calculated from the concentrations of the feed solution and permeate using the following equation;

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

where C_f and C_p are the concentrations of the feed solution and permeate, respectively. The C_f and C_p were measured by using a high-performance liquid chromatography (HPLC) (model Waters 501) that attached with a differential refractometer R401 as a detector.
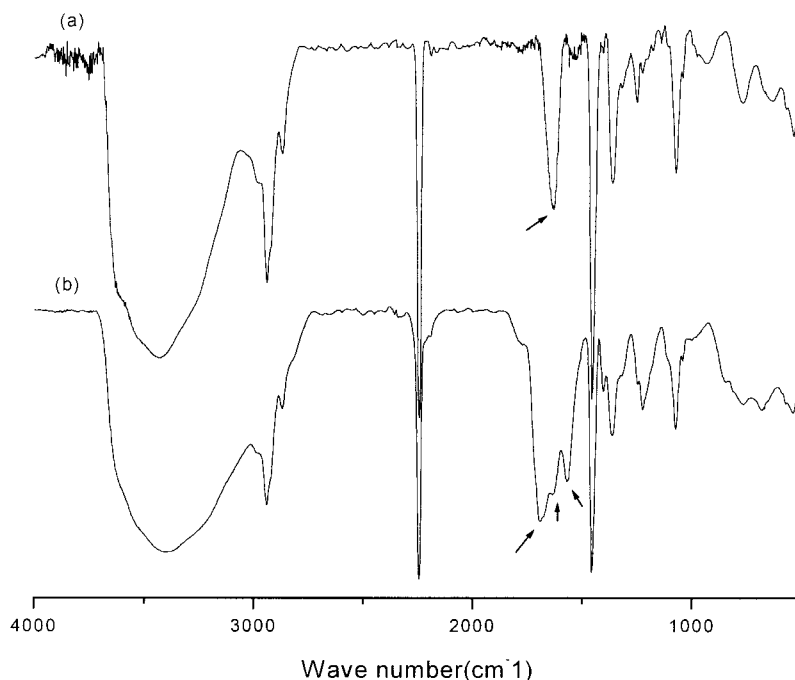
Figure 1 FTIR-ATR spectra of the polyamide composite membranes prepared by using different PAN supports: (a) unmodified PAN support, (b) modified PAN support with 2-*M* NaOH solution for 1 h at 40°C. (The PAN supports were made from 15 wt % PAN solution.)

RESULTS AND DISCUSSION

Preparation of PA Composite Membranes

PA composite membranes that have ionic bonds between their active layers and microporous supports were prepared by the interfacial polymerization of PIP and TMC on the PAN supports containing —COOH groups on their surfaces. The supports with carboxylic acid were prepared by the modification of PAN supports with a 2-*M* NaOH solution as explained in the previous article.[7] The PAN supports prepared from different compositions of the PAN/NMP solutions [10/90, 15/85, and 20/80 (in wt%)] by the phase inversion and used for this experiment had different permeation characteristics. The detailed permeation performances of the PAN supports were already described in the previous article.[7]

Chemical Structures

The FTIR-ATR spectrum of the surface of the PA composite membrane that has ionic bonds is presented in Figure 1. In this case, the support was the one prepared from 15 wt % PAN solution, and contained carboxylic acid groups on its surface. As

one can see, it shows three separate peaks ranging from 1600 to 1800 cm^{-1}, which indicates the C=O stretching peaks under different chemical circumstances as shown in Scheme 1. The three peaks at 1570, 1630, and 1700 cm^{-1} correspond to the carboxylic acid salt, amide (in solid state), and carboxylic acid monomer, respectively.

