Nanofiltration Membranes Based on Poly(vinyl alcohol) and Ionic Polymers

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ABSTRACT: Nanofiltration membranes based on poly(vinyl alcohol) (PVA) and ionic polymers, such as sodium alginate (SA) and chitosan, were prepared by casting the respective polymer solutions. The membranes prepared from PVA or PVA–ionic polymer blend were crosslinked in a isopropanol solution using glutaraldehyde as a crosslinking agent. The membranes were characterized with Fourier transform infrared spectroscopy and X-ray diffractometry and swelling test. The membranes crosslinked through the acetal linkage formation between the —OH groups of PVA and the ionomer and glutaraldehyde appeared to be semicrystalline. To study the permeation properties, the membranes were tested with various feed solutions [sodium sulfate, sodium chloride, poly(ethylene glycol) with 600 g/mol of molecular weight (PEG 600), and isopropyl alcohol]. For example, the permeance and the solute rejection of the 1000 ppm sodium sulfate at 600 psi of upstream pressure through the PVA membrane were 0.55 m^3/m^2 day and over 99%, respectively. The effects of the ionomers on the permeation properties of the PVA membranes were studied using the PVA–SA and PVA–chitosan blend membranes. The addition of small amount of ionic polymers (5 wt %) made the PVA membranes more effective for the organic solute rejection without decrease in their fluxes. The rejection ratios of the PEG 600 and isopropanol were increased substantially. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1755–1762, 1999

Key words: nanofiltration; poly(vinyl alcohol); ionic polymer; glutaraldehyde; sodium alginate; chitosan

INTRODUCTION

With good physical and chemical properties as a membrane material, poly(vinyl alcohol) (PVA) has been widely used for the preparation of several kinds of membranes for different applications.[1–11] Specifically, PVA has frequently been used for the formation of pervaporation membranes to separate water–alcohol mixtures due to its good hydrophilicity.[6–10] Knowing such good physical and chemical properties, people have

tried to use it for the formation of reverse osmosis (RO) membranes with a good chemical stability as well as high flux and high rejection. However, unfortunately, the performance of the RO membranes based on PVA has not been satisfactory yet. The PVA RO membranes thermally crosslinked have shown very low flux and relatively low salt rejection.[11] According to the Cadotte et al., the flux of the PVA membranes crosslinked via the acetal formation by heat curing was low, and they suggested the following two factors as reasons for the low flux. (1) The first one is that because of hydrogen bonding force, the linear PVA chains could have packed tightly during drying. Most of the crosslinking reaction prob-

ably took place in the later stages of drying, when the densely packed configuration had already been reached. (2) Second, most of the reaction with the aldehyde may have been intermolecular to form essentially a poly(vinyl formal) with only minor interchain crosslinking. Poly(vinyl formal) would probably exhibit low flux because of the softness and excessive creep under compression.[11]

On this basis, two approaches have been made in this study to develop good PVA nanofiltration (NF) membranes, whose permeation properties are in between UF and RO membranes, high rejection of organic solute with low molecular weight, and low rejection of NaCl. For the first, to avoid the close packing and crystallization of the PVA molecules during the thermal crosslinking, as reported by Cadotte, the PVA membranes were crosslinked in a crosslinking solution without heating, using glutaraldehyde as a crosslinking agent. To protect the formation of the crystals after crosslinking, the membranes were kept in distilled water before test. Second, ionomers, such as sodium alginate and chitosan, were considered to be used to improve solute rejection without a decrease in the flux of PVA membranes. Since the ionomers have excellent water affinity due to the ionic character, they have been expected to reject the multivalent ions effectively. In this study, small amounts of sodium alginate and chitosan were blended with PVA for the formation of PVA–SA and PVA–chitosan blend membranes. In this study, homogeneous NF membranes were prepared and used for the study on the relationship between the permeation properties and the chemical properties of the membranes.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (PVA) 99% hydrolyzed with molecular weight of 50,000 g/mol bought from Aldrich Co., and sodium alginate and chitosan from Sigma Co. were used as membrane materials. Na_2SO_4, NaCl, poly(ethylene glycol) with a molecular weight of 600 g/mol (PEG 600), and isopropanol were bought from Tokyo Kasei Co. and used as solutes for permeation tests of the membranes. Glutaraldehyde with a content of 25 wt % bought from Tokyo Kasei Co. was used as a crosslinking agent.

