

Preparation and Characterization of Nanofiltration Composite Membranes Using Polyacrylonitrile (PAN). I. Preparation and Modification of PAN Supports

NAM-WUN OH, JONGGEON JEGAL, KEW-HO LEE

Membrane and Separation Research Center, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusong, Taejeon, 305-606, South Korea

Received 1 February 2000; accepted 28 July 2000

ABSTRACT: Polyacrylonitrile (PAN) supports useful for the formation of nanofiltration (NF) composite membranes were prepared from PAN solutions in *N*-methylpyrrolidone (NMP), using a phase-inversion method. The compositions of the PAN/NMP solutions used were as follows: 10/90, 15/85, and 20/80 (in wt %). The PAN supports were treated with various concentrations of NaOH aqueous solutions (0.1, 0.5, 1, and 2 mol) for certain periods of times (0.5, 1, 2, and 3 h) in order to modify their surface chemically and morphologically. The characteristics of the supports, modified or unmodified, were carefully studied. The morphology of those were observed with field-emission scanning electron microscopy (FESEM) and atomic force microscopy (AFM). The change of the chemical structure of those by the NaOH treatment was studied using FTIR-ATR spectroscopy and ESCA. The permeation properties of those were also determined at 1–5 bar of operation pressure using a PEG 35,000 aqueous feed solution. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1854–1862, 2001

Key words: Nanofiltration; composite membrane; polyacrylonitrile; morphology; phase inversion

INTRODUCTION

For nanofiltration (NF), several types of composite membranes have been used. They are usually composed of thin active layers and microporous supports. Among the polymers most often used for the formation of the supports of NF composite membranes are polysulfone (PSf), polyethersulfone, polyimide, and polyetherimide. They have been known to have good mechanical and chemical properties. However, the supports prepared from those polymers are usually hydrophobic and do not have any functional groups that can react with active layers to form chemical bonds such as

a hydrogen bond, ionic bond, or covalent bond. Generally, active layers of composite membranes just physically adhered to the support.

The hydrophobicity of the supports is sometimes troublesome in the formation of NF composite membranes with hydrophilic materials such as poly(vinyl alcohol) (PVA). For instance, the formation of a thin PVA active layer on the hydrophobic PSf support without defects is not easy because of the very different surface properties of both materials. So, the thickness of the active layers of the PVA composite membranes is usually thick and their flux is low.^{1–5}

In this article, it was considered that the supports with hydrophilic functional groups such as —COOH would be good for the formation of NF composite membranes that have very thin active layers and good permeation performances. The

Correspondence to: J. Jegal.

Journal of Applied Polymer Science, Vol. 80, 1854–1862 (2001)
© 2001 John Wiley & Sons, Inc.

hydrophilic surfaces of the supports could be favorable for the formation of active layers on it with hydrophilic and chemically stable materials such as PVA to fabricate chemically stable composite membranes. Such functional groups as —COOH on the support will increase the physical and chemical stability of the resulting composite membranes through the formation of chemical bonds with the active layers.

To realize the purpose of this study, polyacrylonitrile (PAN) was used as a support material. PAN has been often used for the formation of ultrafiltration (UF) membranes.^{6,7} In addition, the surface morphology of the PAN support can be also controlled by the modification with NaOH without loss in its porosity, since the —CN groups of PAN can be transformed into —COOH groups by NaOH and the molecules that have —COOH groups can be swollen by water and move to decrease the pore size.^{8,9} The decrease of the pore size without loss in the porosity would be favorable for the formation of thinner active layers, which will be good for the higher flux of the composite membrane.

In this study, various PAN supports were fabricated from different PAN/NMP compositions and modified with NaOH. The PAN supports, modified or unmodified, were characterized with various methods with respect to their morphology, chemical structure, and permeation properties.

EXPERIMENTAL

Materials

PAN ($M_w = 168,000$ daltons) was kindly supplied by the Hanil Synthetic Fiber Co. (Ulsan, South Korea) and used for the formation of the PAN supports. Sodium hydroxide purchased from the Showa Chemical Co. (Tokyo, Japan) and hydrochloric acid from the Junsei Chemical Co. (Tokyo, Japan) were used for the modification of the PAN supports. Poly(ethylene glycol) with 35,000 g/mol of molecular weight (PEG 35,000) bought from the Fluka Co. (Buchs, Switzerland) was used for the formation of a feed solution.