On the other hand, the spectrum (b) obtained from the one without the ionic bonds, prepared by using the unmodified PAN support, shows only one strong amide (in solid state) stretching peak at 1630 cm^{-1}.
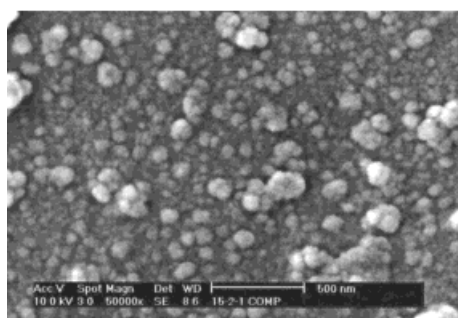
From this result, it strongly suggests that the carboxylic acid groups of the modified PAN sup-
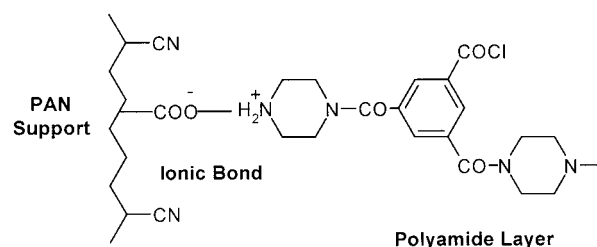
Scheme 1 Schematic representation of the ionic bond formation between the PIP of PA active layer and —COOH on the PAN support
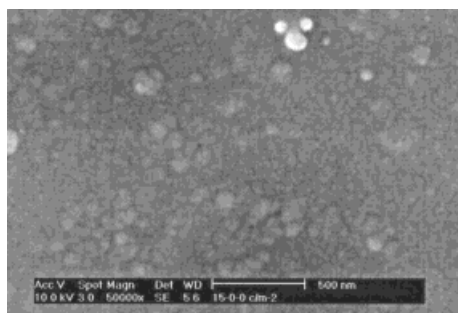
(a)

(b)

Figure 2 FE SEM photographs of the surfaces of the PA composite membranes: (a) unmodified PAN support, (b) modified PAN support with 2-*M* NaOH solution for 1 h at 40°C. (The PAN supports were made from 15 wt % PAN solution.)

port are able to form the ionic bonds with the PIP of the PA layer.

Morphology

To see how the surface morphology of the PA composite membranes is affected by the chemical property of the supports (with or without presence of the carboxylic acid groups) and how it influences on their permeation performance, its photographs were taken as shown in Figure 2, using a FESEM.

The surface of the one with the carboxylic acid groups appears to be more rough than that of the one without the carboxylic acid groups. This result suggests that the surface morphology be influenced by the chemical property of the support, but the exact reason is not clear yet in this study. Possibly, the —COOH groups on the modified PAN support that can form ionic bonds with the PIP during the interfacial poly-

merization process would affect on the surface morphology.

Figure 3 presents the AFM pictures of the surfaces of the PA composite membranes. The PAN supports used for the formation of those PA composite membranes were the ones prepared from the PAN solutions with different PAN concentrations such as 10, 15, and 20 wt % by the phase inversion, followed by the NaOH treatment. The surface roughness of those were different from each other and the one prepared from higher PAN
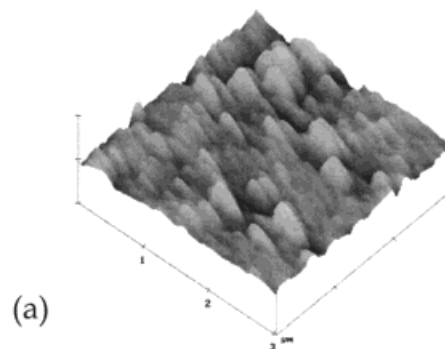
(a)
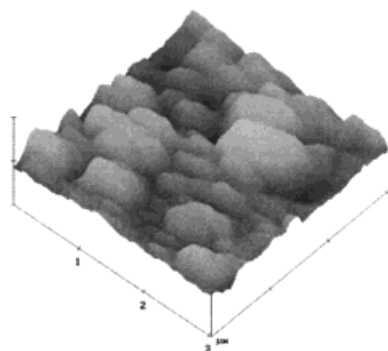
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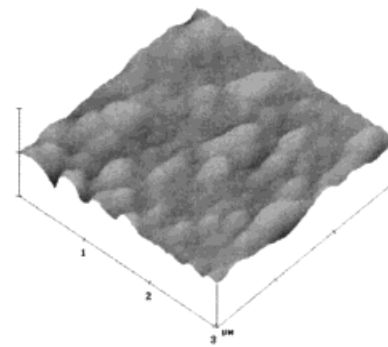
(c)

