Characteristics of the Nanofiltration Composite Membranes Based on PVA and Sodium Alginate

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ABSTRACT: Chemically stable nanofiltration (NF) composite membranes based on poly-(vinyl alcohol) (PVA) and sodium alginate (SA) (hereafter, these membranes are called PVA/SA composite membranes) were prepared by coating microporous polysulfone (PSF) supports with dilute PVA/SA blend solutions. The PSF supports were pretreated with small monomeric compounds to reduce their pore size and to improve their hydrophilicity before coating with the PVA/SA blend solutions. The concentration of the PVA/SA blend solutions ranged from 0.1 to 0.3 wt %. The membranes prepared in this study were characterized with various methods such as SEM, FTIR, permeation tests, and z-potential measurements. Especially, chemical stabilities of the membranes were tested, using three aqueous solutions with different pHs such as a HCl solution (pH 1), a K_2CO_3 solution (pH 12.5), and a NaOH solution (pH 13). Their chemical stabilities were compared with that of a polyamide (PA) composite membrane prepared from piperazine (PIP) and trimesoyl chloride (TMC). In this study, it was found that the PVA/SA composite membranes prepared showed not only good chemical stabilities but also good permeation performances in the range from pH 1 to 13. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 2471–2479, 2001

Key words: nanofiltration; composite membrane; PVA; sodium alginate; chemical stability

INTRODUCTION

In spite of its good membrane performance, a polyamide (PA) composite membrane has limitations in its application because of its low chemical stability. Consisting of a PA active layer and a microporous polysulfone (PSF) support, the PA composite membrane seems unstable in strong base conditions such as a NaOH solution, since the PA active layer is very easy to be hydrolyzed at over pH 12. It has been then naturally recommended that if a chemically stable material is used for the formation of an active layer the resulting composite membrane could be chemically stable.

On this basis, to prepare a chemically stable nanofiltration (NF) membrane, hydrophilic PVA was used in this study as a material for the formation of an active layer of the NF composite membrane since the poly(vinyl alcohol) (PVA) comprised a C—C backbone structure that is very well known as chemically stable. However, there has been some problems in the formation of a good NF composite membrane with PVA. The PVA composite membranes prepared so far have low water fluxes and relatively low solute rejections, possibly due to the relatively thick PVA active layer and improper degree of crosslinking.[1–4]

The main subject to be considered were how to form on the PS support a very thin PVA active layer without defects and how to optimize the degree of crosslinking of the active layer. The size of the pore of the PSF support with a molecular weight cutoff (MWCO) of 30,000 g/mol that has been often used as a support of a composite membrane was found too large to be covered with a dilute PVA solution (0.1 wt %). A large difference between the solubility parameters of the PVA and the PSF was another difficulty to be solved for the formation of a homogeneous PVA thin layer on a hydrophobic PSF layer.

In this study, to solve such difficulties, pretreatment of the PSF support with monomeric chemicals was tried to reduce the pore size and to increase the hydrophilicity of the PSF support without a large decrease in its flux. The pretreated PSF support was then coated with a very dilute PVA/sodium alginate (SA) blend solution, followed by crosslinking with glutaraldehyde and obtained much better permeation performances than those of the other PVA composite membranes.[5,6] In this article, details of the characteristics of the PVA/SA composite membranes such as chemical stabilities and permeation performances were elaborated.

EXPERIMENTAL

Materials

PVA (molecular weight of 50,000 g/mol, 99% hydrolyzed) and SA, purchased from the Aldrich Co. (Milwaukee, WI), were used for the formation of active layers of the PVA/SA composite membranes. Piperazine (PIP) and trimesoyl chloride (TMC) purchased from the Aldrich Co. were used as monomers for the formation of a PA composite membrane. A PSF UF membrane (MWCO: 30,000 g/mol] bought from the Fluid System Co. (San Diego, CA) was used as a support of the composite membrane prepared. Na_2SO_4, $MgSO_4$, $MgCl_2$, NaCl, and poly(ethylene glycol)s (molecular weights of 600, 400, 200 g/mol) (hereafter, called PEG600, PEG400, PEG200, respectively) were bought from the Tokyo Kasei Co. (Tokyo, Japan) and used as solutes for the permeation tests. Glutaraldehyde (GA) (concentration: 25 wt %) was bought from the Tokyo Kasei Co. and used as a crosslinking agent. Hexane and acetone purchased from the Junsei Co. (Tokyo, Japan) were used as solvents without further purification.

HCl, K_2CO_3, and NaOH bought from the Junsei Co. were used to make solutions with different pHs.

