

Preparation and Characterization of PVA/SA Composite Nanofiltration Membranes

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

Membrane and Separation Research Center, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusong, 305-600, South Korea

Received 25 March 1999; accepted 14 October 1999

ABSTRACT: Nanofiltration (NF) composite membranes based on poly(vinyl alcohol) (PVA) and sodium alginate (SA) were prepared by coating PVA/SA (95/5 in wt %) mixture solutions on microporous polysulfone (PSF) supports. For the formation of a defect free thin active layer on a support, the PSF support was multi-coated with a dilute PVA/SA blend solution. The PVA/SA active layer formed was crosslinked at room temperature by using an acetone solution containing glutaraldehyde as a crosslinking agent. The prepared composite membranes were characterized with a scanning electron microscopy (SEM), a Fourier transform infrared spectroscopy (FTIR), an electrokinetic analyzer (EKA) and permeation tests: The thicknesses of the active layers were about 0.25 μm and 0.01 μm depending on the preparation conditions. The crosslinking reaction of the active layers were completed in less than three minutes via the formation of acetal linkage. The surface of the PVA/SA composite membrane was found to be anionic. The permeation properties of the composite membrane were as follows: 1.3 m^3/m^2 day of flux and $> 95\%$ of rejection at 200 psi for 1000 ppm PEG600 solution. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 347–354, 2000

Key words: PVA/SA composite; PSF

INTRODUCTION

Nanofiltration (NF) is a pressure-driven process that is used to separate multivalent ions and small organic molecules from water. The NF process has broad applications, like water softening, instantaneous concentration, and desalting of cheese whey. With increasing applications, the NF membrane is being considered as an effective tool for water treatment. Now, a few NF membranes such as TS-10 of the Trisep Co. (USA) and MPF-series of MPF (Israel) are commercialized. Generally, those membranes are polyamide composite membranes with high flux and moderate

rejection of multivalent ions and low rejection of NaCl. It has been well known that the polyamide NF membranes have low chemical stability. Especially, their chlorine tolerance and stability in base solution are very poor because of their amide linkage, which is labile to hydrolysis reaction. Their chemical instability limits their applications substantially, so we have selected poly(vinyl alcohol) (PVA) as a membrane material to prepare chemically stable NF membranes.

In fact, PVA is a very well-known material to have good chemical stability and hydrophilicity.^{1–5} There have been many experiments using PVA for the fabrication of reverse osmosis (RO) or NF membranes.^{2–6} However, their flux and rejection have been rarely satisfactory. Mostly, they have shown low flux and low rejection. Their poor performance was due to the improper crosslinking reaction (thermal crosslinking) and relatively

Correspondence to: J. Jegal and K.-H. Lee.
Contract grant sponsor: Ministry of Science and Technology of Korea.

Journal of Applied Polymer Science, Vol. 77, 347–354 (2000)
© 2000 John Wiley & Sons, Inc.

thick membrane thickness (or thick PVA active layer in the case of a composite membrane). The thermal crosslinking reaction made the membrane hydrophobic, and resulted in low flux, and the thickness of the PVA layer became one of the reasons for the low flux.

To develop PVA NF membranes with good performances for the separation of multivalent ions and small organic molecules by avoiding such problems that were encountered in the formation of PVA membranes, composite type membranes consisting of very thin PVA/SA active layers with an optimum degree of crosslinking and microporous PSF supports were prepared in this study. (1) First, thin defect-free PVA/SA active layers were successfully coated on the PSF supports by multicoating with dilute polymer solutions. Defect formation that occurred in the formation of thin PVA layer was usually due to the different hydrophilicity between PVA and PSF. In other words, it was not easy for the hydrophilic PVA solution to cover homogeneously across the surface of the hydrophobic PSF support. In this study, to prevent the defect formation and minimize the thickness increase, the PSF support was coated with multiple dilute polymer solution without insolubilization between each coating step, and succeeded in forming a defect-free thin PVA/SA layer. (2) Second, to avoid several negative effects encountered in the high-temperature crosslinking as explained in the previous articles,^{1,2,4} the active layers were crosslinked at room temperature, using a crosslinking solution.