Figure 3 AFM photographs of the PA composite membranes prepared by using modified PAN supports that were prepared from different PAN concentrations: (a) 10, (b) 15, and (c) 20 wt %.

concentration showed a smoother surface.[7] Generally speaking, the surfaces of the polymeric membranes made from the solutions with higher polymer concentrations by the phase inversion method are smoother, and have smaller pores on their surfaces compared to the ones made from lower concentrations of polymer solutions. This is due to the different phase inversion processes during the solidification of the polymer solution in a coagulant bath.[8] The surface roughness of the resulting PA composite membranes seems to be dependent on the smoothness of the supports. The rougher the surface of the support, the rougher the surface of the resulting composite membrane. For instance, the surface of the PA composite membrane by using the support with the smoother surface was even smoother.

From these results, it was found that the surface morphology of the PA composite membranes is in close relationship with that of the supports, as well as their chemical property.

Permeation Properties

Effect of Chemical Modifications

Figures 4 and 5 present the permeation test results through the PA composite membranes prepared from the modified and the unmodified supports (hereafter the PA composite membrane prepared from the modified support will be called MPACM, and that from the unmodified one will be called UPACM). The supports used for those PA composite membranes were prepared from the 15 wt % PAN solution.

For both the membranes, it was found that they showed typical nanofiltration performances, high rejections of multivalent ions, and low rejections of monovalent ions with high fluxes at moderate pressures. In the case of the UPACM, the flux at 200 psi of the PEG 600 solution was about 1.5 m^3/m^2 day, and it did not vary with different feed solutions. However, the rejection, as expected, depended strongly on the feed solution. Because of the anionic character of the active layer containing the —COOH groups, the rejections of multivalent anions such as Na_2SO_4 and $MgSO_4$ were high, while those of monovalent anions such as NaCl, and $MgCl_2$ were relatively low. From these results, including a rejection behavior according to the different ions and PEG 600, it was found that the steric hindrance of the solutes (sieving mechanism) should be considered as well as the Donnan exclusion for the explanation of the rejection mechanism.
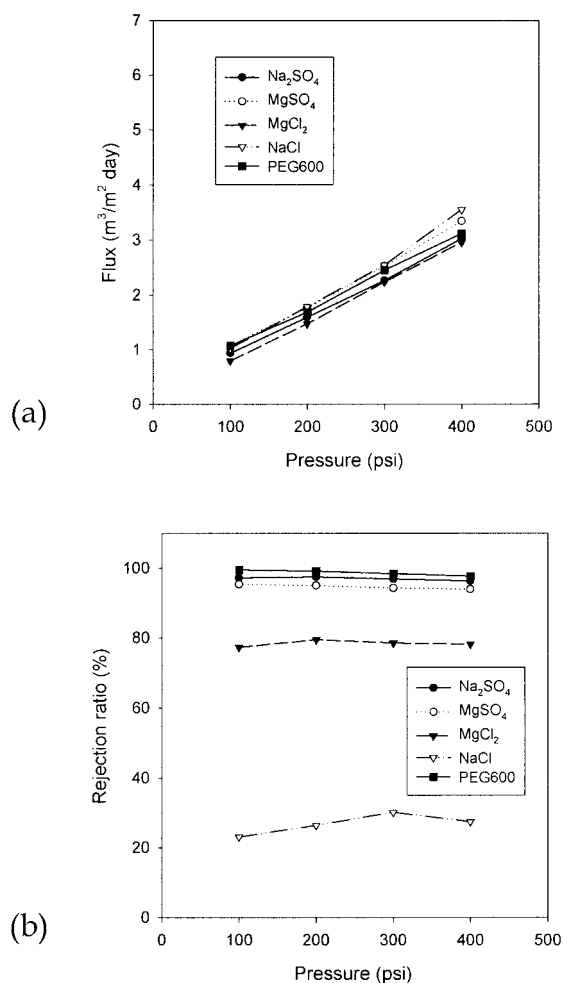

