

Preparation and Characterization of PVA/SA Blend Nanofiltration Membranes

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(Received November 8, 1999, Accepted December 28, 1999)

Abstract : The nanofiltration (NF) membranes based on poly(vinyl alcohol) (PVA) and sodium alginate (SA) were prepared. Homogeneous PVA/SA blend membranes were prepared by casting a PVA/SA (95/5 in wt.%) mixture solution on an acryl plate, followed by drying at a room temperature and by crosslinking with glutaraldehyde (GA) for 20 minutes. PVA/SA blend composite membranes were also prepared by coating a PVA/SA (95/5 in wt.%) mixture solution on microporous polysulfone (PSF) supports. The PVA/SA active layer of the composite membrane was crosslinked at room temperature by using an acetone solution containing GA as a crosslinking agent. The both prepared homogeneous and composite membranes were characterized with a scanning electron microscopy (SEM), a fourier transform infrared spectroscopy (FTIR), and permeation tests. The permeation properties of the composite membrane were as follows: $1.3 \text{ m}^3/\text{m}^2\text{day}$ of flux and $>95\%$ of rejection at 200 psi for a 1000 ppm PEG600 solution.

1. Introduction

In order to prepare chemically stable nanofiltration (NF) composite membranes, poly(vinyl alcohol) (PVA) has been used as a material of the active layer of NF composite membranes [1-5]. Even though PVA has good features as a membrane material like good mechanical property, hydrophilicity and easy to make thin film, it is true that there are some problems in the formation of composite membranes with PVA such as improper crosslinking method and relatively thick thickness of the active layer. The conventional crosslinking method, thermal crosslinking, is not proper since that is not easy to control the degree of crosslinking and develops crystallites in the PVA active layer, which can result in a low flux and a low rejection [1-4].

To develop the PVA NF membranes with good performances in the separation of multivalent ions

and small organic molecules, the PVA/SA blend membranes with thin active layers having an optimum degree of crosslinking were prepared. In this study, to prevent defect formation and to minimize thickness increase in the formation of a PVA active layer on a microporous polysulfone (PSF) support, the PSF support was multiple-coated with a dilute PVA/SA blend solution without insolubilization between coating steps. Also, to avoid the several negative effects encountered in the high temperature crosslinking as explained in the previous papers [1,2,4], the PVA active layers were crosslinked at room temperature in a crosslinking solution containing glutaraldehyde (GA) as a crosslinking agent [5]. The prepared membranes were characterized with several analytical methods (SEM, FTIR). NF properties of the membranes were determined through the tests with various feed solutions (PEG 600, Na_2SO_4 , MgCl , NaCl).

2. Experimental

2.1. 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 the NF membranes. A PSF UF membrane (MWCO: 30,000 g/mol) bought from Fluid System Co. was used as a support of the composite membrane. Na_2SO_4 , MgCl_2 , NaCl , and poly(ethylene glycol) with a molecular weight of 600 g/mol (PEG600) were bought from Tokyo Kasei Co. and used for permeation tests. Glutaraldehyde (GA) with a 25 wt.% content bought from Tokyo Kasei Co. was used as a crosslinking agent. Acetone was purchased from Junsei Co. and used as a solvent of a crosslinking solution without further purification.

2.2. Membrane Formation

2.2.1. Homogeneous membranes

Free standing symmetric homogeneous membranes were prepared by casting a 5 wt.% solutions of PVA/SA (95/5 in wt.%) mixture on an acrylic plate, followed by drying at room temperature. The polymer solution was containing 5 vol.% of glutaraldehyde (GA) as a crosslinking agent. For the crosslinking, the prepared PVA/SA blend membranes were immersed for 40 minutes at room temperature into an isopropanol/water (90/10 in vol.%) mixture solution containing 1 vol.% of hydrochloric acid as a catalyst. After which, the membranes were kept in distilled water at room temperature for 24 hrs to completely remove any unreacted GA that could remain in the membranes [5].