The prepared membranes were characterized with several analytical methods (SEM, FTIR, EKA). NF properties of the membranes were determined through the tests with various feed solutions (PEG 600, Na_2SO_4 , MgCl_2 , NaCl).

EXPERIMENTAL

Materials

PVA with molecular weight of 50,000 g/mol, 99% hydrolyzed, purchased from Aldrich Co., and sodium alginate and chitosan from Sigma Co. were used for the formation of active layers of the NF composite membranes. PSF UF membrane (MWCO: 30,000 g/mol) bought from Fluid System Co. was used as supports of the composite membranes. Na_2SO_4 , MgCl_2 , NaCl , and Poly(ethylene glycol)s with molecular weights of 600 g/mol (PEG600) were bought from Tokyo Kasei Co. and

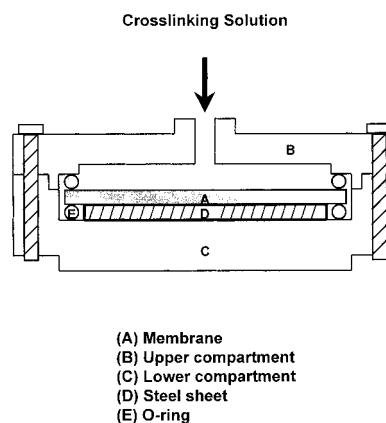


Figure 1 Schematic representation of the crosslinking reaction cell.

used for permeation tests. Glutaraldehyde (GA) with 25 wt % content bought from Tokyo Kasei Co. was used as a crosslinking agent. Acetone was purchased from Junsei Co. and used without further purification as a solvent of a crosslinking solution.

Membrane Formation

Composite membranes consisting of PVA/SA blend (95/5 in wt %) active layers and microporous PSF supports were prepared by coating the PSF support multiply with PVA/SA solutions having different concentrations, followed by drying at room temperature. The composition of the PVA/SA was 95/5 in wt % and the concentrations of the solutions were varied from 0.1 to 0.5 wt %. The multiple coating process was as follows: the PSF support was dipped into the polymer solution for 10 min and taken out to dry. The support first coated was immersed into the polymer solution again for 10 s for the second coating and then taken out to dry. The third coating was also carried out by the same way as the second coating. The active layers formed were crosslinked at room temperature by contacting them with a crosslinking solution as shown schematically in Figure 1. The crosslinking solution used was an acetone containing 5 vol % of GA as a crosslinking agent and trace amount of HCl as a catalyst.⁷ The contacting time was adjusted from 1 to 3 min to control the degree of crosslinking. After crosslinking, the composite membranes were washed with an excess amount of water and kept in distilled water for a day to remove any unreacted GA remaining in the membranes. The prepared com-

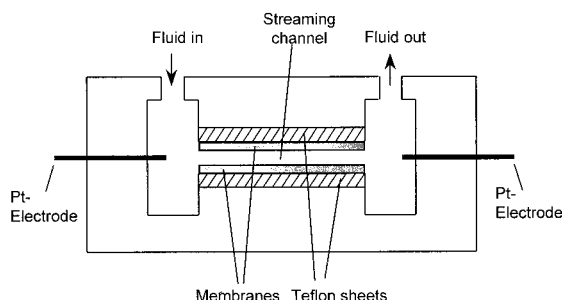


Figure 2 Schematic representation of the electrokinetic analyzer.

posite membranes were kept in distilled water before using for permeation tests.

Characterization

The morphology and thickness of the active layers of the composite membranes were observed with a scanning electron microscopy (SEM) (model: JSM-80A, JEOL). The crosslinking reaction of the PVA/SA active layer with GA was confirmed with a FTIR spectrophotometry (Bio-Rad, Digilab Division, model FTS-80, FTIR).