(a)

(b)

Figure 4 Permeation properties of the PA composite membrane prepared by using the unmodified PAN support that was made from 15 wt % PAN solution: (a) flux, (b) rejection ratio. (Feed solution; 1000 ppm PEG600, Na_2SO_4, $MgSO_4$, $MgCl_2$, and NaCl aqueous solutions.)

For the MPACM, the permeation behavior was very similar to that of the UPACM except the higher flux. The flux of the MPACM appeared to be improved, as shown in Figure 5. For instance, the flux of the PEG 600 solution at 200 psi was increased by 1.5 times to 2.5 m^3/m^2 day. This improved flux might be related strongly with the increase in the flux of the PAN support by the modification with NaOH explained in the previous article.[7] It can be explained that the carboxylic groups on the modified PAN support (increased hydrophilicity) acted positively for the better flux of the resulting MPACM.

Effect of PAN Supports

Figure 6 exhibits the permeation test results with 1000 ppm PEG 600 feed solution through the
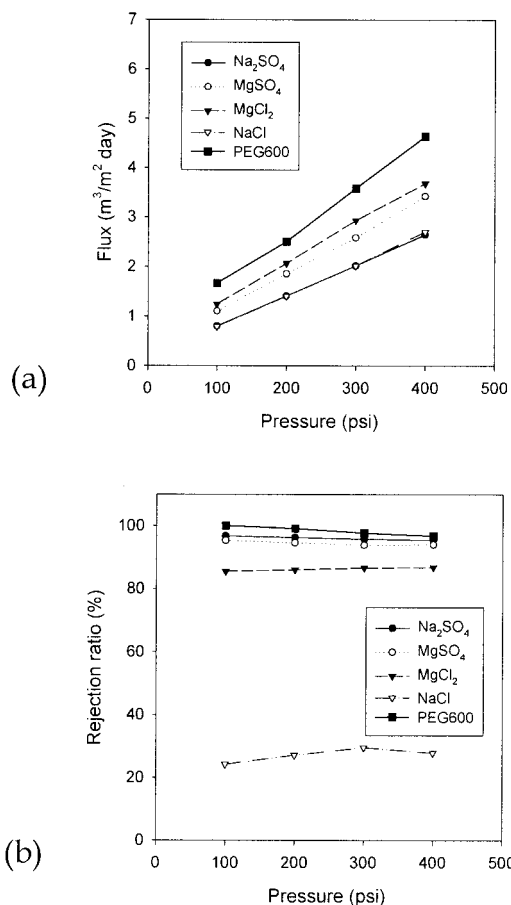
(a)

(b)

Figure 5 Permeation properties of the PA composite membrane prepared by using the PAN support modified with 2-*M* NaOH solution for 1 h at 40°C after formation of the one from 15 wt % PAN solution: (a) flux, (b) rejection ratio. (Feed solution; 1000 ppm PEG600, Na_2SO_4, $MgSO_4$, $MgCl_2$, and NaCl aqueous solutions.)