2.2.2. Composite membranes

The composite membranes consisting of PVA/SA blend (95/5 in wt.%) active layers and microporous PSF supports were prepared by the multiple coating of PSF supports with PVA/SA solutions having different concentrations, followed by drying at room temperature. A composition of the PVA/SA blend 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 minutes and taken out to dry. The support first coated was then immersed into the polymer solution again for 10 second 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. The used crosslinking solution was an acetone solution containing 5 vol.% of GA as a crosslinking agent and trace amount of HCl as a catalyst [6]. The contacting time was adjusted from 1 to 3 minutes to control degrees of crosslinking. After crosslinking, the composite membranes were washed with excess amount of water and kept in distilled water for a day to remove any unreacted GA that could remain in the membranes. The prepared composite membranes were then kept in distilled water before using for permeation tests.

2.3. Characterization

The morphology and the chemical structures of the membranes prepared in this study were characterized with a scanning electron microscopy (SEM) (model: JSM-80A, JEOL) and FTIR (Bio-Rad, Digilab Division, model FTS-80, FTIR), respectively.

2.4. Permeation Test

To test the performances of the membranes prepared, a nanofiltration test set was used. The concentration of feed solutions was 1,000 ppm and an upstream pressure was controlled by using back-pressure regulators (100, 200, 300, and 400 psi). Before measuring the flux and rejection, the pressure was kept at 400 psi for 2 hours to get rid of any fluctuation of data due to the membrane compaction. All test was 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:

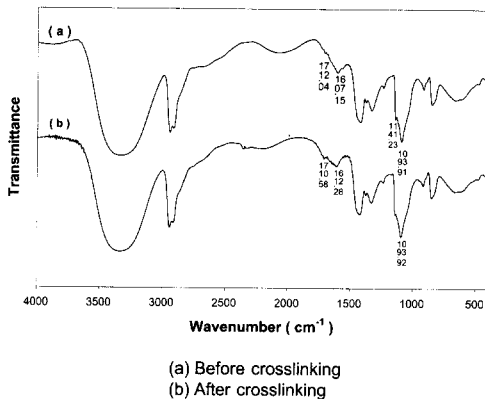


Fig. 1. FTIR spectra of the PVA/SA (95/5 in wt.%) active layers before (a) and after (b) crosslinking with GA.

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

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.

3. Results and Discussion

3.1. Characterization

3.1.1. FTIR

The crosslinking mechanism of PVA with GA is very well known that the -OH group of PVA reacts with the -CHO group of GA with aid of an acid catalyst at a room temperature to form acetal linkage [5]. The FTIR spectra of the PVA/SA films were obtained as shown in Fig. 1 to see the difference in the spectra of the films before and after crosslinking with GA [7]. The spectrum (a) obtained from the uncrosslinked one shows a weak C=O stretching peak at 1712 cm^{-1} that comes from the $-\text{COO}^- \text{Na}^+$ group of the SA, indicating that the SA is well mixed with the PVA. The weak intensity of the C=O stretching peak is due to the small amount (5 wt.%) of SA in the PVA/SA blend film. However, the spectrum did not show much

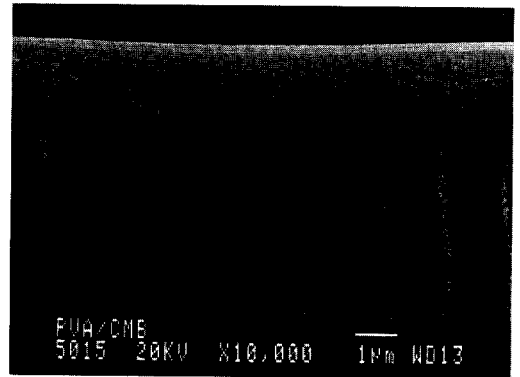


Fig. 2. SEM photograph of the PVA/SA (95/5 in wt.%) composite membrane prepared by coating a 0.5 wt.% PVA/SA solution three times on the PS support, followed by crosslinking for two minutes.

difference after the crosslinking reaction as shown in a spectrum (b). In the crosslinking reaction, The -OH groups of the PVA and SA react with the -CH=O group of the GA to form -C-O-C-O- acetal linkages. The characteristic -C-O- stretching peaks of the PVA and SA are so similar to the -C-O- stretching peak of the acetal linkage formed by the crosslinking reaction that there is no significant change in the spectrum.