Preparation of PAN Supports

PAN supports were prepared by casting PAN solutions in NMP on nonwoven polyester fabrics (NWPF) followed by solidification in water. The

compositions of the PAN/NMP solutions were as follows: 10/90, 15/85, and 20/80 in weight percent. The thickness of the supports was controlled to about 50 μm , adjusting the gap of the casting knife (Model YBA-5, Yoshimitsu, Japan). Immediately after casting the PAN solution on the NWPFs, they were plunged into the water controlled at 20°C. After complete phase inversion in the water, the PAN supports were kept in hot water (50°C) for 2 h to remove any remaining NMP.

Modification

The PAN supports were modified chemically and physically, using NaOH solutions. Different concentrations (0.1, 0.5, 1, and 2 mol) of the NaOH solutions were prepared. For the modification, the PAN supports were heated in the NaOH solutions at 40°C for certain periods of times such as 0.5, 1, 2, and 3 h, after which they were immersed into a HCl solution (2 mol) at room temperature for 30 min. The PAN supports were then washed with an excess amount of distilled water three times to remove any remaining chemicals.

Characterization

For the characterization of the PAN supports before and after the modification, various analytical methods were used. The morphology of the supports before and after modification, prepared from different concentrations of the PAN solution in NMP, was observed with field-emission scanning electron microscopy (FESEM) (XL30, Philips Co., USA) and atomic force microscopy (AFM) (NanoScope IIIa, DI Co., USA). The change of the chemical structure of the surface of the PAN supports by the reaction with NaOH was studied using FTIR-ATR spectroscopy. An ESCA (ESCALAB MK-II, VG Scientific Ltd., UK) was also used to confirm the degree of the reaction (from the —CN group to the —COOH group) of PAN with NaOH.

Permeation Test

The permeation properties of the PAN supports, modified or unmodified, were determined from the tests with a 1000 ppm PEG 35,000 aqueous solution, using a general NF test setup. The operating pressure ranged from 1 to 5 bar, controlled by using back-pressure regulators. Other test conditions were as same as in the previous report.⁴ Flux was measured by weighing the permeate penetrated through the supports per unit time and solute rejection was calculated from the

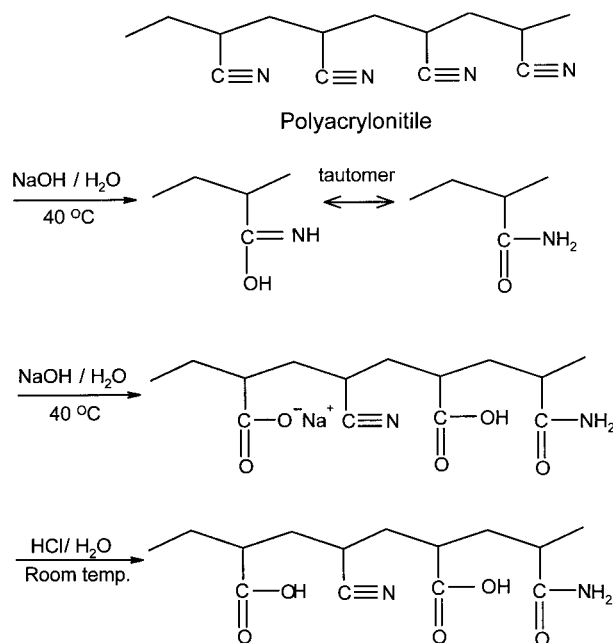


Figure 1 Reaction mechanism of PAN with NaOH.

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 the permeate, respectively. C_f and C_p were measured using a high-performance liquid chromatograph (HPLC) (Model Waters 501) that was attached to a differential refractometer R401 as a detector.

RESULTS AND DISCUSSION

Preparation of PAN Supports

To prepare PAN supports suitable for the formation of NF composite membranes, PAN membranes with an ultrafiltration performance were prepared by the phase-inversion method from different compositions of PAN/NMP. The compositions of the PAN/NMP solutions used were 10/90, 15/85, and 20/80 (in weight percent). All the membranes had an asymmetric structure consisting of a dense skin layer and a supporting layer with a fingerlike structure. The thickness of those was about 50–55 μm .

Modification with NaOH Solutions

The PAN supports prepared were chemically modified with NaOH solutions to control their surface morphology and hydrophilicity. As explained in the Introduction, the $-\text{CN}$ group of PAN can be converted into a $-\text{COO}^- \text{Na}^+$ group by the reaction with NaOH. The modified PAN molecules with a certain content of the $-\text{COO}^- \text{Na}^+$ group will be definitely more hydrophilic and be swollen by water during the reaction process. The swollen molecules then become more mobile and enable one to move toward the pores to decrease the pore size, making the surface of the membrane smoother.