MPACM. The PAN supports used for the formation of those were prepared from PAN solutions with such different PAN contents as 10, 15, and 20 in wt %, followed by the subsequent modification with a 2-*M* NaOH solution for 1 h. As one can see, the flux and rejection appeared to be very dependent on the characteristics of the supports used (see Fig. 7).[7] With increasing PAN content in the PAN solution, the flux and rejection of the resulting MPACM decreased and increased, respectively, as expected. This is very closely related to the morphology of the supports used for the formation of the respective composite membranes. In other words, the composite membranes with smoother surface made by using the supports prepared from the higher concentrations of polymer solutions have lower flux but higher rejection, and vice versa.[8]

For the membrane prepared from 10 wt % PAN solution, the flux was very high (about 5.5 m^3/m^2 day at 200 psi) and the rejection was low (about 55% at 200 psi). However, the membrane prepared from 15 wt % PAN solution showed about 2.5 m^3/m^2 day of flux and 97% of rejection at 200 psi. When the PAN content was further increased to 20 wt %, the flux was further decreased to 0.2 m^3/m^2 day without substantial increase in the rejection of 97%. This result indicates that the optimum PAN concentration for the formation of the proper PAN support for the good PA NF composite membrane is about 15 wt % in NMP.

Chemical Stabilities

To see the effect of the presence of ionic bonds between the active layer and support on the
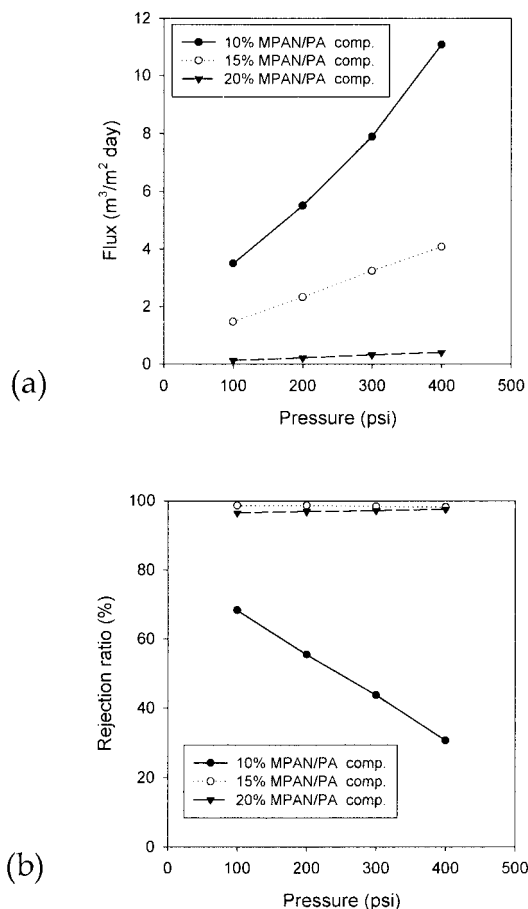

(a)

(b)