Membrane Formation

Free-standing symmetric homogeneous membranes were prepared by casting the respective polymer solutions, followed by drying at room temperature for 24 h and crosslinking in solution for different times (20, 40, 60, 120, and 240 min). The polymer solutions used were 5 wt % solutions of PVA, PVA–SA (95/5 in wt %), and PVA–chitosan (95/5 in wt %). The polymer solutions contained 5 vol % of glutaraldehyde as a crosslinking agent. The solution used for the crosslinking of the polymer film was an isopropanol–water (90 : 10 in vol %) mixture containing 1 vol % of hydrochloric acid as a catalyst at room temperature. After crosslinking for a certain time, the membranes were kept in distilled water at room temperature for 24 h to remove the glutaraldehyde remaining unreacted in the membranes, and further crosslinking was prevented. Before the permeation tests, membranes were kept in water to prevent crystal formation.

Characterization

The morphology and the chemical structures of the membranes were characterized with X-ray diffractometry (XRD; model D/MAX IIIB Rigaku) and Fourier transform infrared (FTIR) spectroscopy (Bio-Rad, Digilab Division, model FTS-80, FTIR), respectively. Swelling indices of the membranes were measured to obtain relative degrees of crosslinking.

Permeation Test

To test the performances of the membranes, a nanofiltration test set was used. The concentration of feed solutions was 1000 ppm, and the upstream pressure was controlled using back-pressure regulators (100, 200, 300, 400, 500, and 600 psi). All tests were carried out at room temperature. The flux of the membrane was measured by weighing the permeate penetrated through the membrane per unit time (g/min) and solute rejection was obtained from the data from the high-performance liquid chromatography (HPLC) using the following equation;

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

where C_f and C_p are the concentration of the feed solution and permeate, respectively, calculated from the peak area of HPLC.
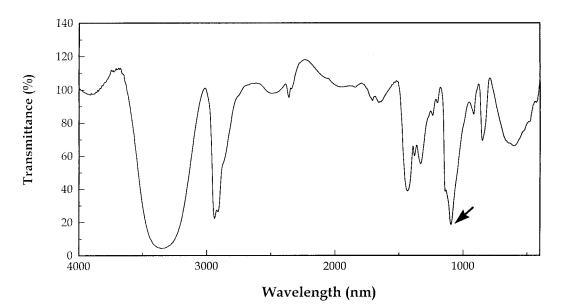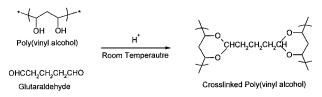
Figure 1   FTIR spectrum of the PVA membrane crosslinked with glutaraldehyde.

RESULTS AND DISCUSSION

Characterization

Fourier Transform Infrared Spectroscopy

Figure 1 presents the FTIR spectrum of PVA membrane crosslinked with glutaraldehyde. The PVA membrane containing 5 vol % of glutaraldehyde as crosslinking agent was crosslinked by dipping into the isopropanol–water (90 : 10 in vol %) mixtures containing 1 vol % of HCl as a catalyst. The crosslinking reaction between the PVA and glutaraldehyde occurred only after the diffusion of the HCl into the membrane in the presence of water from the crosslinking solution because the reaction of the hydroxyl groups of the PVA with aldehyde groups of the glutaraldehyde took place only with the aid of protons (H^+) as catalyst (see Scheme 1). In other words, the crosslinking degree of the PVA membrane was possible to be controlled by adjusting the dipping time in the

Scheme 1   Schematic representation of the crosslinking reaction of the PVA with glutaraldehyde in the isopropanol–water (90 : 10 in vol %) mixtures containing 5 vol % HCl as a catalyst.

crosslinking solution, increasing with increasing dipping time. The acetal linkage was formed from the crosslinking reaction, and its formation was confirmed by the strong C—O—C stretching peak at 1110 cm^{-1} of the FTIR spectrum.