The possible reaction scheme of PAN with NaOH is as shown in Figure 1, in which the $-\text{COO}^- \text{Na}^+$ group produced in the NaOH solution was transformed into a $-\text{COOH}$ group by treatment with HCl. The $-\text{COOH}$ group formed on the surface of the membrane will be used for the formation of ionic bonds with piperazine (PIP) during the formation of polyamide (PA) composite membranes and for the formation of an ester linkage with PVA during the formation of PVA composite membranes. To optimize the reaction condition for the formation of proper morphology and hydrophilicity, the modification reaction was carried out under different concentrations of NaOH for different reaction times.

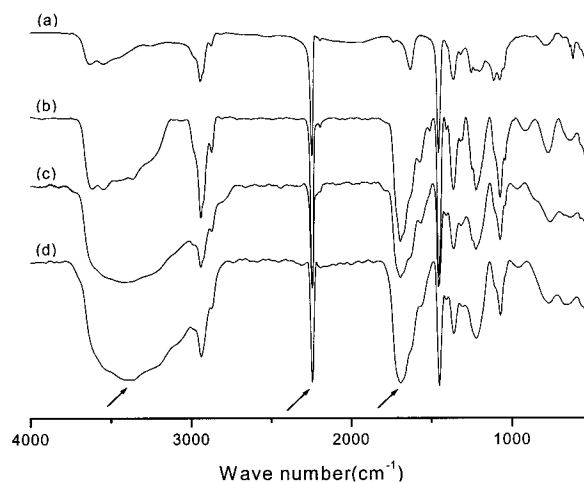


Figure 2 FTIR-ATR spectra of PAN membranes modified with a 2M NaOH solution at 40°C for different reaction times: (a) 0, (b) 0.5, (c) 1, and (d) 3 h, after their formation from a 15 wt % PAN solution.

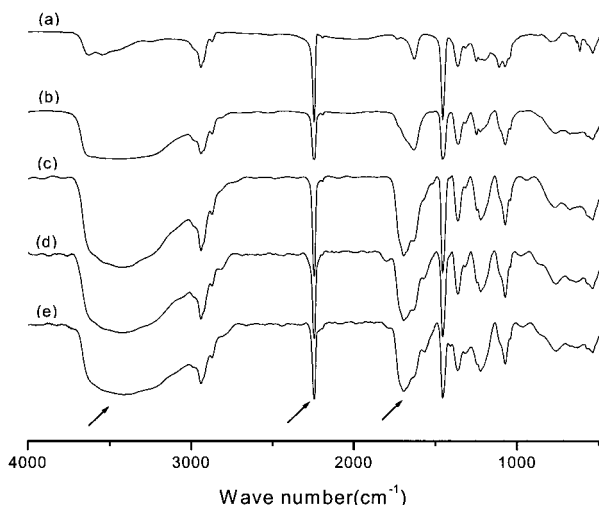


Figure 3 FTIR-ATR spectra of PAN membranes modified with various NaOH concentrations: (a) 0, (b) 0.1, (c) 0.5, (d) 1, and (e) 2M for 1 h at 40°C, after their formation from a 15 wt % PAN solution.

Characterization

Chemical Structure

FTIR-ATR. Figures 2 and 3 show the FTIR-ATR spectra of the PAN membranes modified under different reaction conditions after phase inversion of a 15 wt % PAN solution. One can see clearly from Figure 2 that by the modification with 2M of the NaOH solution at 40°C the intensity of the —CN stretching peak at 2240 cm^{-1} decreases slightly, while the respective intensities of the —OH stretching peak (3300 cm^{-1}) and the —C=O stretching peak (1710 cm^{-1}) increase gradually with the reaction time, indicating that the —CN of PAN transformed into —COOH. With an increasing reaction time, the peaks at 3300 and 1710 cm^{-1} corresponding to the —COOH group increased further, suggesting that more reaction occurred with an increasing reaction time.

The results shown in Figure 3, FTIR-ATR spectra of the PAN membranes after 1 h of reaction with different NaOH concentrations, show that as the concentration increases the degree of reaction increases. This result is very general but confirms that the NaOH concentration is one of the important factors for the modification of PAN as well.

ESCA. Tables I and II present the atomic compositions of the surfaces of the PAN membranes modified under the conditions mentioned above.

As shown in the FTIR-ATR result, Tables I and II also exhibit a change of the chemical structure of the surface of the PAN membrane. Table I shows that with an increasing reaction time the oxygen content increased and the nitrogen content decreased gradually from the surface of the PAN membrane. Table II shows a higher conversion of —CN into —COOH at a higher concentration of NaOH. These results also indicate that the degree of the conversion of —CN into —COOH is very dependent on the reaction condition such as the reaction time and concentration of NaOH.