Figure 6 Permeation properties of the PA composite membrane prepared from the modified PAN supports that were prepared from different PAN content in PAN solution in NMP: (a) flux, (b) rejection ratio. (Feed solution; 1000 ppm PEG 600 aqueous solution, concentrations of PAN solutions; 10, 15, and 20 wt %.)
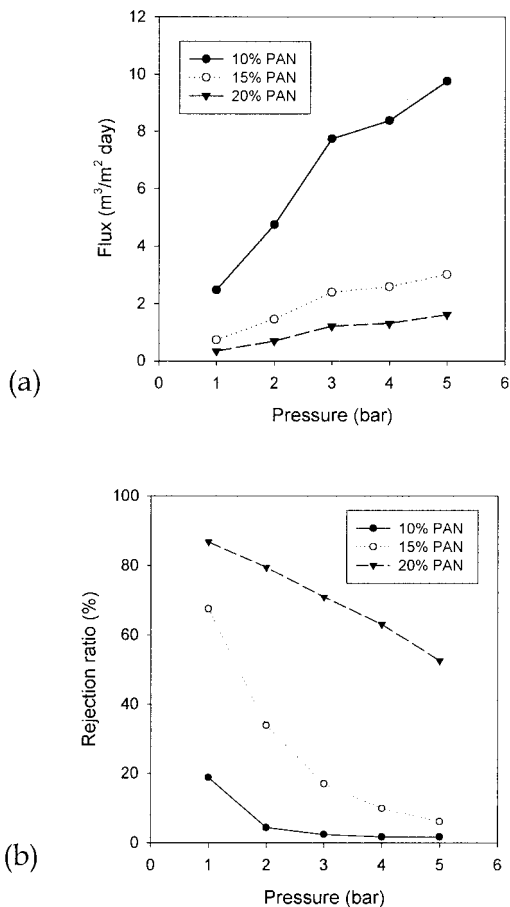
The test results with MPACM and UPACM are shown in Figures 8 and 9. The most distinct difference between those membranes were in their flux behavior before and after treatment with alcohol solutions. In the case of the UPACM, by the treatment with alcohols, the flux changed in a large scale; especially, when treated in ethanol, the flux increased almost two times to 3.5 m^3/m^2 day (see Fig. 8). There were some variations in the flux according to the different alcohols. However, despite the large change in the flux, there was no substantial changes in the rejection ratio. This result might be explained with the swelling
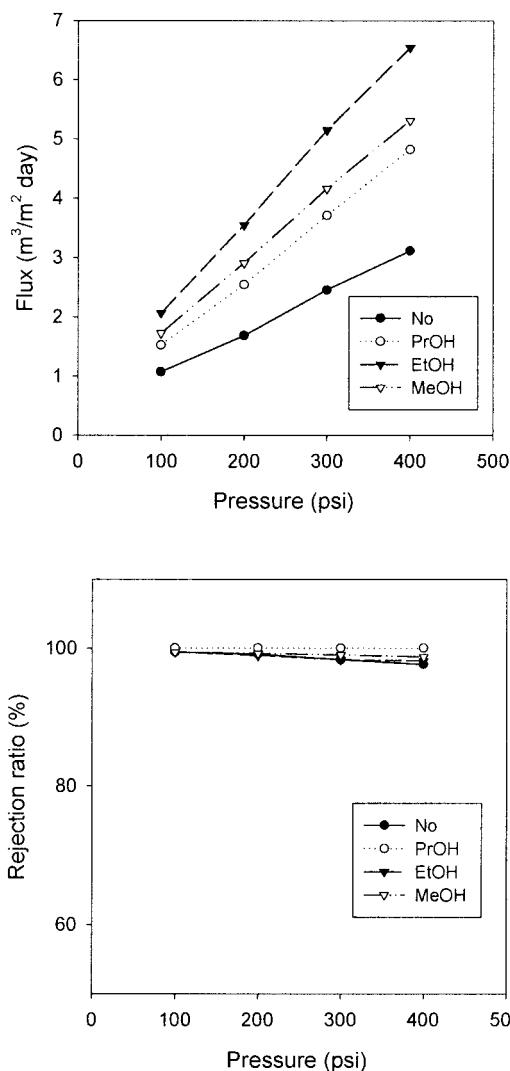
(a)

(b)

Figure 7 Permeation properties of the PAN membranes prepared from different concentrations of PAN solutions: (a) flux, (b) rejection ratio. (Feed solution; 1000 ppm PEG 35,000 aqueous solution.)

chemical stability of the composite membrane, MPACM and UPACM were tested with a 1000 ppm PEG 600 feed solution after chemical treatment in alcohol solutions such as methanol, ethanol, and isopropanol. Those alcohol solutions were used because they swell but do not seriously destroy the morphological characteristics of the PAN support. Water/alcohol mixtures (50/50 in vol %) were used in this study. It is expected that the swelling of the support by the solvents might cause the active layer to be detached from the support, and resulted in the variation of the permeation performance of the composite membranes.