3.1.2. SEM

In order to see the thickness and state of the active layer of the PVA composite membrane, a SEM photograph was taken as shown in Fig. 2. The PVA/SA blend composite membrane prepared by coating a microporous PSF support three times with a 0.5 wt.% PVA/SA solution was in good shape and the thickness of the active layer was about $0.25 \mu\text{m}$. The surface of the composite membrane was looked smooth.

3.2. Permeation Test

SA, an 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 a PVA membrane. Especially, the SA was expected to improve a solute rejection through the Donnan

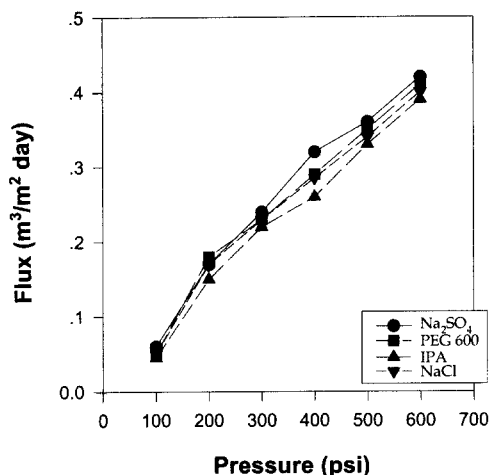


Fig. 3. Flux as a function of pressure through the PVA/SA homogeneous membrane.

exclusion because of its anionic character. The composition of the PVA/SA blend used was determined as 95/5 in wt.%, since this composition was approved to be the best one with respect to the homogeneous blending and proper crosslinking reaction [5].

3.2.1. Homogeneous PVA/SA blend membrane

A PVA/SA blend membrane containing 5 wt.% of SA was prepared. The PVA/SA blend membrane crosslinked with GA for 40 minutes in the crosslinking solution showed 370% of water swelling index [5]. The thickness of the dried PVA/SA blend membrane was about 10 μm . Figs. 3 and 4 exhibit the permeances and rejection ratios through the PVA/SA blend membrane [5]. The permeances increased with an increasing pressure from 0.06 (at 100 psi) to 0.43 $\text{m}^3/\text{m}^2 \text{ day}$ (at 600 psi). The permeances as a function of the upstream pressure were almost same regardless of the different feed solutions. However, the rejection ratios varied with the different solutes. For sodium sulfate and sodium chloride, the rejection ratios increased gradually with the increasing pressure. For sodium sulfate, they were above 99% at all the pressures. For sodium chloride, they increased from 65 to 80% with the increasing pressure from 100 to 600 psi. On the other hand, the rejections of PEG 600 and

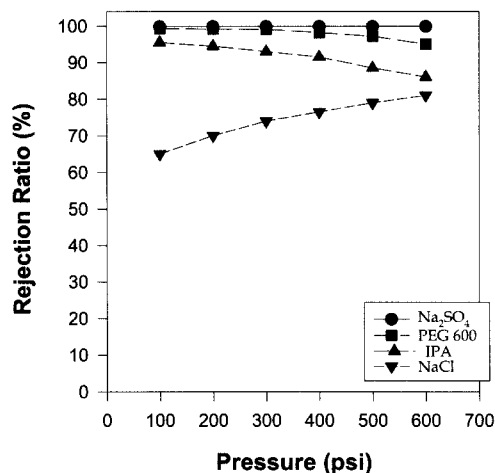


Fig. 4. Rejection as a function of pressure through the PVA/SA homogeneous membrane.

isopropanol decreased with the increasing upstream pressure. The rejection ratio of PEG 600 varied from 98 to 95% and that of isopropanol from 95 to 86% with the increasing pressure. This result might have some relationship with chemical interactions between the organic solutes and the ionic surfaces of the membranes that were introduced by using small amount of SA. Since the ionic surfaces of the PVA/SA blend membranes had relatively lower affinity with the organic solutes, the solute rejections of those membranes were relatively high.