Zeta Potential Measurement

Zeta potentials of the membranes were measured by using an electrokinetic analyzer (Model: EKA, Brookhaven). The setup to determine zeta-potentials are as shown in Figure 2. With this setup, zeta potentials could be measured along the surface. The concentrations of the electrolyte solutions used were in the range of 0.001 to 0.1 M for NaCl.

Permeation Test

To test the performances of the membranes, a nanofiltration test set was used. The concentration of feed solutions was 1000 ppm, and upstream pressure was controlled by using back-pressure regulators (100, 200, 300, and 400 psi). All test was conducted at 25°C. Flux was measured by weighing the permeate penetrated through the membranes per unit time, and solute rejection was calculated from the concentrations of the feed solution and permeate using the following equation:

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

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.

RESULTS AND DISCUSSION

Membrane Formation

To avoid the formation of defects during the coating of the active layers on the support, the PSF supports were coated multiple times with a 0.5 wt % PVA/SA (95/5 in wt %) solution as explained in the experimental part. In fact, it was found in this experiment that the composite membrane made by coating one time with a 1.0 wt % solution showed defects, but the membrane made by coating three times with a 0.5 wt % solution showed no defect. From this result, it was found that the multiple coating with a dilute polymer solution was effective for the formation of a thin active layer without defects.

The PVA/SA layers coated on the microporous support should be insolubilized to act as active layers of the microporous support should be insolubilized to act as active layers of the composite membranes. For crosslinking the PVA/SA layers, a room-temperature crosslinking method using GA as a crosslinking agent was used in this study. The acetone solution containing 5 vol % of GA and trace amount of HCl made it possible to crosslink the active layer at room temperature through the formation of acetal linkages. The hydroxyl group of PVA and SA reacted with GA with the aid of an acid catalyst at room temperature. Its reaction mechanism is very well known.⁶ This room-temperature crosslinking reaction made it possible to avoid several negative effects such as crystallization and serious dehydration of PVA, which were encountered in the high-temperature crosslinking in the dry state and resulted in low flux.^{1,2,4}

In this study, a specially designed cell (Fig. 1) was used to crosslink the active layer. Because the PSF support was found to be damaged by the acetone solution, the composite membranes could not be immersed in the acetone solution for crosslinking. When coming in contact with acetone, the surface of the PSF support seriously swelled, making small bubbles on its skin layer. Only the active layer was allowed to make contact with the acetone, using the specially designed

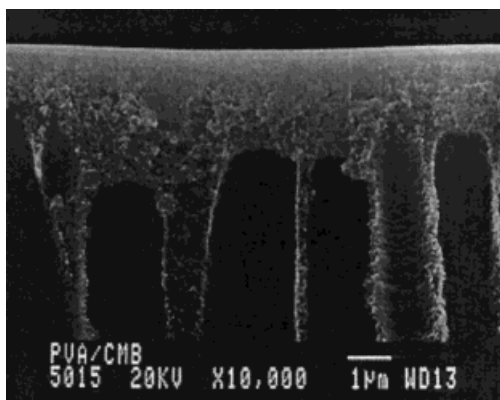


Figure 3 SEM photograph of the PVA/SA (95/5 in wt %) composite membrane prepared by coating a 0.5 wt % PVA/SA solution three times on the PS support, followed by crosslinking 2 min.

cell. The crosslinking cell was effective, and only the active layer was crosslinked without damaging the support.

In this crosslinking setup, GA in the acetone diffused into the active layer, and the crosslinking reaction started to occur from the surface of the active layer and spreaded into the inner part. After a few minutes, the whole active layer was crosslinked to reach an optimum degree of crosslinking. The degree of crosslinking was controlled by adjusting the contacting time of the active layer with the crosslinking solution. As the time increased, it increased, indicating that the degree of crosslinking depended strongly on the amount of the GA diffused into the active layer.