Swelling Test

For the study on the relative crosslinking degree of the membranes, swelling indices of the membranes crosslinked for different reaction time were obtained, as shown in Table I. The swelling index was calculated by using the following equation:

$$\text{Swelling index } (\%) = 100 \times (W_s - W_d)/W_d$$

Table I   Swelling Indices of the Membranes Based on the Poly(vinyl alcohol), Sodium Alginate, and Chitosan

Reaction Time (min)	Swelling Index (%)		
	PVA	PVA–SA[a]	PVA–Chitosan[b]
20	260	partially soluble	partially soluble
40	220	370	360
60	90	—	—
120	70	360	350
240	—	330	330

[a] Composition of PVA–SA = 95 : 5 in wt %.
[b] Composition of PVA–chitosan = 95 : 5 in wt %.

where W_s and W_d were weights of swollen samples and dried samples, respectively.

The swelling indices of the prepared membranes decreased with increasing crosslinking reaction time, indicating that with increasing reaction time, the crosslinking degree increased. From the table I, it seems that the crosslinking reaction rate depends on the membrane composition, especially on the content of ionomers. For instance, the swelling indices of the PVA–SA and PVA–chitosan blend membranes in which the ionomer content was only 5 wt % did not decrease with the reaction time as fast as that of the PVA membrane. The PVA–SA blend membranes showed a swelling index of 330% after crosslinking for 240 min. This slow crosslinking reaction of the PVA–SA and PVA–chitosan blend membranes might be due to the competition between the swelling and crosslinking reaction in the isopropanol–water mixture.

In this study, since the crosslinking of the membranes was carried out in the isopropanol–water mixture containing HCl as a catalyst, the crosslinking reaction started with diffusion of proton (H^+) with water molecules into the membranes. The absorbed protons initiate the crosslinking reaction between —OH groups of the membrane materials and aldehyde groups, while the absorbed water molecules were swelling the membrane. Therefore, the two reactions, crosslinking and swelling, were occurring at the same time. In the case of PVA–SA blend membrane, since the hydrophilicity of the SA was so high, the water absorption rate of the membrane was faster than the crosslinking reaction. Consequently crosslinking reaction should be proceeded after the membrane swelled pretty much. The swelling reaction induced the increase of intermolecular distances of the membrane material so that the distance between the —OH groups in different molecules that should be involved in the crosslinking reaction became longer. The longer distance between —OH groups in the swollen state was unfavorable for the crosslinking reaction and eventually the crosslinking reaction of the blend membranes was relatively slower than
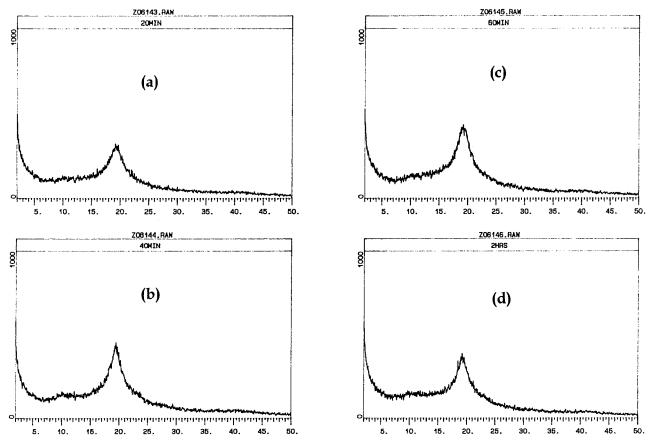

