Preparation and Characterization of Crosslinked Sodium Alginate Membranes for the Dehydration of Organic Solvents

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Abstract: In recent years, an increasing interest in membrane technology has been observed in chemical and environmental industry. Membrane technology has advantages of low cost, energy saving and environmental clean technology comparing to conventional separation processes. Pervaporation is one of new advanced membrane technology applied for separation of azeotropic mixtures, aqueous organic mixtures, organic solvent and petrochemical mixtures. Sodium alginate composite membranes were prepared for the enhancement of long-term stability of pervaporation performance of water-ethanol mixture using pervaporation. Sodium alginate membranes were crosslinked with $CaCl_2$ and coated with polyelectrolyte chitosan to protect washing out of calcium ions from the polymer. The surface structures of PAN and hydrolysed PAN membrane were confirmed by ATR Fourier transform infrared (FT-IR). A field emission scanning electron microscopy (FE-SEM; Jeol 6340F) operated at 15 kV. Concentration profiles for Ca in the membrane surface and membrane cross-section were taken by an energy dispersive X-ray (EDX) analyser (Jeol) attached to the field emission scanning electron microscopy (Jeol 6340F). Pervaporation experiments were done with several operation run times to investigate long-term stability of the membranes.

Keywords: pervaporation, sodium alginate, chitosan, ethanol, self diffusion coefficient

1. Introduction

When organic solvent is used in chemical process, high purification is essential. There are several methods that can be used in separation of liquid mixtures: 1) membrane permeation, 2) simple distillation, 3) azeotropic/extractive distillation, 4) liquid-liquid extraction, 5) stripping, 6) adsorption and 7) melt crystallization. Pervaporation has received much attention as an efficient separation technique for organic mixtures, especially for dehydration from aqueous organic mixtures. In the cases of separation of high boiling point compounds mixtures, azeotropic mixtures and heat sensitive mixtures, pervaporation is preferred to simple distillation process[1]. For an advantage of energy savings and elimination of entrainer, pervaporation is now available commercially to separate the ethanol-water azeotrope.

Since an American Oil Company invented polyethylene-based pervaporation membrane, many researchers have studied in pervaporation membrane. As membrane research has been developed to make hollow fiber and composite membrane, separation of aqueous

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MM : Manuronic acid block
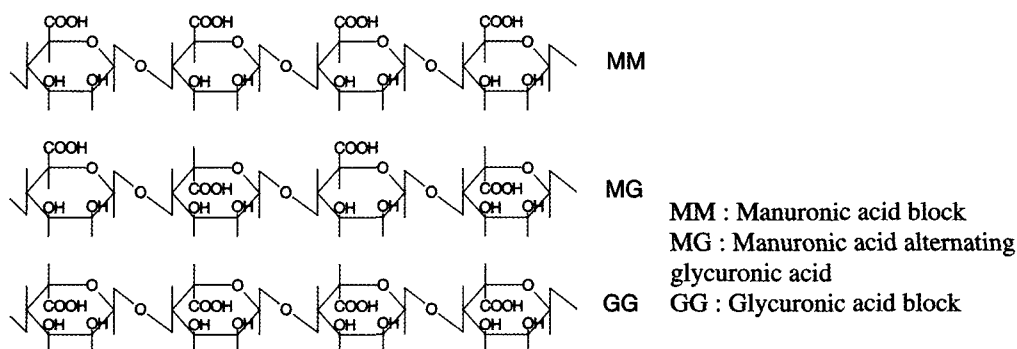MG : Manuronic acid alternating glycuronic acid
GG : Glycuronic acid block

Fig. 1. Chemical structures of sodium alginate.

organic mixture has been focused on. Indeed, poly (vinyl alcohol)-based pervaporation membrane was invented by GFT company in Germany and it came true to dehydrate organic solvent or its mixture.

Sodium alginate (SA), which is a highly hydrophilic natural polymer obtained from seaweeds, has recently aroused a great interest in view of its industrial and biomedical applications. Three kinds of repeating structures for SA are shown in Figure 1.

