NOTE

Chitosan Membranes Crosslinked with Sulfosuccinic Acid for the Pervaporation Separation of Water/Alcohol Mixtures

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INTRODUCTION

Hydrophilic polymer membranes have been widely used for dehydration of alcohol solutions by pervaporation.¹⁻⁹ Polysaccharides, consisting of relatively rigid backbone structure and ionic side groups, have been used very often and have shown good membrane performance. Chitosan is one of the polysaccharides and consists of a six-membered ring structure backbone and amine side groups. The chitosan has also been used by a few researchers to form pervaporation membranes for the separation of water/alcohol mixtures. Mostly, they insolublized the chitosan membranes by dipping them into a NaOH solution or by neutralizing them with sulfuric acid.⁸ Although the chitosan membranes made as previously described had shown good performance in the dehydration of alcohol solutions, we came to think that bulky and hydrophilic crosslinking agents other than sulfuric acid would be better for the formation of chitosan membrane. The bulky crosslinking agent is favorable for the formation of membranes with more free volume, resulting in higher fluxes, whereas crosslinking with small size crosslinking agents decreases the free volume and results in the decrease in the flux. Hydrophilicity of the crosslinking agent is also expected to be important for the membrane, because that affects the hydrophilicity of membranes. For instance, when the crosslinking agent, consisting of long hydrophobic alkyl chains without hydrophilic groups, is used, the resulting membrane becomes less hydrophilic after crosslinking. In many cases, the polysaccharide membranes became less hydrophilic by crosslinking with general organic crosslinking agents, such as glu-

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taraldehyde, and the resulting membranes showed lower permselectivity.

On this basis, it can be suggested that the bulky crosslinking agent with strong hydrophilicity be good for the chitosan membrane, and we chose sulfosuccinic acid (SSA) as a crosslinking agent for this study. It has three crosslinkable sites (two carboxylic acid groups and one sulfuric acid group) and a relatively bulky chemical structure. The three acidic groups will be good for ionic crosslinking with chitosan molecules and also good for keeping the membrane hydrophilic. In this study, the chitosan membranes crosslinked with SSA were prepared and characterized with Fourier transform infrared (FTIR) spectroscopy and X-ray diffractometry. For the study on permselective properties, three different kinds of alcohol solutions (methanol, ethanol, and isopropanol) were used.

EXPERIMENTAL

Materials

Chitosan, purchased from Sigma Co., and SSA and hydrochloric acid, purchased from Aldrich, were used for the formation of membranes. Acetone, methanol, ethanol, and isopropanol, purchased from Merck Co., were used for the permeation test.

Preparation of Membranes

Chitosan membranes were prepared by casting 2 wt % aqueous solution of chitosan, prepared by dissolving 2 g of chitosan into 100 mL of distilled water containing 2 mL of acetic acid, followed by drying at room tempera-

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Figure 1 FTIR spectrum of the chitosan membrane crosslinked with SSA.

ture for 24 h. Chitosan membranes with 10 μ m thickness were kept in the methanol solution containing 2 mol % of SSA as a crosslinking agent for 10 h and dried at room temperature for crosslinking of the membranes. They were kept in the feed solutions for 10 h before use for the pervaporation test.

Characterization

FTIR Spectroscopy. Chemical structures of the chitosan membrane crosslinked with the SSA were characterized by using an infrared spectrophotometer (model: Bio-Rad, Digilab Division FTS-80; FTIR). Thickness of the chitosan membrane was $\sim 10 \ \mu$ m.

X-ray Diffractometry. Morphologies of the chitosan membranes under different crosslinking conditions were studied with an X-ray diffractometer (model: D/MAX IIIB Rigaku) using nickel-filtered Cu-K α radiation with wavelength of 1.54 Å. Sample thickness was $\sim 20 \ \mu$ m.