Membrane Formations

PVA/SA Composite Membrane

PVA/SA composite membranes were prepared by coating PVA/SA (95/5 in wt %) mixture solutions on the microporous PSF supports that were pretreated with monomeric chemicals such as piperazine and trimesoyl chloride to reduce the pore size and improve the hydrophilicity of the surface of the supports.[6] The concentrations of the PVA/SA mixture solutions ranged from 0.1 to 0.3 wt %. For coating the PVA/SA active layer, the PSF supports were coated three times with the polymer solutions regardless of their different concentrations. The PVA/SA active layers of the composite membranes formed were crosslinked with GA at room temperature for 1 min using a crosslinking solution as described in previous articles.[5,6]

Polyamide Composite Membrane

A PA composite membrane was prepared by a conventional interfacial polymerization of PIP and TMC on a microporous PSF support.[7] The concentrations of PIP in water and TMC in hexane were 1 and 0.05 wt %, respectively. The respective interfacial polymerization time and reaction temperature were each 10 s at 25°C.

SEM

The morphology and thickness of the active layers of the PVA/SA composite membranes were observed with a scanning electron microscope (SEM) (Model JSM-80A, JEOL).

Zeta-potential Measurements

Zeta-potentials of the composite membranes of PVA/SA and PA were measured to characterize their surface ionic properties using an electrokinetic analyzer (Model: EKA, Brookhaven). The setup of the zeta-potentiometer was as presented in a previous article.[5] With this setup, zeta-potentials were measured along a surface of the membranes. The thickness of the membranes used was about 100 μm. The driving pressure was applied in both directions and, consequently, the electrolyte could pass through the channel from the left to the right or from the right to the left. The pressure difference was varied in the range of 0–0.25 bar and monitored with an accuracy of

0.01 bar. The concentrations of the electrolyte solutions used were in the range of 0.001–0.1M for the two salts, NaCl and Na$_2$SO$_4$. The temperature of the system was kept at 20°C.

Chemical Treatment

To study and compare the chemical stabilities of both the PVA/SA and PA composite membranes, they were treated with solutions with different pHs that ranged from 1 to 13, using a specially designed cell (Fig. 1). In the cell, only the active layer of the composite membrane was in contact directly with the solutions for the chemical treatment. The membranes were treated for 17 h at room temperature with the solutions, after which they were taken out of the cell and washed with an excess amount of distilled water and kept in the water until it was used for permeation tests. The chemical stabilities of the membranes were determined indirectly by measuring their rejection performances. The solutions with different pHs were prepared by dissolving in water proper amounts of the HCl, K$_2$CO$_3$, and NaOH at room temperature, using a pH meter for the exact adjustment of the pHs (HCl solution: pH 1; K$_2$CO$_3$ solution: pH 12.5; NaOH solution: pH 13).

Permeation Test

To test the performances of the membranes prepared, an NF test setup was used. The concentration of all the feed solutions used in this experiment was 1000 ppm and an upstream pressure was controlled by using back-pressure regulators (100, 200, 300, and 400 psi). All tests were conducted at 25°C. A flux was measured by weighing the permeate penetrated through the membranes 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 chromatograph (HPLC) (Model Waters 501) that was attached to a differential refractometer R401 as a detector.

RESULTS AND DISCUSSION

Morphology

Figure 2 shows SEM photographs of the cross section and surface of the PVA/SA composite mem-

Chemical Solution

(A) Membrane
(B) Upper compartment
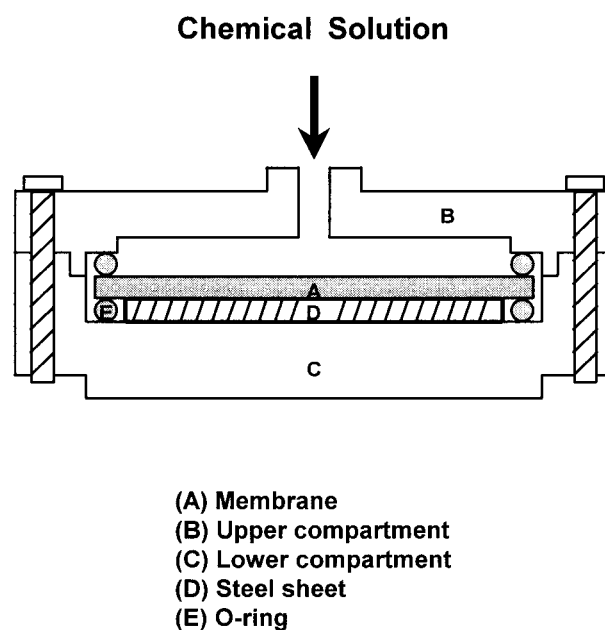(C) Lower compartment
(D) Steel sheet
(E) O-ring

Figure 1 Schematic representation of a cell used for chemical treatment.