G. Golemme et al.[2] has been studied sodium alginate dense and composite membranes for the separation of water/ethanol mixtures using pervaporation. Sodium alginate membranes was modified through ion exchange of sodium with multivalent metal ions and their permselectivities have been tested for the water-ethanol mixture.

C.K. Yeom et al.[3] investigated long-term stability of sodium alginate reverse osmosis membrane using protective polyelectrolyte complexes formed at the membrane surface. They reported the polyelectrolyte complex layer between sodium alginate and chitosan in the complex membrane is a protective covering of the crosslinked interior layer without affecting membrane performance, protecting the inside of the membrane from washing out the divalent ion, Ca^+ by feed flow.

In this study, two kinds of sodium alginate composite membranes have been prepared to investigate long-term stability of sodium alginate membranes for the pervaporation separation of water-ethanol mixtures. In order to enhance the long-term stability of sodium alginate membrane, polyelectrolyte complex protective layer

between chitosan and sodium alginate was adopted. Pervaporation performance of water-ethanol mixtures through two kinds of sodium alginate membranes with different crosslinking method with several run have been investigated.

2. Experimental

Sodium alginate mixed manuronic acid and glycuronic acid unit was purchased from Fluka. PAN UF membrane for preparing the composite membrane was purchased from GKSS. Ethanol was supplied by Merck (Darmstadt, Germany). Calcium chloride and chitosan were purchased from Aldrich. Ultrapure deionized water was used. All chemicals were used without any further purification. A PAN UF membrane was hydrolized in 1 N NaOH aqueous solution to enhance adhesion between sodium alginate and PAN UF membrane and to promote pervaporation performance at 60°C for 15 min, and then transferred into deionized warm water to continue the hydrolytic reaction until the brown color disappeared. Sodium alginate solution was prepared by dissolving 2 wt% sodium alginate powder into deionized water. Then they were cast onto hydrolized PAN UF membrane using casting knife and dried in a fume hood for 24 h. After drying, the membrane were cross-lniked by $CaCl_2$ aqueous solution and $CaCl_2$/chitosan aqueous solution for 10 min. The concentration of $CaCl_2$ in the crosslinking solutions was fixed 0.05 M. pH of the $CaCl_2$/chitosan solution was adjusted at 5.4 with 0.1 M NaOH.
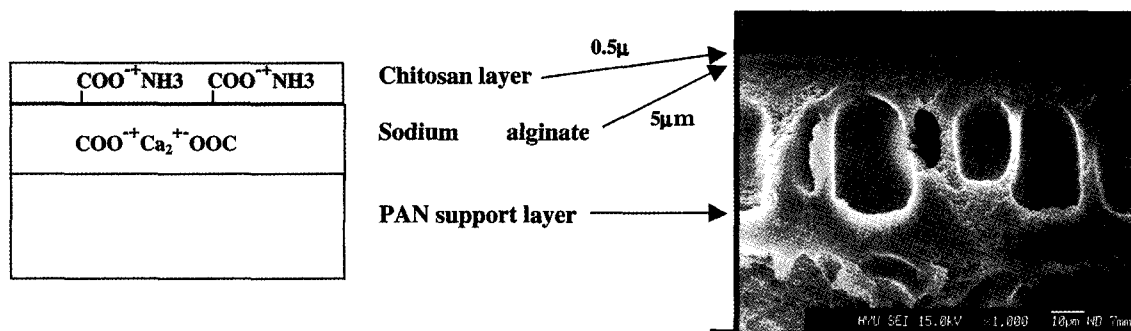
Fig. 2. Cross-section of SA composite membrane coated with diluted chitosan.

Equipment used to conduct pervaporation experiments is described in previous paper[1]. Effective membrane area in contact with feed liquid is about 180 cm^2 and the volume of feed chamber is 3 L. Downstream pressure was maintained below 3 mbar. The permeate was condensed and collected in a cold trap immersed in liquid nitrogen, and the flux was determined from the amount of permeate sample collected for a given time. Separation analysis was carried out by Hewlett-Packard Gas Chromatography equipped with a column packed with Porapak-Q and with thermal conductivity detector.