Figure 2 X-ray diffractograms of PVA membranes in a dry state crosslinked for different periods of time: (a) 20, (b) 40, (c) 60, and (d) 120 min.
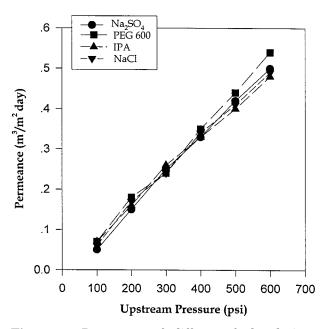
Figure 3 Permeance of different feed solutions through the PVA membrane crosslinked for 20 min as a function of upstream pressure.

that of PVA membrane. As results, the swelling indices of those two membranes crosslinked for the same reaction time were larger than that of PVA membrane.

X-ray Diffraction

The microstructures of the PVA membranes crosslinked under different conditions were studied with XRD. In this study, dried samples and swollen samples with thickness of 20 μm were used. Figure 2 presents the XRD patterns of crosslinked, dried PVA membranes.

All dried PVA membranes showed very similar XRD patterns and appeared to be semicrystalline, despite their different degrees of crosslinking. All the XRDs showed broad peaks at around 10° of 2θ, indicating the average intermolecular distance of the amorphous part and relatively sharp semicrystalline peaks centered at around 20° of 2θ. From this result, one can find that average intermolecular distances of the PVA membranes are almost the same, in spite of the different degrees of crosslinking. This result suggests that the differences of the average intermolecular distances of the PVA membranes with different degrees of crosslinking are not large enough to be detected by the XRD.

Permeation Test

The permeation properties of the prepared membranes were tested with aqueous solutions con-

taining 1000 ppm of solutes, such as sodium sulfate, sodium chloride, PEG 600, and isopropanol.

PVA Membrane

The physical properties of the PVA membranes crosslinked with glutaraldehyde, as explained above, were dependent on their crosslinking degrees. As the crosslinking degree increased, the rigidity of the membrane increased. After 1 h of crosslinking, the membrane became rigid, and cracks developed on the membrane during the permeation test at about 400 psi. Therefore, to avoid this problem, membranes with 260% of swelling index crosslinked for 20 min were used for permeation tests. The membranes, after crosslinking, were kept in distilled water for swelling and for protection of crystal formation. The thickness of the dried membranes was about 10 μm.

Figures 3 and 4 show the permeances and the rejection ratios of the PVA membranes, respectively. The permeance of 1000-ppm Na_2SO_4 feed solution was about 0.07 m^3/m^2 day at 100 psi of the pressure and increased almost linearly up to 0.55 m^3/m^2 day as the pressure increased to 600 psi. The permeances as a function of upstream pressure were almost independent to the feed solution species and almost the same at the same pressures. Those permeances obtained through the PVA membranes crosslinked in the solution
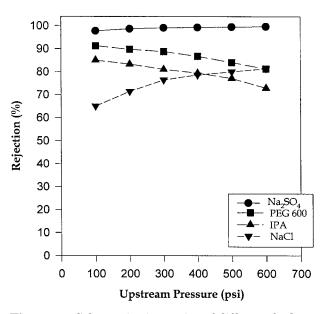

Figure 4 Solute rejection ratios of different feed solutions through the PVA membrane crosslinked for 20 min, as a function of upstream pressure.
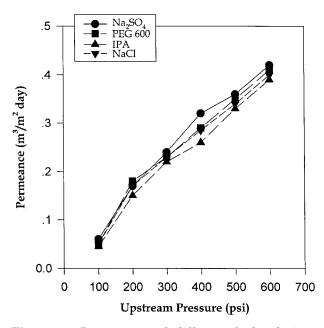
Figure 5 Permeances of different feed solutions through the PVA–SA (95 : 5 in wt %) blend membrane crosslinked for 40 min as a function of upstream pressure.

without heating appeared to be much higher than those obtained through the thermally crosslinked PVA membranes published in the article.[11] The higher permeances of these membranes would be mainly attributed to the different crosslinking method. Crosslinking in the solution at room temperature rather than thermal crosslinking prevented the membranes from the crystal formation and dehydration reaction of PVA molecules, resulting in the higher permeances compared to the thermally crosslinked PVA membranes.