3.2.2. PVA/SA blend composite membranes

Figs. 5 and 6 show the permeation properties of the PVA/SA blend composite membrane prepared by coating the PSF support three times with a 0.5 wt.% PVA/SA blend solution, followed by crosslinking with GA for two minutes [7]. From these results, one can find that this membrane is a typical NF membrane; showing relatively good fluxes and high rejections of the PEG 600 and Na_2SO_4 and very low rejections of the NaCl and MgCl_2 . The flux was not affected substantially by the different feed solutions, however, the rejection depended strongly. The flux increased almost linearly with the increasing operating pressure and became about 0.5 $\text{m}^3/\text{m}^2 \text{ day}$ at 200 psi which was

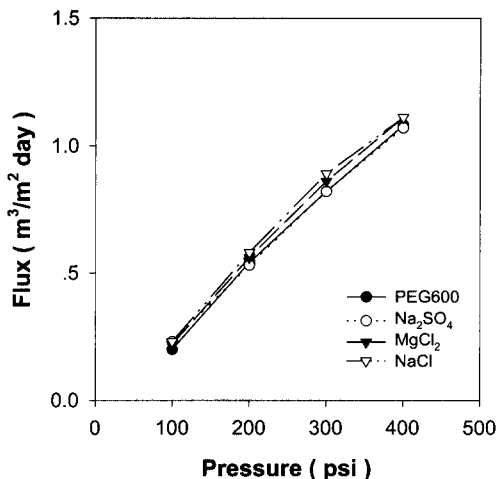


Fig. 5. Flux as a function of pressure through the PVA/SA composite membrane (0.5 wt.% PVA/SA solution, crosslinking for 2 minutes).

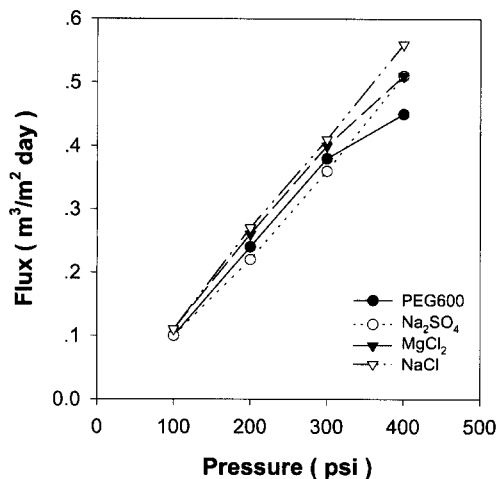


Fig. 7. Flux as a function of pressure through the PVA/SA composite membrane (0.5 wt.% PVA/SA solution, crosslinking for 3 minutes).

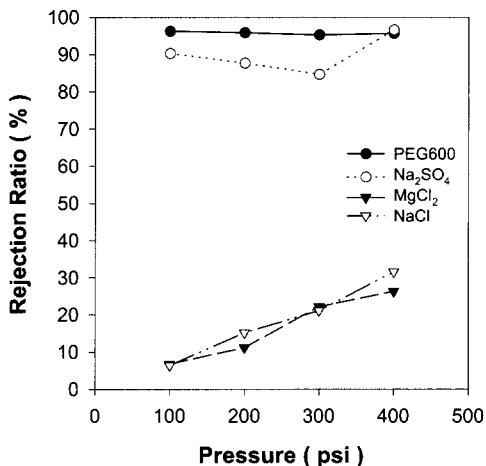


Fig. 6. Rejection as a function of pressure through the PVA/SA composite membrane (0.5 wt.% PVA/SA solution, crosslinking for 2 minutes).

about half of that of commercially available NF membranes such as NF-40 [8].

The rejection behavior as a function of the operating pressure depended on the solutes. For the solutions of PEG 600 and Na₂SO₄, it decreased slightly with the increasing pressure, while it

increased for the MgCl₂ and NaCl. The increase in the rejection of the MgCl₂ 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 the PEG 600, Na₂SO₄, MgCl₂, and NaCl were 90, 88, 15 and 10%, respectively. This result suggests that the mechanism of solute rejection be combination of the size exclusion and Donnan exclusion.

High rejection of the Na₂SO₄ and relatively low rejection of the MgCl₂ and NaCl also suggest that the surface of the membrane have anionic character.