Characterization

Morphology

Figure 3 presents the SEM photograph of the PVA/SA composite membrane prepared by coating the microporous PSF support three times with a 0.5 wt % PVA/SA solution. The thickness of the active layer was about $0.25 \mu\text{m}$, and its surface was smooth.

FTIR

Figure 4 presents the FTIR spectra of the PVA/SA film before and after crosslinking with GA. Spectrum (a) obtained from the uncrosslinked one shows weak C=O stretch peak at 1712 cm^{-1} that comes from the $-\text{COO}^- \text{Na}^+$ group of SA, indicating that SA is well mixed with PVA. The weak

intensity of the C=O stretch peak is due to the small amount (5 wt %) of SA in the PVA/SA blend. Its spectrum, however, did not show much difference after the crosslinking reaction, as shown in spectrum (b). In the crosslinking reaction, $-\text{OH}$ groups of PVA and SA reacts with the $-\text{CH}=\text{O}$ group of GA to form the $-\text{C}-\text{O}-\text{C}-\text{O}-$ (acetal linkage). The characteristic $-\text{C}-\text{O}-$ stretch peak of PVA and SA is so similar to the $-\text{C}-\text{O}-$ stretch peak of the acetal linkage formed by the crosslinking reaction that there is no significant change in the spectrum.

Zeta Potential Measurement

To characterize the ionic character of the PVA/SA membrane, its zeta potentials were measured. Figure 5 shows the zeta potentials as a function of the concentration of NaCl (electrolyte) of the PVA/SA composite membrane and polyamide (PA) composite membrane prepared by the interfacial polymerization of piperazine with trimesoyl chloride on the PSF support.

The zeta potential of the PVA/SA membrane was all negative in the range of concentration of NaCl, and decreased with increasing the concentration. Its decreasing zeta potential with concentration can be explained by more ions in the solution, which may compensate the surface charge of the membrane.⁸

From the comparison between the values and behaviors of the zeta potentials of both the PVA/SA membrane and PA membrane, it can be

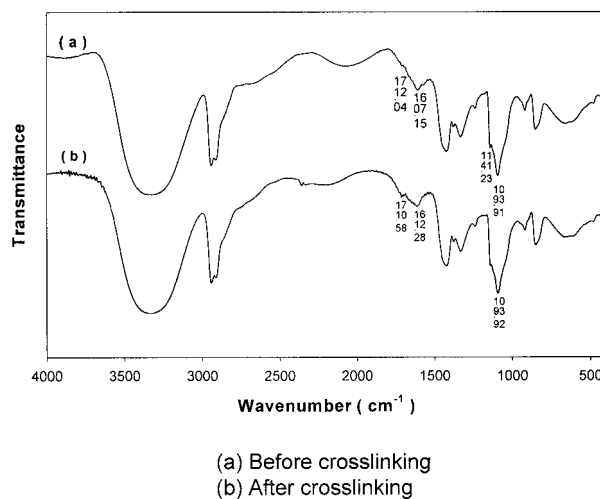


Figure 4 FTIR spectra of the PVA/SA (95/5 in wt %) active layers before (a) and after (b) crosslinking with GA.

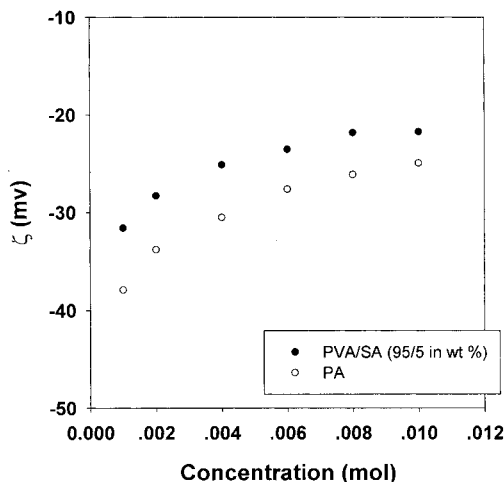


Figure 5 Zeta potentials of a PVA/SA composite membrane and a PA composite membrane as a function of the concentration of electrolyte, NaCl.

suggested that the PVA/SA composite membrane also have anionic character like the PA membrane. However, the lower zeta potentials of the PVA/SA membrane indicate that it has less ionic character than the PA membrane.