brane that was prepared by coating three times with a 0.1 wt % PVA/SA mixture solution. Even after magnification to 20,000 times, the interface between the active layer and support of the membrane was not clear so that the thickness of the active layer could not be measured exactly from the cross-section view of the SEM photographs shown in Figure 2. The surface of the PVA/SA composite membrane was found to be rather rough, which was much different from the smooth surface of the PVA/SA composite membrane prepared from a 0.5 wt % PVA/SA mixture solution.[5]

Zeta-potential Measurement

To study the ionic characteristics of the surfaces of the PVA/SA and PA composite membranes, their zeta-potentials were measured, using an electrokinetic analyzer. Figure 3 shows the zeta-potentials of the PVA/SA and PA composite membranes as a function of the concentration of the solutions of Na$_2$SO$_4$ and NaCl. The zeta-potentials of those were all negative in the range of the concentration of the electrolyte solutions and decreased with the increasing concentrations. The negative zeta-potentials indicate that the surfaces of the both membranes are anionic and the decreasing zeta-potentials with the increasing concentrations of the electrolytes are due to the narrow double-layer thickness formed in the concentrated electrolyte solution.[8]
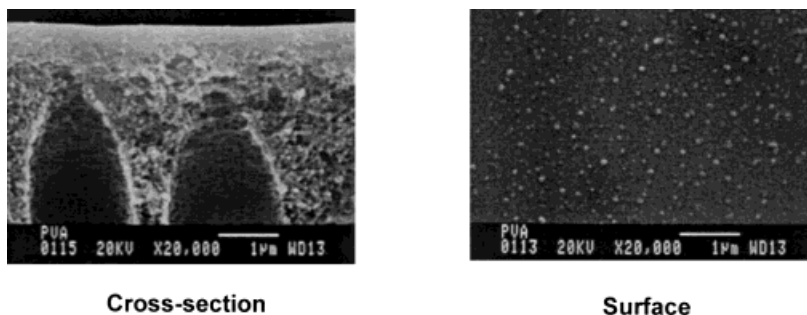
Figure 2 SEM photographs of a PVA/SA (95/5 in wt %) composite membrane prepared by coating a 0.1 wt % PVA/SA solution three times on a PSF support, followed by crosslinking for 1 min.

From the lower zeta-potentials of the PVA/SA composite membrane than that of the PA composite membrane, it is indicated that the anionic character of the surface of the PVA/SA composite membrane is less than that of the PA composite membrane. This result suggests that a relatively large amount of acyl chloride (—COCl) of the TMC that was not involved in the interfacial polymerization with PIP during the formation of the PA composite membrane was transformed into the carboxylic acid (—COOH) and acted as an anionic site.

The difference between the zeta-potentials measured with NaCl and Na_2SO_4 is related to the ionic strength of the electrolytes. Since the ionic strength of the Na_2SO_4 is higher than that of NaCl, the zeta-potentials measured with a Na_2SO_4 solution appeared to be lower.[8]

Permeation Properties

Effect of Thickness of Active Layers

To determine the proper thickness of the active layer, several PVA/SA composite membranes were prepared from different concentrations of PVA/SA mixture solutions (0.1, 0.2, and 0.3 wt %), since the solution with a higher concentration would give a thicker active layer. For those membranes, the crosslinking time of the active layer with GA was fixed at 1 min, considering the results reported in a previous article.[5]

Figure 4 shows the permeation performances of those membranes as a function of the operating pressure. The feed solution used was a 1000 ppm PEG 600 aqueous solution. As expected, the flux of the membranes decreased as the concentration of the PVA/SA mixture solution increased, but the rejection remained almost constant. The flux of the membrane made from the 0.1 wt % solution was about 1.3 $m^3 \ m^{-2} \ day^{-1}$ at 200 psi, but it was only 0.2 $m^3 \ m^{-2} \ day^{-1}$ for the one made from the 0.3 wt

% solution. The rejection, however, was about 96 wt % for those, regardless of the thickness of the active layers. From this study, the 0.1 wt % solution was found to be the optimum concentration for the formation of a PVA/SA NF composite membrane.

Effect of Molecular Weight of Solutes

For the determination of the MWCO of the PVA/SA composite membrane prepared from a 0.1 wt % PVA/SA mixture solution, permeation tests were carried out with 1000 ppm aqueous solutions of PEGs having different molecular weights such as 200, 400, and 600 g/mol. Figure 5 shows the permeation results. As one can see, for all the feed solutions, the flux, without dependence on the molecular weight of the solutes, was about 1.3 $m^3 \ m^{-2} \ day^{-1}$ at 200 psi. The independence of the flux on the molecular weight of PEG may be due to that the permeate is almost water itself containing a very little amount of PEG and the PEG used is not in the molecular size which causes a clogging effect during the permeation test. However, the rejection of the solute, decreasing with an increasing upstream pressure, was very dependent on the molecular weight as expected, showing a higher rejection for the higher molecular weight and a lower rejection for the lower molecular weight. In the case of PEG 600, it was about 96%, but it was only about 60% for PEG 200. This result suggests that size exclusion is dominant for the rejection of the PEG and that the MWCO of this membrane is about 400.