Morphology

FESEM. Figure 4 shows FESEM photographs of the surfaces of the PAN membranes prepared from PAN/NMP compositions such as 10/90, 15/85, and 80/20. As one can see, the surface became denser and smoother as the content of PAN in the solution increased. This result is considered very general in the formation of microporous membranes by the phase inversion of polymer solutions. Usually, when the concentration of the polymer solution is higher, the phase-inversion speed is faster and less porous membranes with smaller pores in the skin layer are formed.

To show the change in the surface morphology by the modification with NaOH, Figure 5 was prepared. From that, one can see that the surface of the PAN membranes prepared from the 15 wt % PAN solution is becomes denser with an increasing reaction time (from 0.5 to 3 h) in the modification process with a 2M NaOH solution. From (b) and (c) of Figure 5, it is found that for a substantial change in the morphology a certain period of reaction time is required. In this case, the critical time for the substantial change

Table I Atomic Compositions (%) of the Surface of the PAN Membranes as a Function of the Reaction Time in the Modification Reaction with a 2M NaOH Solution at 40°C

Time (h)	C	O	N	C/O	C/N
0	75.523	2.061	22.416	36.644	3.369
0.5	74.796	3.717	21.487	20.123	3.481
1	74.013	5.292	20.695	13.986	3.576
2	73.103	6.200	20.695	11.791	3.532
3	74.082	8.840	17.438	8.380	4.248

Table II Atomic Compositions (%) of the Surface of the PAN Membranes as a Function of the NaOH Concentration in the Modification Reaction for 1 h at 40°C

Concentration (<i>M</i>)	C	O	N	C/O	C/N
0	75.523	2.061	22.416	36.644	3.369
0.1	75.140	2.366	22.494	31.758	3.340
0.5	75.033	2.731	22.236	27.475	3.374
1	75.167	3.076	21.757	24.437	3.455
2	74.013	5.292	20.695	13.986	3.576

seemed to be about 2 h. Other than this, all the other PAN membranes prepared from other PAN solutions also became smoother with an

increasing reaction time by the reaction with NaOH.

This result strongly indicates that the modified surface became more hydrophilic and some of the molecules that have —COOH groups were capable of being swollen in water and to move to make the surface smoother. The pore size of the surface naturally became smaller. This explanation was confirmed from the permeation tests with those membranes which will be described in the following part of this article.

AFM. Figure 6 shows AFM pictures of the surfaces of the PAN membranes modified for 1 h with different NaOH concentrations at 40°C after phase inversion of a 15 wt % PAN solution. In this case, AFM was used instead of FESEM to determine the small morphological differences more clearly.

From Figure 6, one can see the difference in the surface morphology between those membranes modified with different NaOH concentrations. As in the case of different reaction times, the surface became smoother as the concentration of NaOH increased.

From these morphology studies by FESEM and AFM, it is suggested that for a substantial change in the surface morphology the reaction time is more important than is the concentration of NaOH, even though the critical reaction time for a substantial morphological change is a function of the NaOH concentration. This is because the molecules of modified PAN take some time to move to cause a morphological change.

Permeation Properties

Effect of PAN/NMP Compositions

Figure 7 shows the permeation properties of the PAN membranes prepared from different compositions of PAN/NMP. The permeation properties appeared to be closely related to the concentra-