Permeation Test

SA, anionic polymer, containing sodium carboxylate groups attached to the six-membered ring backbone structure was used to blend with PVA and expected to improve the NF performance of PVA membranes. Especially, the SA was expected to improve the solute rejection through the Donnan exclusion because of its anionic character. The composition of the PVA/SA blend used was determined as 95/5 in wt %, because this composition was approved to be the best one with respect to the homogeneous blending and proper crosslinking reaction.⁶

Figures 6 and 7 show the permeation properties of the membrane prepared by coating the PSF support three times with a 0.5 wt % PVA/SA blend solution, followed by crosslinking for 2 min. From these results, one can find that this membrane is a typical NF membrane, showing relatively good flux and high rejection of PEG 600 and Na_2SO_4 and very low rejection of NaCl and MgCl_2 . The flux was not substantially affected by different feed solutions; however, the rejection depended strongly on the feed solutions. The flux increased almost linearly with increasing operating pressure, and became about $0.5 \text{ m}^3/\text{m}^2 \text{ day}$ at

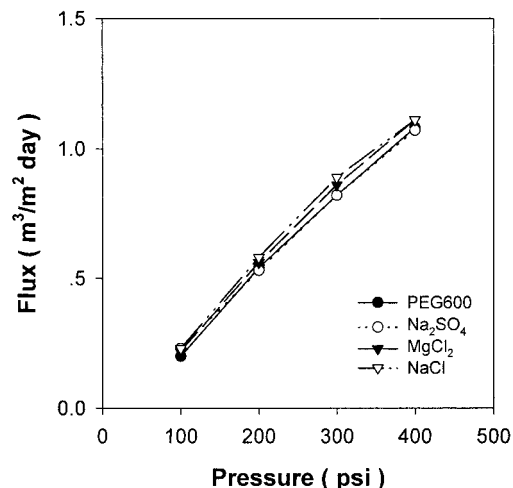


Figure 6 Flux as a function of pressure through the PVA/SA composite membrane (0.5 wt % PVA/SA solution, crosslinking for 2 min).

200 psi, which was about half of that of commercially available NF membranes such as NF-40.⁹

The rejection behavior as a function of operating pressure depended on the solutes. For the solutions of PEG 600 and Na_2SO_4 , it slightly decreased with increasing pressure, while it increased for MgCl_2 and NaCl. The increase in the rejection of MgCl_2 and NaCl can be explained by the fact that the flux of the ions is almost constant, while the flux of water increases proportionally to the increasing pressure. At 200 psi, the rejections of PEG 600, Na_2SO_4 , MgCl_2 , and NaCl were 90, 88, 15, and 10%, respectively. This result

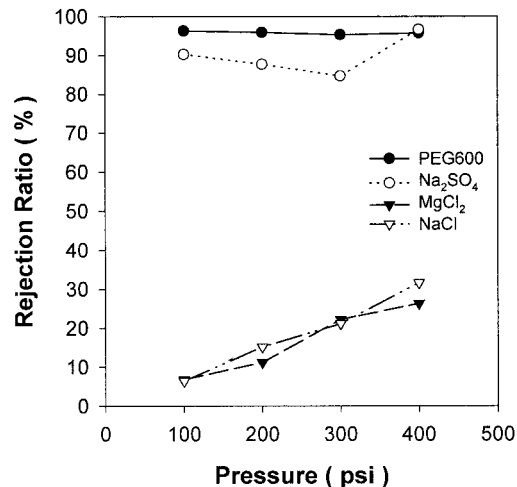


Figure 7 Rejection as a function of pressure through the PVA/SA composite membrane (0.5 wt % PVA/SA solution, crosslinking for 2 min).