Effect of Different Salts

Four kinds of salt (Na_2SO_4, $MgSO_4$, $MgCl_2$, and NaCl) were used for the permeation tests to determine the effect of the characteristics of the salts such as ion size and number of ion charges
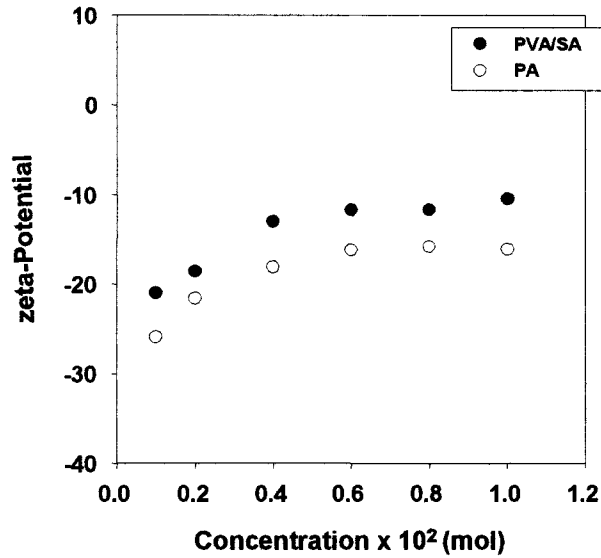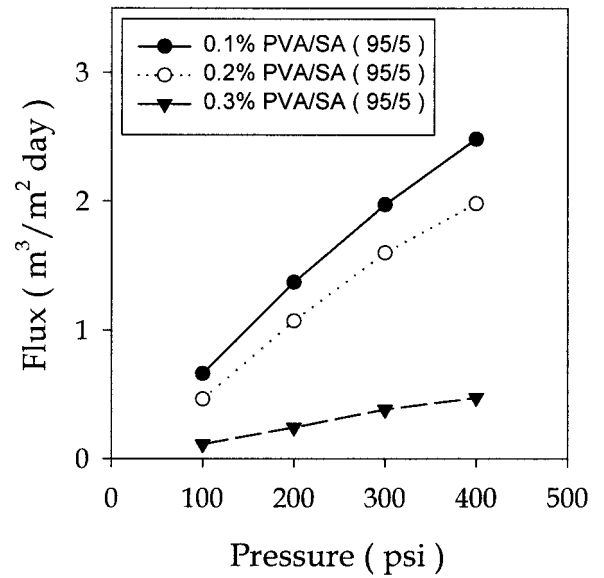
(a)
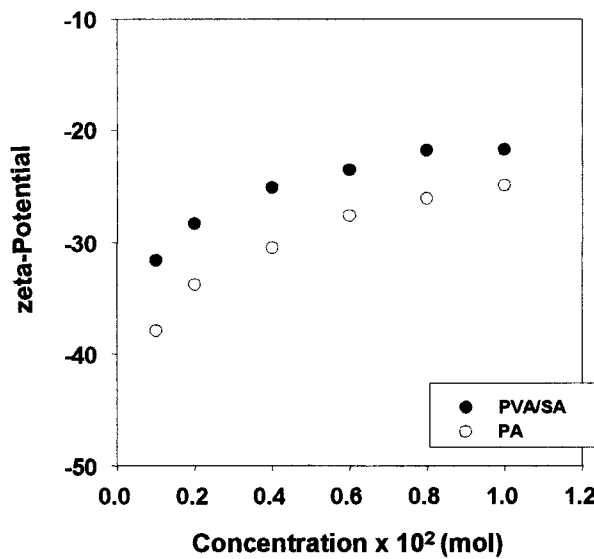
(b)