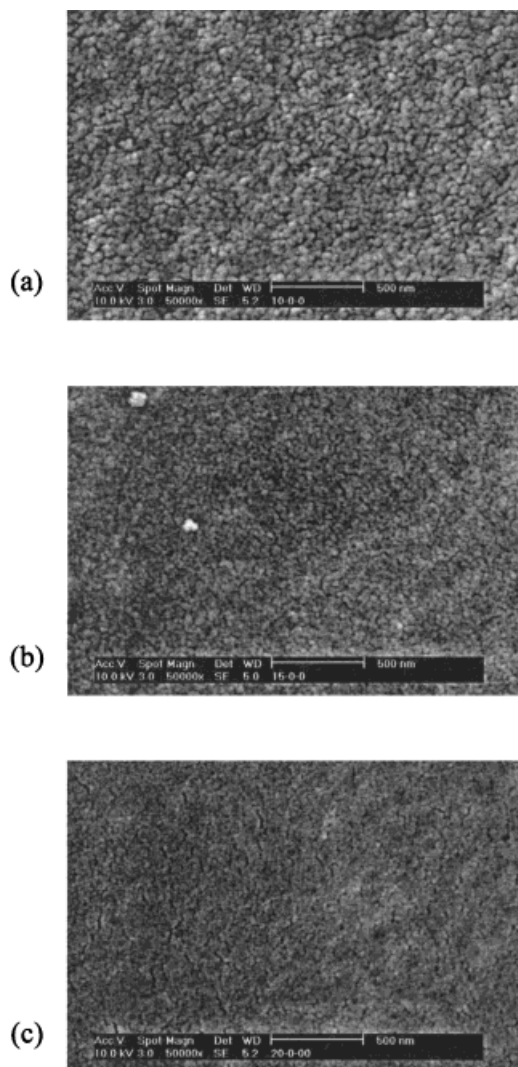


Figure 4 FESEM photographs of the surfaces of PAN membranes prepared from different PAN concentrations: (a) 10, (b) 15, and (c) 20 wt %.

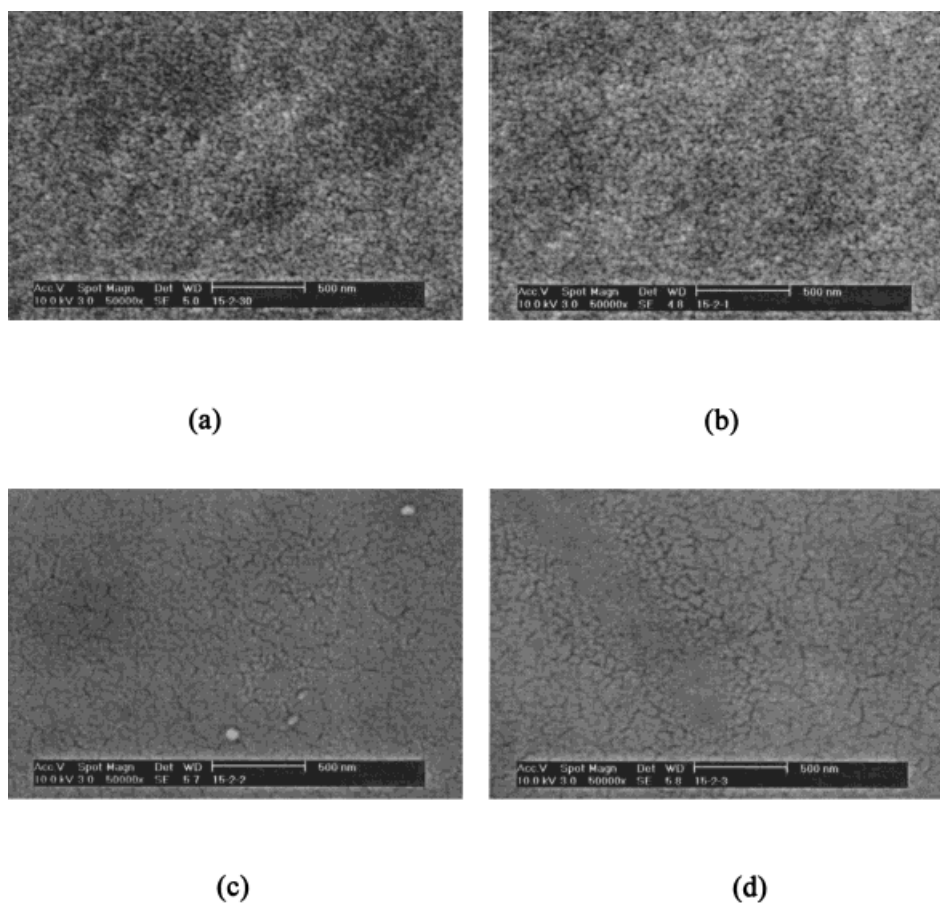


Figure 5 FESEM photographs of the surfaces of PAN membranes modified with a 2M NaOH solution for different reaction times: (a) 0.5, (b) 1, (c) 2, and (d) 3 h, after their formation from a 15 wt % PAN solution.

tion of the PAN in the solutions. As expected from the results obtained from the morphology study with FESEM, the flux decreased and rejection increased with increasing concentrations of PAN. For this permeation test, a 1000 ppm PEG 35,000 aqueous feed solution was used and the operating pressure was varied from 1 to 5 bar.

When the PAN content in the solution was 10 wt %, the respective flux and rejection at 1 bar were about $2.5 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$ and 20%. As the content of PAN increased, the flux decreased and rejection increased. They were about $0.8 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$ and 70%, respectively, at 15 wt % of PAN content and $0.4 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$ and 90% at 20 wt % of PAN content.