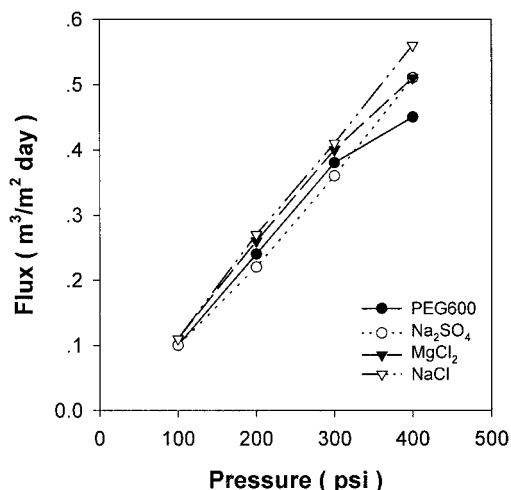


Figure 8 Flux as a function of pressure through the PVA/SA composite membrane (0.5 wt % PVA/SA solution, crosslinking for 3 min).

suggests that the mechanism of solutes rejection was a combination of the size exclusion and Donnan exclusion.

High rejection of Na_2SO_4 and relatively low rejection of MgCl_2 and NaCl also suggest that the surface of the membrane have anionic character. This permeation result agrees with the surface characteristics observed with the zeta potential measurement. The slight anionic character of the membrane surface might be due to the SA located in the surface of the active layer.

Effect of Crosslinking Time

To study the effect of crosslinking reaction time, the contacting time of the active layer with the crosslinking solution was varied from 2 min to 3. The membrane performance after 3 min of crosslinking is shown in Figures 8 and 9. As the crosslinking time increased, the flux decreased and rejection increased. At 200 psi, the flux was about $0.25 \text{ m}^3/\text{m}^2 \text{ day}$, almost half of that obtained after 2 min of crosslinking, but the rejections increased as follows: 97% for PEG 600, 95% for Na_2SO_4 , 31% for MgCl_2 , and 27% for NaCl . The variation in the flux and rejection with the increasing reaction time can be explained by the increase in the degree of crosslinking of the active layer.

Effect of Morphology of Active Layer

Considering the thickness and degree of crosslinking of the active layer as main factors

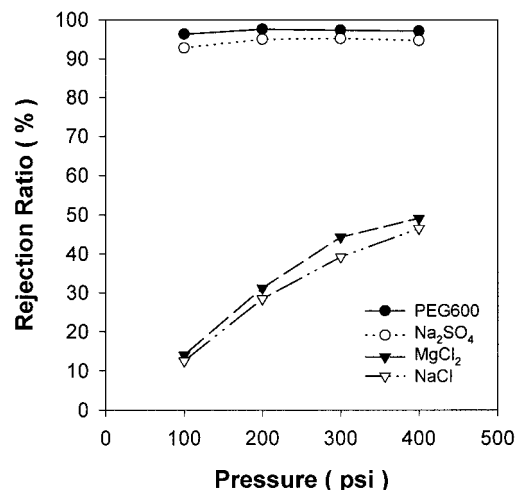


Figure 9 Rejection as a function of pressure through the PVA/SA composite membrane (0.5 wt % PVA/SA solution, crosslinking for 3 min).

affecting on the flux, we tried to form a crosslinking gradient in the PVA/SA active layer rather than homogeneous crosslinking. The schematic representation of the crosslinking gradient morphology with high crosslinking in the surface layer and low crosslinking in the innerpart would give the same effect as a thickness decrease.¹⁰ In fact, $0.25 \mu\text{m}$ of the PVA/SA active layers was still thicker than the $0.01 \mu\text{m}$ of the PA composite membrane.