Figure 3   Zeta-potentials of the PVA/SA and PA composite membranes as a function of the concentration of electrolytes: (a) Na_2SO_4; (b) NaCl.
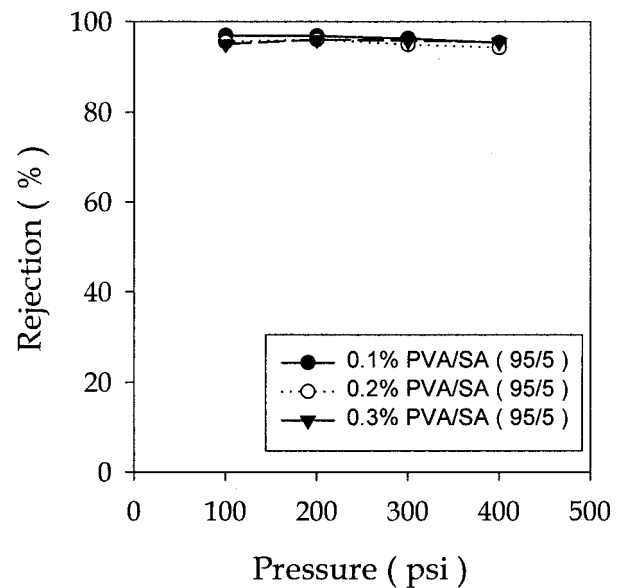
tion. Not like the flux in the test with the PEG solutions, the flux of the salt solution varied. The differences in the flux among different salt solutions were even more significant at high pressure
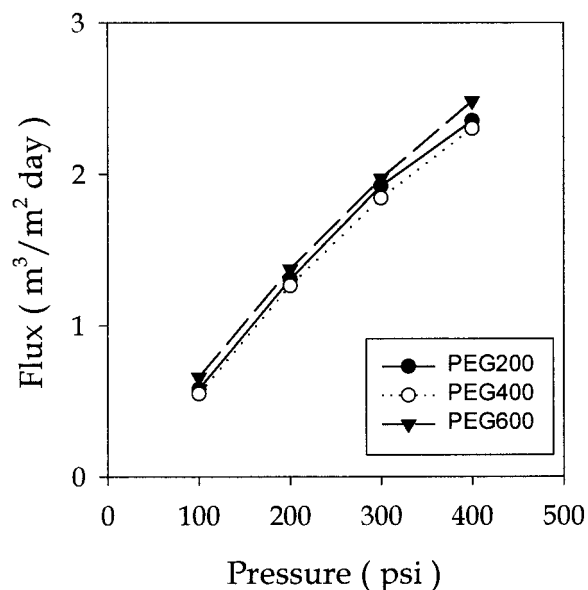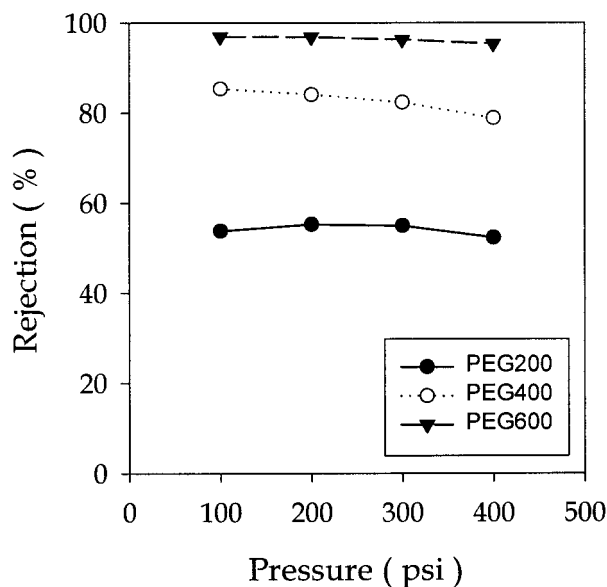

(a)

(b)

Figure 4   Permeation performances of PVA/SA composite membranes prepared from different concentrations of PVA/SA mixture solution as a function of pressure: (a) flux; (b) rejection. Feed solution: 1000 ppm PEG 600 aqueous solution.

on the performance of the PVA/SA composite membrane made from a 0.1 wt % PVA/SA mixture solution. The size of the ions of the salts used are as shown in Table I.[9]

The permeation results, shown in Figure 6, turned out to be very dependent on the feed solu-

(a)

(b)

Figure 5 Permeation performances of the PVA/SA composite membrane prepared from a 0.1 wt % PVA/SA mixture solution as a function of molecular weights of solute: (a) flux; (b) rejection. Feed solutions: 1000 ppm PEG600, PEG400, and PEG200 aqueous solutions.

such as 400 psi. The order of the flux is as follows: $NaCl > MgCl_2 > Na_2SO_4 > MgSO_4$, suggesting the dependence of the flux on the hydrated ion size. The flux of the solutions of the Na_2SO_4 or $MgSO_4$ with relatively bigger hydrated ions was lower than that of the solution of the NaCl or $MgCl_2$ consisting of small ions. However, the exact reason for the dependence of the flux on the different salt solution is not yet clear.