From this result, it was considered that the optimum PAN content for the formation of the membranes useful as a support of the composite membranes would be 15 wt % in the consideration of their pore sizes (rejections) and fluxes. Even though the membrane from 20% PAN con-

tent has a high rejection, the flux is too low to form an NF composite membrane with a flux over $2.5 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$ at 200 psi.⁵ A further permeation study was then carried out with the PAN membranes prepared from the 15 wt % PAN solution.

Effect of Reaction Times

Figure 8 shows the permeation performance of the PAN membranes as a function of the reaction time for the modification. From these graphs, one can see the effect of the modification on the performance of the membrane. First, it was found that by the modification for more than 1 h both the flux and rejection were increased. When compared with the data, $0.8 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$ of flux and 70% of rejection at 1 bar, which were obtained from the unmodified membrane, the membrane after 2 h of modification showed much better results such as $1.5 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$ of flux and 80% of

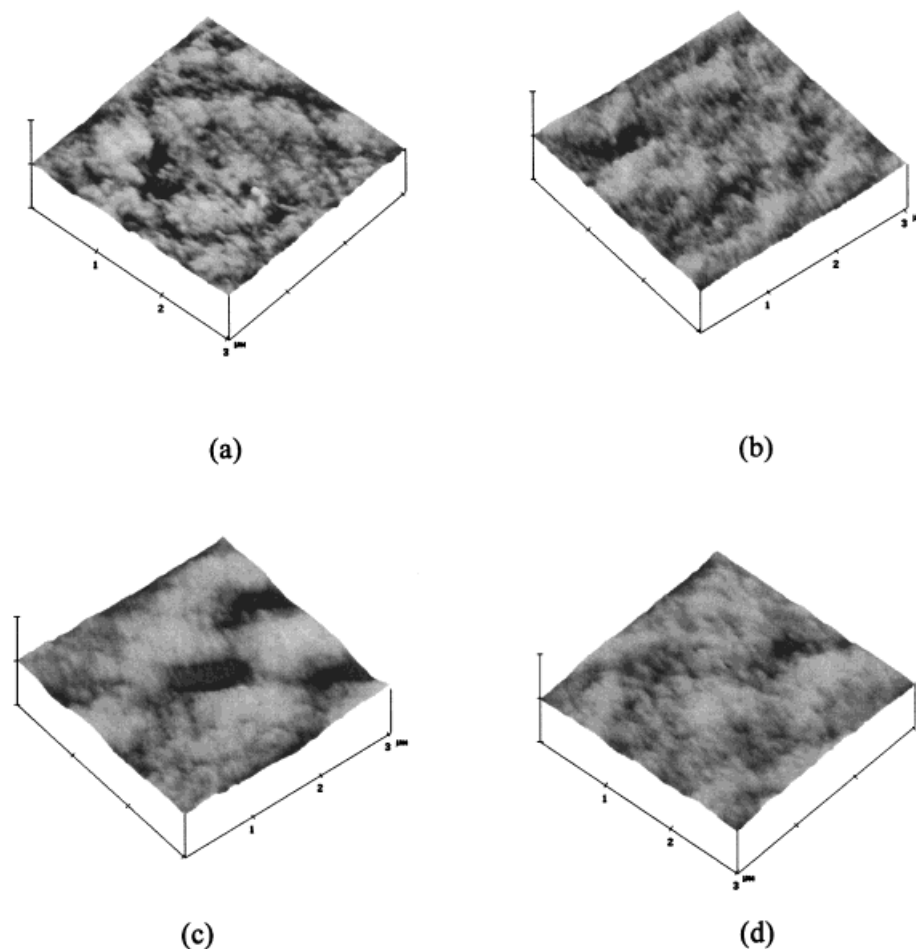


Figure 6 AFM photographs of PAN membranes treated for 1 h with different NaOH concentrations: (a) 0.1, (b) 0.5, (c) 1, and (d) 2M, after their formation from a 15 wt % PAN solution.

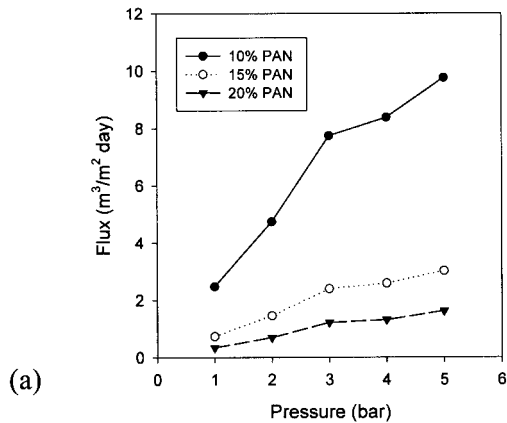
rejection. The flux increased almost twice and the rejection increased by 10%.