The solute rejection ratios depended strongly on the feed solutions, as shown in Figure 4. For the sodium sulfate, the rejection ratios were high and almost above 99% over 100 to 600 psi of pressures. On the other hand, the rejection ratios of sodium chloride were relatively low and ranged from 65 to almost 80%, increasing with increasing pressure. The increasing rejection ratios of inorganic salts with increasing pressures were as usual as the case of general reverse osmosis membranes. It was also found from the high rejection ratios of the multivalent ions, such as SO_4^{-2}, and low rejections of monovalent ions, such as Cl^{-1}, that the surfaces of these membranes had anionic character, which could be explained by the Donnan exclusion.

The rejection ratio behaviors of the organic solutes, such as PEG 600 and isopropanol, were dif-

ferent from those of the inorganic salts. The rejection ratios of PEG 600 ranged from 80 to 90% and decreased with increasing pressure. For the isopropanol solution, the rejection ratios ranged from 70 to 85% and decreased with increasing pressure. The relatively low rejection ratios of the organic solutes, compared with those of the inorganic salts, were due to the better chemical affinity of the membrane material with the organic solutes than the inorganic salts. The better affinity with the membrane material made the organic solutes able to approach the membrane surfaces more easily, and then the concentrations of them near the membrane surfaces would be higher than in the bulk of the feed solutions, which was responsible for the low rejection ratios of the organic solutes. The decreasing rejection ratios of organic solutes with increasing pressure also could be explained by the same way with better affinity of the organic solutes with the membrane material. The high operation pressure could be favorable for the solutes to approach the membrane surface and to penetrate the membrane easily.

PVA–Sodium Alginate (SA) Blend Membrane

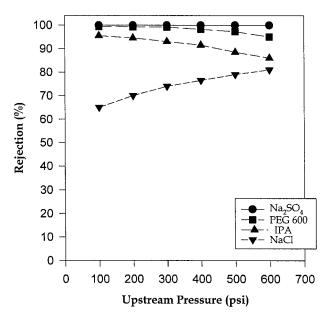To study the effect of the anionic ionomer on the permeation properties of the PVA membrane, the

Figure 6 Solute rejection ratios of different solutions through the PVA–SA (95 : 5 in wt %) blend membrane crosslinked for 40 min as a function of upstream pressure.
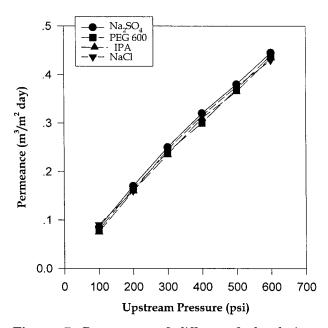
Figure 7 Permeances of different feed solutions through the PVA–chitosan (95 : 5 in wt %) blend membrane crosslinked for 40 min as a function of upstream pressure.

PVA–SA blend membranes containing 5 wt % of SA were used. The PVA–SA blend membranes were crosslinked for 40 min in the crosslinking solution and showed 370% of the swelling index. The thickness of the dried blend membranes was about 10 μm.