The rejection of the salt solution also appeared very dependent on the properties of the salts used by the combined effect of electrostatic repulsion and size exclusion, higher rejection (over 90%) for the salts with a higher amount of anion charge, and bigger ion size such as Na_2SO_4 and $MgSO_4$. Especially, this membrane showed a very low rejection of NaCl (less than 20%).
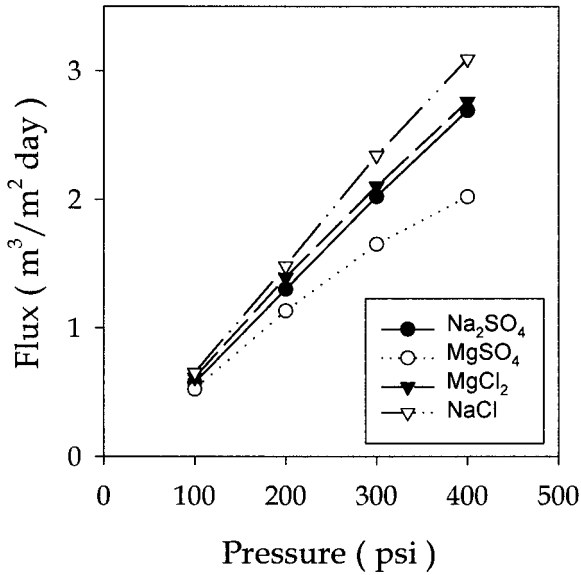
Chemical Stability

A PVA composite membrane consisting of a PVA active layer and a microporous PSF support has been expected to have good chemical stability due to the good chemical stability of PVA. However, the detailed chemical stability of the PVA composite membrane has rarely been tested and confirmed so far.
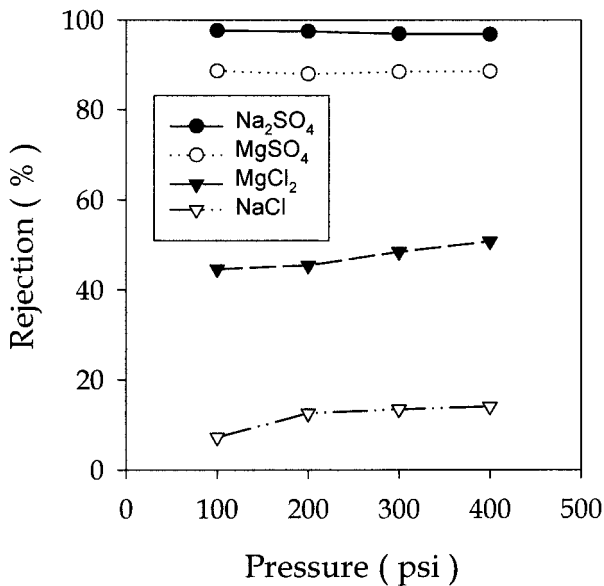
In this study, three aqueous solutions with different pH values such as a HCl solution (pH 1), a K_2CO_3 solution (pH 12.5), and a NaOH solution (pH 13) were prepared to confirm the stable chemical property of the PVA/SA composite membrane prepared in this study. The active layer of the PVA/SA composite membrane made from a 0.1 wt % PVA/SA mixture solution was allowed to contact with each of the chemical solutions prepared in the specially designed cell for 17 h at room temperature. The PA composite membranes, prepared by the interfacial polymerization of piperazine and trimesoyl chloride on the porous PSF support as explained in the Experimental part, were also treated with each of those solutions in the same condition as was the PVA/SA membrane to compare their chemical stabilities. After treatment with the chemical solutions, the membranes were washed with an excess amount of distilled water and kept in distilled water until they were tested with a 1000 ppm PEG600 aqueous solution.

Table I   Effective Ionic Radii[9]