This result could be explained by the combination of the increased hydrophilicity and decreased pore size of the surface of the PAN membrane as explained above with the results from FTIR-ATR and FESEM. The increased hydrophilicity due to the formation of —COOH by the modification could make the resistance that occurs at the interface between the feed solution and the membrane surface decrease, resulting in increased flux. The decreased pore size observed with FESEM could act positively to increase the rejection of the solute (PEG 35,000).

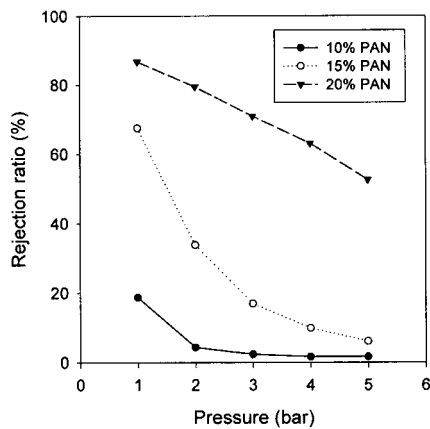
This explanation can be understood more clearly from the study on the flux and rejection as a function of the reaction time. When the modification time is relatively short, such as 0.5 h, the

surface of the membrane first becomes hydrophilic due to the —COOH groups developed but the morphology change is little, since the chemical reaction from —CN to —COOH is fairly fast, but it takes time for the PAN molecules to move to change the morphology, as shown in Figure 5. This phenomenon was exactly reflected in the permeation test. As one can see, the flux is highly increased to $1.9 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$ (almost 2.5 times of the unmodified one) but the rejection is about the same.

The flux highly increased after modification for 0.5 h, then decreased with a further increasing reaction time, but the rejection increased due to the substantial change of the morphology (decrease in pore size) of the membrane surface with increasing reaction time. After 3 h of modification, the flux became about $1.2 \text{ m}^3 \text{ m}^{-2} \text{ day}^{-1}$ and the rejection about 83%. These results coincide



(a)



(b)

Figure 7 Permeation properties of PAN membranes prepared from different concentrations of PAN solutions: (a) flux; (b) rejection ratio. Feed solution: 1000 ppm PEG 35000 aqueous solution.

exactly with the results obtained from the study on the chemical structure and morphology. From these results, it was confirmed that even though the chemical reaction of —CN with NaOH to form —COOH is fast, the morphology change does take time for the movement of the PAN molecules in the swollen state during the chemical modification.

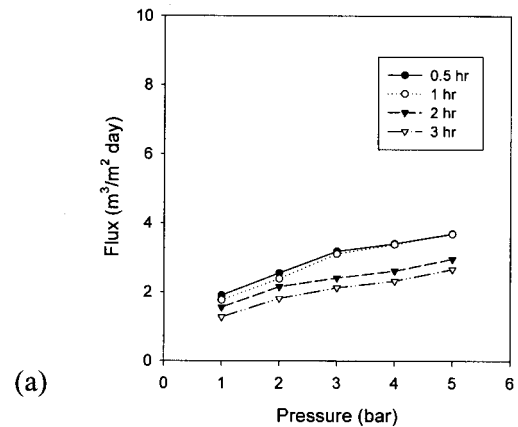
Effect of Concentrations

Figure 9 shows the effect of the NaOH concentrations on the performance of the modified membranes. For this study, the modification was carried out for 1 h at 40°C.

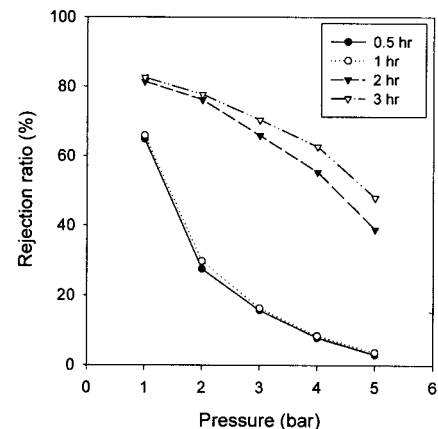
This result shown in Figure 9 suggests that as the concentration of the NaOH decreases the

morphological change (pore size change) of the membrane is negligible and the hydrophilicity change is dominant and that when the concentration of NaOH is high enough the morphological change becomes evident with increased hydrophilicity.