For chemical treatment, the MPACMs were immersed in the alcohol solutions for 12 h to let the membranes be swollen fully, after which they were washed with an excess amount of water to remove any remaining alcohols and then used for the permeation tests.

Figure 8 Permeation properties of the PA composite membrane prepared from the unmodified PAN support, after treatment with several alcohol solutions (MeOH, EtOH, and PrOH) for 12 h at room temperature. (Feed solution; 1000 ppm PEG 600.)

Figure 9 Permeation properties of the PA composite membrane prepared from the modified PAN support, after treatment with several alcohol solutions (MeOH, EtOH, and PrOH) for 12 h at room temperature. (Feed solution; 1000 ppm PEG 600.)
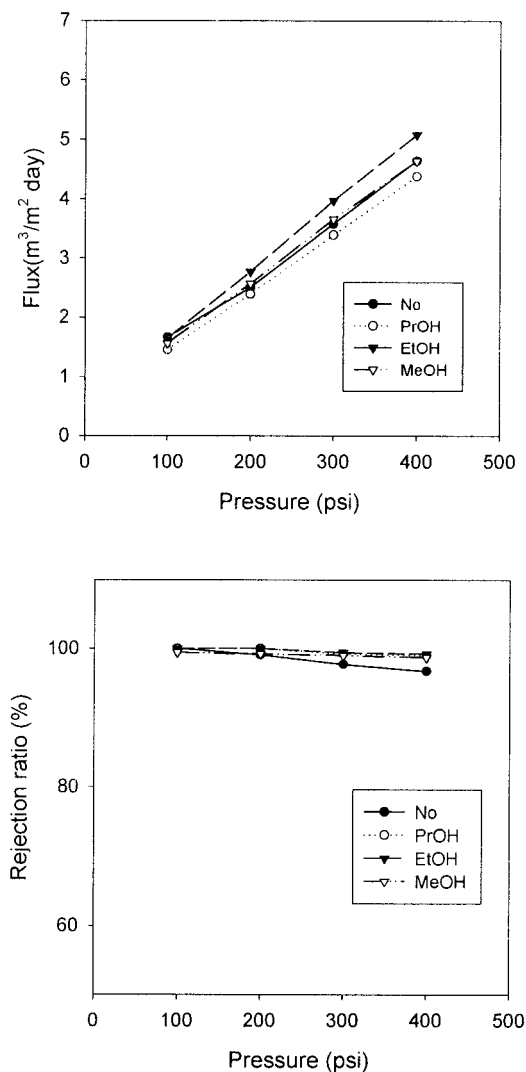
of the support without defect formation in the active layer, including the detachment between the two layers due to the different degrees of swelling.

However, for the MPACM, there were no changes in either the flux or rejection ratio before and after the treatment. They were almost the same regardless of the chemical treatment, indicating that the morphology of MPACM was not affected by the alcohol solutions and it is more stable than the UPACM.

The stability of the membrane in the alcohol solutions might be attributed to the presence of the ionic bonds between the PA active layer and the support. As explained before, the modified PAN support have —COOH groups on the surface, and the resulting PA composite membrane has strong ionic bonds between the PIP of active layer and the —COOH, while there is only physical adsorption between the active layer and the unmodified PAN support. Consequently the MPACM definitely will have better chemical stability than the UPACM.

CONCLUSIONS

PA NF composite membranes with ionic bonds between the active layer and the support are able to be prepared by the interfacial polymerization of thin PA active layers on the PAN supports containing —COOH groups on their surfaces. The —COOH groups can be easily formed on the surface of the PAN support by the modification with NaOH at ambient temperature. The ionic bonds formed between the two layers positively affects the flux and rejection of the PA composite membranes. The PA composite membranes prepared by using modified PAN support show typical NF performance, high rejections of multivalent ions, and low rejections of monovalent ions with relatively high fluxes at moderate operating pressure. The chemical stability of the PA composite membranes can be improved by the introduction of ionic bonds (strong interaction) between the active layer and support.

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