Ions	Radius (Å)
Na^+	1.13
Mg^{2+}	0.71
Cl^-	1.67
SO_4^{2-}	2.30

membranes, their fluxes and rejections appeared to be almost the same despite the treatment, suggesting that the both composite membranes are quite stable at the pH 1 condition.
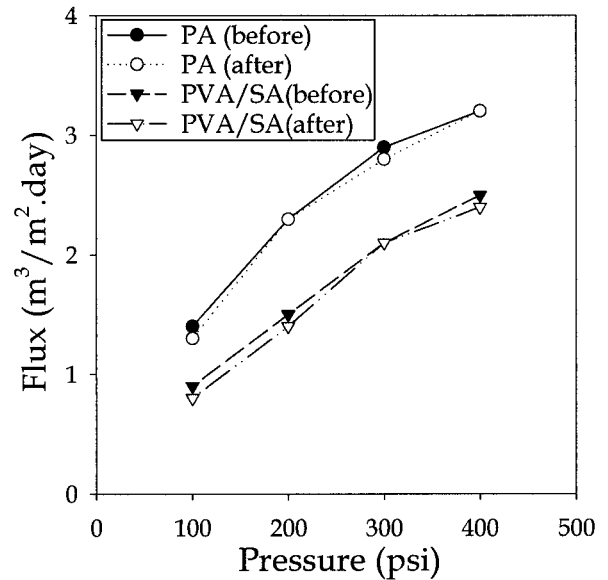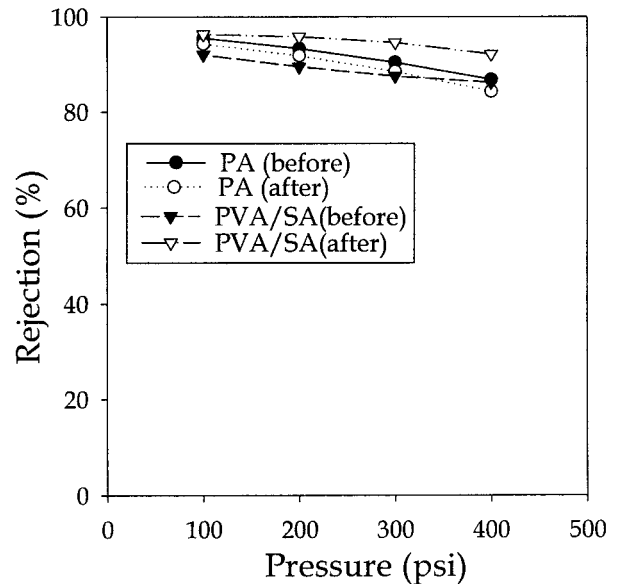

(a)

(b)

Figure 6 Permeation performances of the PVA/SA composite membrane with different salt solutions: (a) flux; (b) rejection. Feed solutions: 1000 ppm aqueous salt solutions such as Na_2SO_4, $MgSO_4$, $MgCl_2$, and NaCl.

Figure 7 presents the permeation properties of the both PVA/SA and PA composite membranes before and after treatment with the HCl solution (pH 1). As one can see, for the PVA/SA and PA

(a)

(b)

Figure 7 Permeation performances of the PVA/SA and PA composite membranes before and after treatment with a HCl solution (pH 1): (a) flux; (b) rejection. Feed solution: 1000 ppm PEG600 aqueous solution.
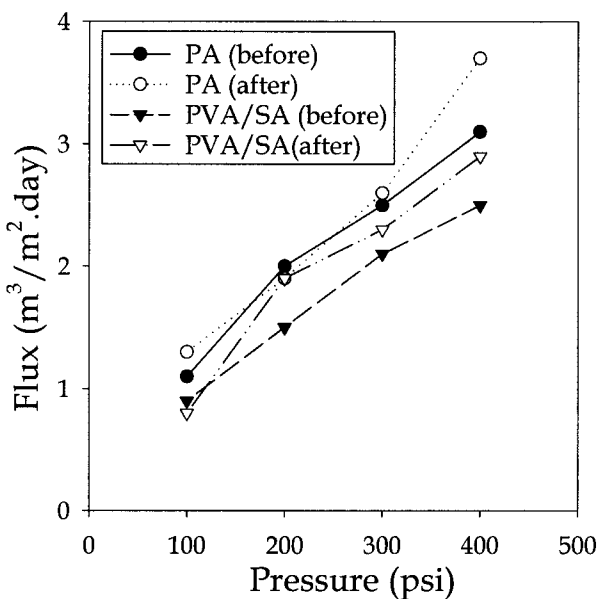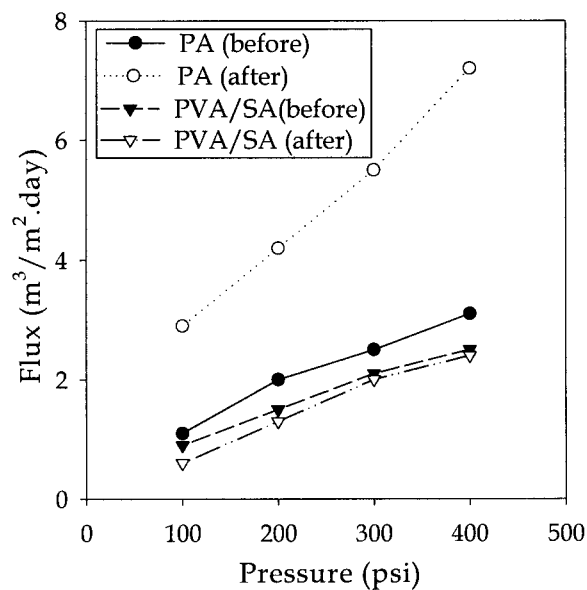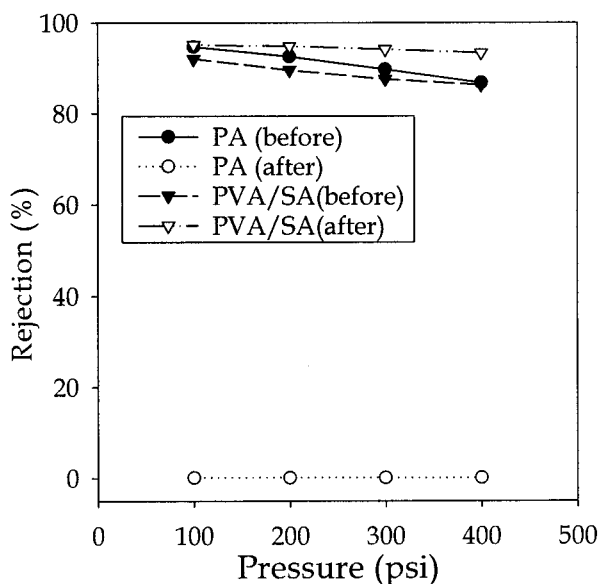
(a)
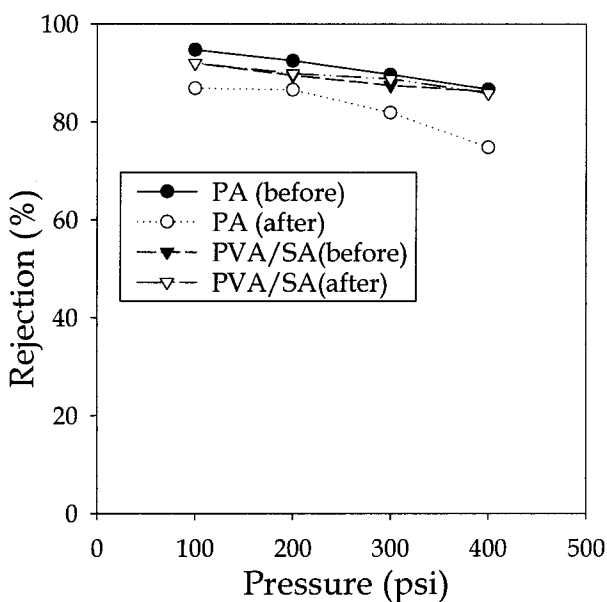
(b)