For instance, when the concentration is very low such as 0.1M, only the hydrophilicity increased with a negligible pore size change so that the flux increased greatly, especially at high pressure (at 5 bar), but the rejection decreased. Generally speaking, with increasing hydrophilicity of the membrane surface, the affinity between the membrane surface and hydrophilic solute such as PEG increases, result-



(a)



(b)

Figure 8 Permeation properties of the PAN membranes modified with a 2M NaOH solution for different reaction times after their formation from a 15 wt % PAN solution: (a) flux; (b) rejection ratio. Feed solution: 1000 ppm PEG 35000 aqueous solution.

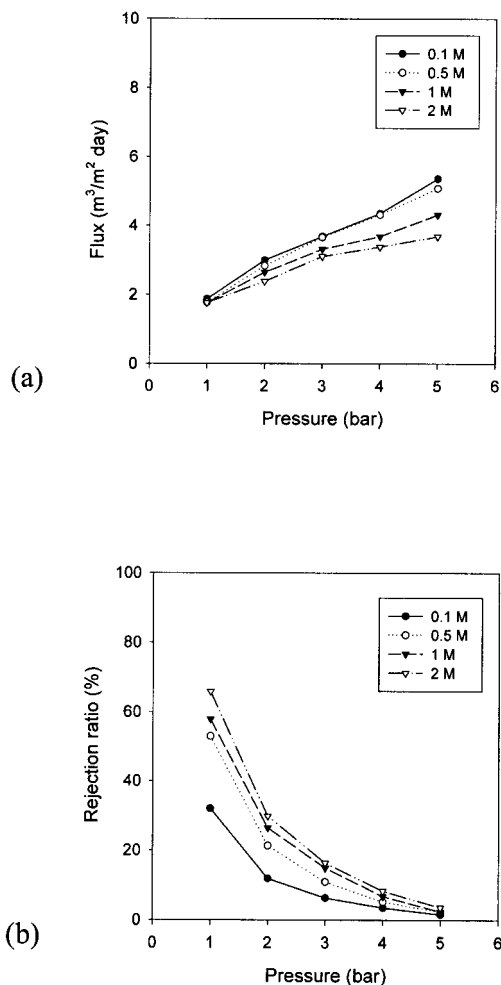


Figure 9 Permeation properties of the PAN membranes modified with various concentrations of NaOH for 1 h after their formation from a 15 wt % PAN solution: (a) flux; (b) rejection ratio. Feed solution: 1000 ppm PEG 35000 aqueous solution.

ing in the increase in flux and the decrease in rejection. However, when the concentration is high enough such as 2M, the change in morphology, such as the pore size, is large enough to affect the permeation performance, so the rejection increases with decrease in the flux, as shown in Figure 9.

CONCLUSIONS

PAN membranes with an MWCO of 35,000 that could be used as supports of NF composite membranes can be prepared by the phase-inversion process of the PAN/NMP solutions with compositions of 15/85 or 20/80, followed by the modification with NaOH. Carboxylic acid ($-\text{COOH}$) groups can be developed on the surface of the PAN membrane by the reaction with NaOH. The modification with NaOH not only changes the hydrophilicity of the membrane surface but also changes the morphology such as the pore size. In the modification, the change of hydrophilicity is fast but the morphological change takes time. By the modification, both the flux and rejection of the PAN membrane can be increased due to the increased hydrophilicity and decreased pore size compared to the unmodified one.

REFERENCES

1. Immelman, E.; Sanderson, R. D.; Jacobs, E. P.; Van Reenen, A. J. *J Appl Polym Sci* 1993, 50, 1013–1034.
2. Koyama, K.; Okada, M.; Nishimura, M. *J Appl Polym Sci* 1982, 27, 2783–2789.
3. Cadotte, J. E.; Steuck, M. J.; Petersen, R. J. *In Situ Formed Condensation Polymer for Reverse Osmosis Membranes*; Office of Water Research and Technology, U.S. Department of the Interior; MRI Project No. 4277-N Final Report, March 1978.
4. Jegal, J. G.; Lee, K. H. *J Appl Polym Sci* 1999, 61, 389.
5. Jegal, J. G.; Oh, N.-W.; Lee, K.-H. *J Appl Polym Sci*, 2000, 77, 347.
6. Cheryan, M. *Ultrafiltration and Microfiltration Handbook*; Technomic: Lancaster, PA, 1998.
7. Paul, D. *Polym News* 1996, 21, 102.
8. Kesting, R. E. *Synthetic Polymeric Membranes, A Structural Perspective*, 2nd ed.; Wiley: New York, 1985.
9. Yang, M.-C.; Tong, J.-H. *J Membr Sci* 1997, 132, 63.