To form a crosslinking gradient in the active layer, different crosslinking reaction rates between PVA and SA were used. In the previous article, it was found that the crosslinking rate of PVA was much faster than that of SA.⁶ So, a 0.1 wt % SA solution was coated first on the PSF support and then a 0.5 wt % PVA was coated on the SA layer to form a PSF/SA/PVA layer-by-layer structure. After that, the SA/PVA layer was

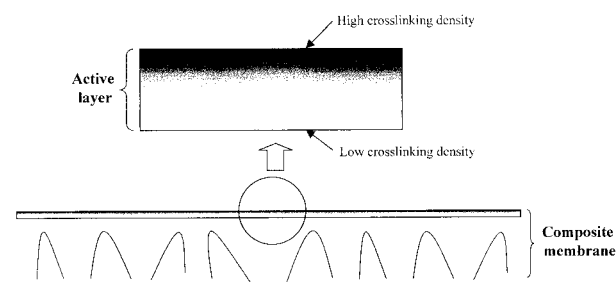


Figure 10 Schematic representation of crosslinking gradient of the PVA/SA active layer.

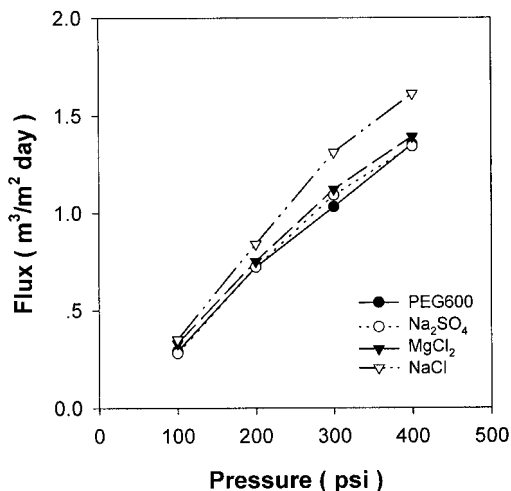


Figure 11 Flux as a function of pressure through the PVA/SA composite membrane with a crosslinking gradient.

crosslinked in the same way as explained above, and the crosslinking time was 1 min to minimize the degree of crosslinking of the SA (inner) layer.

The performance of the membrane prepared as such is shown in Figures 11 and 12. The flux, $0.75 \text{ m}^3/\text{m}^2 \text{ day}$ at 200 psi, is higher than $0.5 \text{ m}^3/\text{m}^2 \text{ day}$ of the one with the homogeneous crosslinking, while the behavior of the solute rejection is comparable. From this result it can be suggested that the formation of the crosslinking gradient in the active layer was favorable for the high flux of the PVA/SA NF membrane.

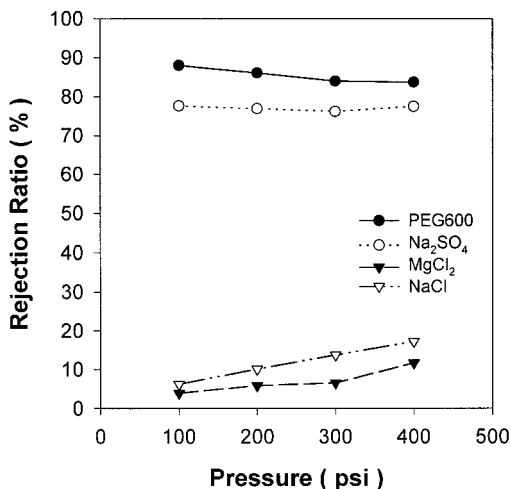


Figure 12 Rejection as a function of pressure through the PVA/SA composite membrane with a crosslinking gradient.

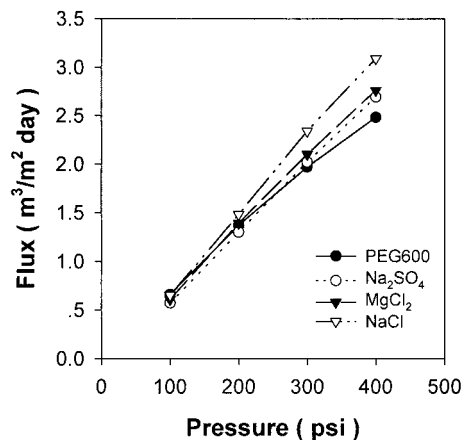


Figure 13 Flux as a function of pressure through the PVA/SA composite membrane (0.1 wt % PVA/SA solution, crosslinking for 2 min).