Figure 8 Permeation performances of the PVA/SA and PA composite membranes before and after treatment with a K_2CO_3 solution (pH 12.5): (a) flux; (b) rejection. Feed solution: 1000 ppm PEG600 aqueous solution.

Figure 8 shows the results of the permeation tests after treatment with the K_2CO_3 solution (pH 12.5). Even though the data of fluxes of the both

membranes were scattered a little, the effect of the K_2CO_3 solution on their stability is not clearly seen. However, the rejection of the PA composite membrane revealed a small decrease after the chemical treatment.

(a)

(b)

Figure 9 Permeation performances of the PVA/SA and PA composite membranes before and after treatment with a NaOH solution (pH 13): (a) flux; (b) rejection. Feed solution: 1000 ppm PEG600 aqueous solution.

Figure 9 shows the permeation results of the membranes after treatment with the NaOH solution (pH 13). Different from the previous two cases, the PA composite membrane was found to be affected seriously by the NaOH solution, whereas the PVA/SA composite membranes were stable. By the treatment, the flux of the PA membrane increased to about 4 m^3 m^{-2} day^{-1} from 2 m^3 m^{-2} day^{-1} at 200 psi with a decrease of rejection from 93% to almost 0%, indicating the degradation of the polyamide active layer by the strong OH^- group of the NaOH solution. These results indicate that even though the polyamide active layer of the PA composite membrane made from piperazine and TMC was pretty stable in strong acid solutions and weak base solutions such as HCl and K_2CO_3 solutions, regardless of pH, it was very unstable in strong base solutions. This phenomenon can be explained by the easy hydrolysis reaction by the OH^- of the amide (—NC=O) linkage to amine (—NH—) and carboxylic (—COOH) acid groups. However, the PVA/SA composite membrane was confirmed to have very good chemical stability in strong acid and base solutions.

CONCLUSIONS

A PVA/SA blend composite NF membrane with a good performance can be prepared by coating a microporous PSF support with a 0.1 wt % PVA/SA mixture solution (95/5 in wt %), followed by crosslinking with GA for 1 min in a crosslinking solution. The PVA/SA composite membrane shows a typical nanofiltration property. The MWCO of the membrane was about 400 and its flux at 200 psi about 1.3 m^3 m^{-2} day^{-1}. The rejection for Na_2SO_4 and PEG 600 is over 95%. The membrane is also chemically stable in the wide range of pH from 1 to 13.

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