Figures 5 and 6 exhibit the permeances and rejection ratios through the PVA–SA blend membrane. The permeances increased with increasing pressure from 0.06 (at 100 psi) to 0.43 m^3/m^2 day (at 600 psi). The permeances as a function of upstream pressure were almost same, regardless of the different feed solutions as in the case of PVA membranes. However, the rejection ratios varied with different solutes. For sodium sulfate and sodium chloride, the rejection ratios increased gradually with increasing pressure. For sodium sulfate, they were above 99% at all the pressures. For sodium chloride, they increased from 65 to 80% with increasing pressures from 100 to 600 psi. On the other hand, the rejections of PEG 600 and isopropanol decreased with increasing upstream pressures. The rejection ratio of PEG 600 varied from 95 to 98% and that of isopropanol from 86 to 95% with increasing pressure. Compared to the PVA membrane, the PVA–SA blend membranes showed higher solute rejections with the aid of SA. Specifically, the organic solute rejections increased substantially.

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 a small amount of SA. Since the ionic surfaces of the PVA–SA blend membranes had relatively lower affinity with the organic solutes than the PVA membranes, the solute rejections of those membranes were relatively higher. However, the tendency of the solute rejections as a function of upstream pressure through the blend membranes was approximately the same as in the case of the PVA membranes.

PVA–Chitosan Blend Membrane

The effects of cationic ionomer on the PVA membranes were studied with PVA–chitosan blend membranes. The PVA–chitosan blend membranes containing 5 wt % of chitosan and crosslinked for 40 min were used. They had 360% of the swelling index. The thickness of the dried membranes was about 10 μm.

Figures 7 and 8 present the permeances and rejection ratios through the PVA–chitosan blend membranes. The permeances were in the range from 0.08 to 0.45 m^3/m^2 day with increasing upstream pressure from 100 to 600 psi. The permeances were almost same, regardless of the different feed solutions as the other membranes. The rejection ratios, however, depended on the
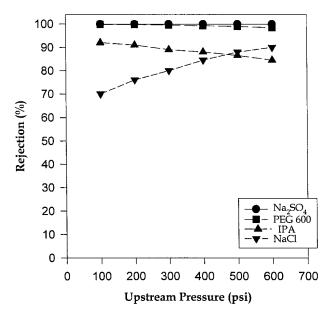

Figure 8 Solute rejection ratios of different feed solutions through the PVA–chitosan (95 : 5 in wt %) blend membrane crosslinked for 40 min as a function of upstream pressure.

feed solutions. For sodium sulfate and sodium chloride, the rejection ratios increased gradually with increasing pressures. For sodium sulfate, they were above 99% at all the pressures. For sodium chloride, they increased from 70 to 88% with increasing pressures. On the other hand, the rejection ratios of organic solutes, such as PEG 600 and isopropanol, decreased with increasing pressures. The rejection ratio of PEG 600 was about 98% at all the pressures, and that of isopropanol ranged from 82% to 90%. From these results, it is found that the chitosan (cationic ionomer) also improved the organic solute rejection of the PVA membrane as effectively as the anionic ionomer did.

From the permeation study, it is found that the membranes based on the PVA and ionomers show nanofiltration properties very well.

CONCLUSIONS

The PVA membranes and the PVA–ionomer blend membranes for nanofiltration can be prepared by casting the respective polymer solutions, followed by drying at room temperature and crosslinking with the glutaraldehyde. The crosslinking of the membranes containing 5 wt % of glutaraldehyde as a crosslinking agent can be done by dipping in the isopropanol–water (90 : 10 in vol %) mixture with 1 vol % of hydrochloric acid as catalyst. The crosslinking degrees of the membranes are able to be controlled by adjustment of the reaction time. The difference in the intermolecular distances of the membranes with different crosslinking degrees is not large enough to be measured by XRD. The permeances through the PVA membranes, crosslinked in the crosslinking solution, are higher than those through the PVA membranes crosslinked by heating in dry states. The membranes based on the PVA and ionomer appear to show nanofiltration properties. The permeances are not dependent on the feed solutions, while the rejection ratios of the membranes seem to depend on the solute species and the chemical property of the membrane surface as well as the crosslinking degree of the membrane. Incorporation of small amount of ionomer into PVA membrane appears to be good for the rejection of organic solutes such as PEG 600 and isopropyl alcohol.

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