Effect of Thickness of Active Layer

To improve the performance of the PVA/SA composite membranes further, a new method to coat a very thin active layer (about $0.01 \mu\text{m}$) on the microporous PSF support was developed.¹¹ Figures 13 and 14 show the permeation properties of the PVA/SA composite membrane prepared by coating three times with a 0.1 wt % PVA/SA blend solution, followed by crosslinking for 2 min as explained above. The flux was highly improved with decreasing thickness of the active layer and about $1.35 \text{ m}^3/\text{m}^2 \text{ day}$ at 200 psi when the feed solution was PEG600, which was very comparable with commercial NF membranes. The rejection was also above 95%.

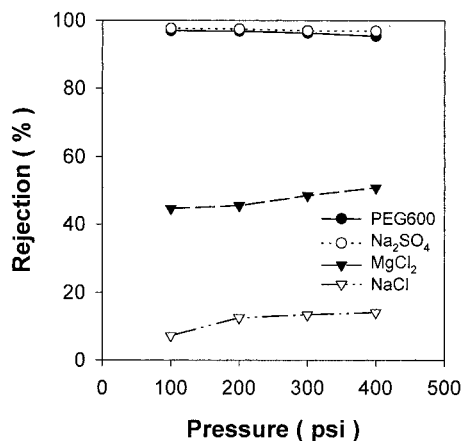


Figure 14 Rejection as a function of pressure through the PVA/SA composite membrane (0.1 wt % PVA/SA solution, crosslinking for 2 min).

CONCLUSIONS

PVA/SA blend composite NF membranes can be prepared by coating PVA/SA mixture solutions (95/5 in wt %) with different concentrations on the microporous PSF support, followed by crosslinking for less than 3 min. Multiple coating with a dilute polymer solution is favorable for the formation of the defect-free thin active layer on the microporous PSF support. PVA/SA blend composite membranes show typical nanofiltration properties with good fluxes and rejections. The flux through the membrane increases with decreasing the active layer thickness. With increasing crosslinking time, the flux decreases, and the solute rejection increases.

Financial support of this work by the Ministry of Science and Technology (MOST) of Korea is gratefully acknowledged. We are also grateful to Professor Tony Fane, Dr. Kyu-Jin Kim, and Mr. Dennis Cho (University of New South Wales) for the use of the Electrokinetic Analyzer.

REFERENCES

1. Sanderson, R. D.; Immelman, E.; Bezuidenhout, D.; Jacobs, E. P.; Van Reenen, A. J. *Desalination* 1993, 90, 15.
2. Immelman, E.; Sanderson, R. D.; Jacobs, E. P.; Van Reenen, A. J. *J Appl Polym Sci* 1993, 50, 1013.
3. Koyama, K.; Okada, M.; Nishimura, M. *J Appl Polym Sci* 1982, 27, 2783.
4. 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.
5. Jegal, J. G.; Lee, K. H. *J Appl Polym Sci* 1996, 61, 389.
6. Jegal, J. G.; Lee, K. H. *J Appl Polym Sci* to appear.
7. Yeom, C. K.; Lee, K. H. *J Membr Sci* 1996, 109, 257.
8. Peeters, J. M. M. Ph.D. Thesis, University of Twente, Netherland (1967).
9. Koo, J. Y.; Petersen, R. J.; Cadotte, J. E. In *Proc. 1987 Int. Congr. on Membranes and Membrane Processes (ICOM '87)*, Tokyo, June 8–12, 1987, p. 350.
10. Yeom, C. K.; Lee, K. H. *J Appl Polym Sci* 1996, 59, 1271.
11. Korea Pat., in preparation.