PFG-NMR measurement in the sodium alginate membranes were carried out only with a Bruker AM 300 NMR spectrometer. The self-diffusion coefficients were determined using the PFGLED sequence. The interval D was fixed at 60 ms, while the intervals t1 and t_e between the rf 90° pulse were fixed to 49.5 and 100 ms, respectively. The magnetic field pulses duration (d) is kept constant and equal to 5 ms, while the magnetic field gradient intensity was varied in the range of 0-25 G/cm[5].

3. Results and Discussion

Yeom et al.[4] reported reverse osmosis preparation method to enhance long term stability of SA membrane. Because of washing out effect of cation in SA membrane, in order to increase long term stability, they used polyelectrolyte, chitosan which has amine groups in main chain. Calcium cation crosslinked SA

membrane can be slightly coated polyelectrolyte and then the coated layer can lessen washing out of the calcium ions out of membrane. Consequently, SA membrane has good long term stability. We also prepapred sodium alginate membrane according to that method. In this method, calcium chloride was used to make a ionic crosslinking between carboxylic groups in sodium alginate polymer chains and chitosan-sodium alginate polyelectrolyte complex layer was coated to prevent from washing out of calcium cations from the sodium alginate membrane during operation of pervaporation experiments.

Figure 2 shows suggested structure and SEM photograph of cross-section of SA composite membrane coated with diluted chitosan. SA layer coated onto PAN support ultrafiltration membrane has less 5 μm thickness and chitosan/alginic acid polyelectrolyte complex layer is shown less 0.5 μm thickness.

Membrane surface was characterized with FE-SEM and FT-IR. Figure 3 shows FE-SEM photographs of SA composite membrane and SA composite membrane coated chitosan, respectively and illustrates the ATR-FT-IR spectra of the membranes. Membrane surface was changed to rough and amide peak of the chitosan was revealed after treating of diluted chitosan solution onto the surface of SA composite membrane. The change of surface characteristics of the membrane can be explained by the ratio Ca/C. The ratio was changed 0.25 to 0.015. It means sodium crosslinked SA surface is coated thin chitosan/alginic acid polyelectrolyte complex layer.

$$\frac{Ca}{C} = 0.25$$

$$\frac{Ca}{C} = 0.015$$

SA crosslinked
with CaCl₂

SA crosslinked
with CaCl₂ and chitosan

-COONa
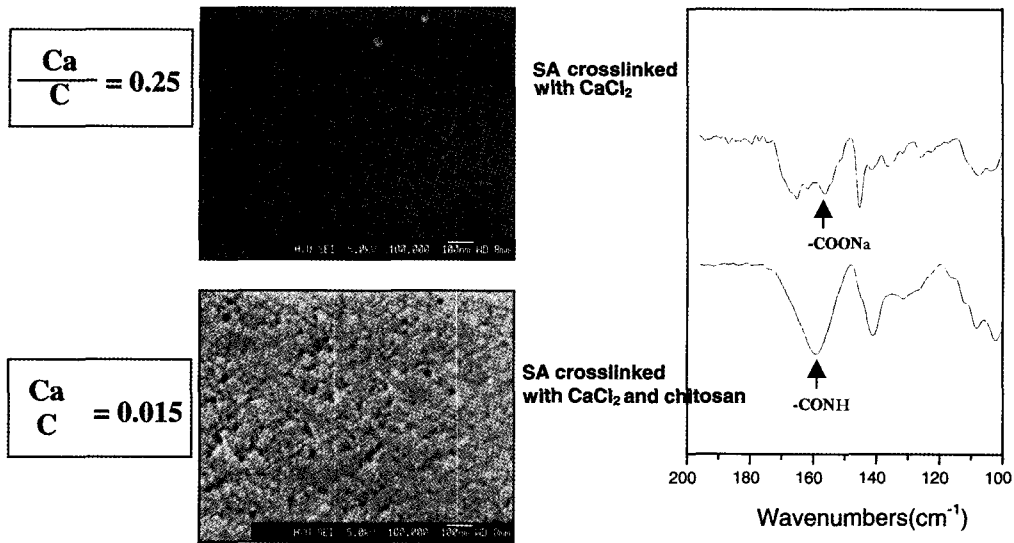
-CONH

Wavenumbers(cm⁻¹)

Fig. 3. FE-SEM photographs and ATR-FT-IR spectra of SA and SA coated with chitosan membranes.