Pervaporation Measurement

Pervaporation measurements were conducted by using a general pervaporation test cell, purchased from Millipore Co. The membrane surface area and downstream pressure were 11.28 cm^2 and 0.3 mm Hg, respectively. Feed solutions used were as follows: water/ethanol mixtures (10/90/, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, and 90/10, in wt %), 80 wt % methanol solution, and 80 wt % isopropanol solution. The volume of the feed solution was 1 L to ensure that the change of the feed composition was negligible during the pervaporation experiment. Pervaporation tests were conducted at different operating temperatures. Total flux through the membrane was measured by weighing the liquid mixtures collected in the sampling test trap. The partial flux and permeate vapor composition were determined by analysis of the condensed permeate, using a gas chromatograph (Perkin-Elmer 8500). The separation factor was defined as follows:

$$\alpha = (W_{\rm H2O}/W_{\rm alcohol})_{permeate}/(W_{\rm H2O}/W_{\rm alcohol})_{feed}$$

where $W_{\rm H2O}$ is the weight fraction of water, and $W_{\rm alcohol}$ is the weight fraction of alcohol.

RESULTS AND DISCUSSION

Characterization

FTIR Spectroscopy. The FTIR spectrum of the chitosan membrane crosslinked with SSA is shown in Figure 1. The chitosan membrane was crosslinked *via* ionic bond formation between the acidic groups of SSA and amine groups of chitosan, as shown in Scheme 1. From Figure 1, the $S(=0)_2$ stretch peak and C=0 stretch peak from SSA appeared at 1250 cm⁻¹ and 1750 cm⁻¹, respectively. A broad NH₃⁺ peak, indicating ionic bond formation, is shown at 2,200–2,000 cm⁻¹.

Wide Angle X-ray Diffractometry. Figure 2 shows the X-ray diffractograms of the chitosan membranes, crosslinked with SSA or just neutralized with HCl. These X-ray diffractograms show the dependence of the membrane morphology on the different kind of chemical agents associated with chitosan. The two kinds of chitosan membranes seemed to be semicrystalline, but with different crystallinities. Crystallinity of the membrane crosslinked with SSA was 5.9%, whereas that of the membrane neutralized with HCl was 8.9%, thus indicating that SSA with the bulky structure was favorable for the formation of more amorphous chitosan membranes. Also, the intermolecular distance of the amorphous part of the chitosan membrane crosslinked with SSA seemed to be longer than that of the membrane



Scheme 1 Schematic representation of the crosslinking reaction of chitosan with SSA.



Figure 2 X-ray diffraction patterns of chitosan membranes (A) crosslinked with SSA (B) and neutralized with hydrochloric acid.

with HCl. These results suggest that a bulky crosslinking agent, such as SSA, be good to make the chitosan membrane with loose molecular packing, which will be good for high flux in the pervaporation process.

Permeation Test

Effect of Feed Solutions. Figures 3 and 4 represent the total fluxes and separation factors toward water through the chitosan membranes, crosslinked with SSA, for different feed solutions [methanol/water mixture (80/20 wt %), ethanol/water mixture (80/20 wt %),

and isopropanol/water mixture (80/20 wt %)]. From Figures 3 and 4, it is found that, as the operation temperature increases, the total fluxes increase whereas separation factors decrease. The behaviors of fluxes and separation factors as a function of temperature are as usual as the case of hydrophilic membranes in the separation of water/alcohol mixtures. However, the interesting point found herein is the high flux and high separation factors, compared with the result obtained through the chitosan membrane crosslinked by





Figure 3 Fluxes for different kinds of feed solution through the chitosan membrane crosslinked with SSA.

Figure 4 Separation factors for different kinds of feed solution through the chitosan membrane cross-linked with SSA.

Membrane	Temperature (°C)	$\begin{array}{c} Feed \\ (H_2O \ wt \ \%) \end{array}$	$\begin{array}{c} Q \\ (\text{kg m}^{-2} \text{ h}^{-1}) \end{array}$	α	Ref.
PVA (GFT)	80	5	0.01	9,500	10
CMC (Na ion)	30	10	0.052	2,430	11
PAA/polyion complex	60	5	1.63	3,500	12
Chitosan	60	10	0.1	6,000	13
Polyimide	75	10	0.01	850	14
Chitosan					
(crosslinked with					
SSA in this study)	60	20	0.45	9,000	