Effect of crosslinking time: In order to study the effect of crosslinking reaction time, the contacting time of the active layer with the crosslinking solution was changed from two minutes to three. The membrane performance after three minutes of crosslinking is shown in Figs. 7 and 8 [7]. As the crosslinking time increased, the flux decreased and the rejection increased. At 200 psi, the flux was about 0.25 m³/m²day, almost half of the one obtained after two minutes of crosslinking but the rejections increased as follows: 97% for the PEG 600, 95% for the Na₂SO₄, 31% for the MgCl₂, and

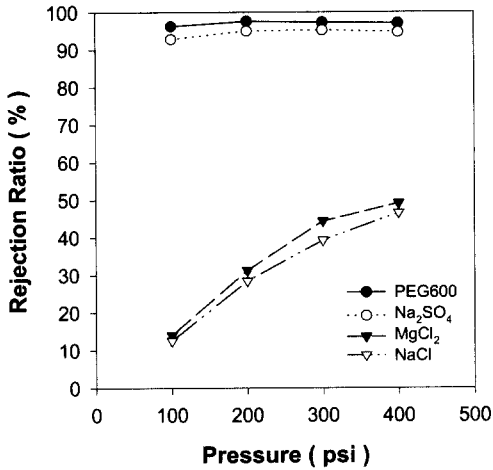


Fig. 8. Rejection as a function of pressure through the PVA/SA composite membrane (0.5 wt.% PVA/SA solution, crosslinking for 3 minutes).

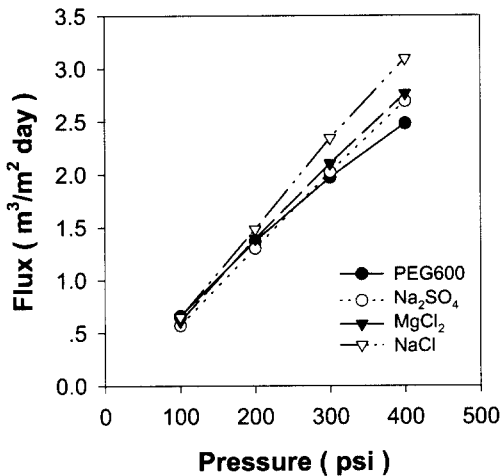


Fig. 9. Flux as a function of pressure through the PVA/SA composite membrane (0.1 wt.% PVA/SA solution, crosslinking for 2 minutes).

27% for the 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 thickness of active layer: To improve the

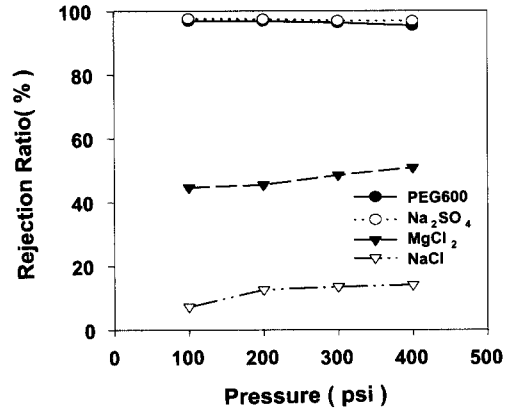


Fig. 10. Rejection as a function of pressure through the PVA/SA composite membrane (0.1 wt.% PVA/SA solution, crosslinking for 2 minutes).

performance of the PVA/SA composite membranes further, a new method to coat a very thin active layer (about 0.01 μm) on the microporous PSF support was developed [6]. Figs. 9 and 10 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 two minutes as explained above [7]. The flux was highly improved with decreasing thickness of the active layer and about 1.35 m³/m² day at 200 psi when the feed solution was PEG600, which was very comparable with commercial NF membranes. The rejection was also above 95%.

4. Conclusions

The performance of the PVA NF membrane can be improved by the incorporation of a small amount of SA into the PVA membrane. A PVA/SA blend homogeneous membrane can be prepared by casting the PVA/SA blend solution (95/5 in wt.%), followed by drying at room temperature and by crosslinking with GA. A PVA/SA blend composite NF membrane also can be prepared by coating a PVA/SA mixture solution (95/5 in wt.%) on a microporous PSF support, followed by crosslinking with GA for less than three minutes. The PVA/SA

blend composite membrane shows typical nanofiltration properties with a good flux and a good rejection. The flux through the membrane increases with decreasing thickness of the active layer. With increasing crosslinking time, the flux decreases and the solute rejection increases.

Acknowledgment

Financial support of this work by the Ministry of Science and Technology (MOST) of Korea is gratefully acknowledged.

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