Table I Pervaporation Performances of Representative Membranes for the Water/Ethanol System

PVA, poly(vinyl alcohol); CMC, carboxymethylcellulose; PAA, poly(acrylic acid).

other crosslinking agents than SSA (see Table I; refs. 10-14 cited therein). For instance, at 70°C, the total flux of the aqueous isopropanol solution was > 1.7 kg $(m^{-2} h^{-1})$. For aqueous ethanol and methanol solutions, that was $0.54 \text{ kg} (\text{m}^{-2} \text{ h}^{-1})$ and $0.3 \text{ kg} (\text{m}^{-2} \text{ h}^{-1})$, respectively. Also, the separation factors at the same operation temperature for different feed solutions were as follows: infinity for the isopropanol solution, 8,000 for the ethanol solution, and 50 for the methanol solution. These pervaporation properties of the chitosan membrane crosslinked with SSA are found to be better than those of the chitosan membranes reported earlier.⁸ The good performances of this membrane may have a strong relationship with chemical and physical properties of the SSA. One can confirm from the high separation factors that the strong hydrophilicity of the SSA affect positively on the membrane to keep good hydrophilicity. Also, the high fluxes confirm indirectly that the free volume of the membrane is relatively large due to the bulky SSA structure.

Figure 5 shows the total flux and separation factor at 40°C through the membrane as a function of the composition of the water/ethanol mixture. As the ethanol content in feed solution increases, the total flux decreases gradually, whereas the separation factor shows a maximum at 80 wt %. From this result, one can find that this membrane shows good performance for the wide range of feed compositions. This membrane shows good pervaporation performance not only at high ethanol content (such as 80 wt %), but also at low ethanol content (such as 10–40 wt %). Interestingly, this membrane shows a particularly low ethanol content in permeate for low ethanol content feed solutions. It was < 0.5 wt %, even though the total flux was very high, whereas that of other membranes (such as the



Figure 5 Permeation properties through the chitosan membrane as a function of ethanol content in feed solutions. EtOH = ethanol.



Figure 6 Effect of ethanol content in feed solution on the pervaporation properties of the chitosan membrane crosslinked with SSA.



Figure 7 Effect of aging on the pervaporation properties of the chitosan membrane crosslinked with SSA.

polyvinyl alcohol membrane and the polyion complex membranes) was > 5 wt %. For high ethanol content solutions, when the feed solution was 80 wt %, the flux was 145 g (m⁻² h⁻¹), and the separation factor was 15,000. The relatively lower ethanol content in the permeate with high flux, compared with other membranes, may be due to the high hydrophilicity of the membrane.

Effect of Aging. The chitosan membrane crosslinked with SSA showed the aging effect as shown in Figures 6 and 7, like the other polysaccharide membranes.⁹ The aging effect of the membrane was studied through observation of the variation of permselective properties with the aging processes. The flux and separation factor through the membrane were measured for 4 days with aging steps between the runs of the pervaporation test. Details of the aging experiment were as follows; after loading the dried membrane on the test cell, pervaporation separation of water/ethanol was conducted with increasing operation temperature from 40°-70°C. Afterward, the membrane was left in the test cell with one side contacted with feed solution and the other with atmosphere for 12 h for aging. After that, pervaporation was conducted under the same condition as the first test and again for the second test. This process was repeated two more times to see the aging effect of the membrane.

As shown in Figures 6 and 7, with repeating runs of the test, the flux decreased and separation factor increased. After the first aging step, the flux and separation factor changed substantially, while not changing much after the second aging step. From this result, one can assume that something happens in the membrane by the aging process. Therefore, the membrane was characterized with X-ray diffractometry before and after the aging process to study if the membrane morphology changed by the aging. However, there was no difference in the X-ray diffractograms of the membrane, which indicate that there was no morphological change, such as development of crystals in the membrane. The effect of aging then has to be explained by the relaxation of the chitosan molecules, as published before from our group.9 From this result, it can be suggested that the decrease in flux and an increase in the separation factor by the aging process resulted from the decrease in the free volume of the membrane due to the relaxation of the molecules by aging.

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