It is reported that pervaporation performance with sodium alginate membranes showed flux and selectivity decline trend in continuous experiment[6]. This phenomena were explained that relaxation of carbohydrate polymer and sweeping out of anions from the membrane. In order to enhance long-term stability of the sodium alginate membrane, we have suggested three ways to modify polymer structure: (1) synthesizing a polymeric materaisl that contains both negative and positive charges on group covalently linked; (2) substituting univalent ions with multivalent species; (3) making a polyelectrolyte complex membranes that has a good separating performance. We already reported pervaporation performance of sodium alginate membrane crosslinked with several multivalent cation according to second method. In this study, combination of second and third method has been used to enhance the stability of the sodium alginate membrane.

Figure 4 shows the effect of feed concentration on pervaporation performance for water/ethanol mixtures through the membrane. As the feed water concentration increases, separation factor decreases which the permeation flux increases. The result of increaing separation factor with feed ethanol concentration, indicated that the SA membrane is permselective to water in the full feed concentration range for experiment[7].
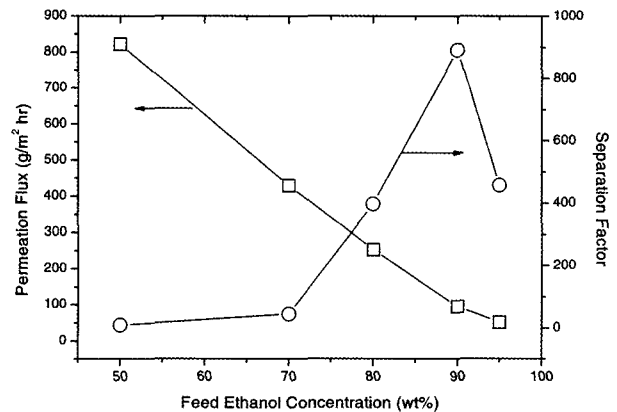

Fig. 4. Effect of feed ethanol concentration on pervaporation performance of water/ethanol mixtures through SA composite membrane.

The effect of operating temperature on pervaporation performance of the SA membrane for 95% water/ethanol mixtures is shown in Figure 5. As the feed temperature increased, the permeate flux also increased and the separation factor decreased. This behavior can be explained with difference in diffusion of the permeating components. At high feed operating temperature, chain mobility in SA membrane is enhanced and ethanol and water molecules can penetrate into the SA chains easily. With increasing operating temperatures, separation factor decreases and the permeation flux increases.
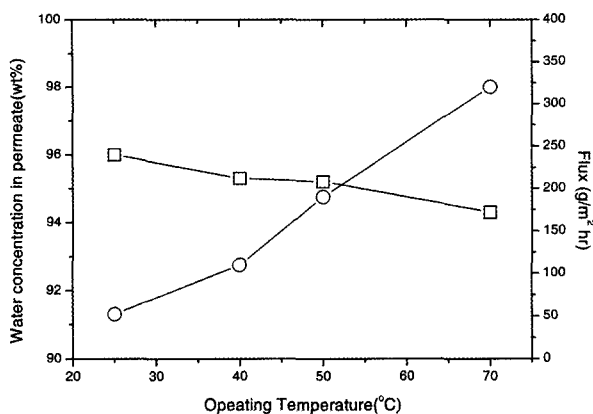
Fig. 5. Effect of operating temperatures on pervaporation performance of 95% water/ethanol mixtures through SA composite membranes.

Yeom et al.[4] reported reverse osmosis preparation method to enhance long term stability of SA membrane. Because of washing out effect of cation in SA mem-

brane, in order to increase long term stability, they used polyelectrolyte, chitosan which has amine groups in main chain. Calcium cation crosslinked SA membrane can be slightly coated polyelectrolyte and then the coated layer can lessen washing out of the calcium ions out of membrane. Consequently, SA membrane has a good long term stability.

Figure 6 shows pervaporation performance of water-ethanol mixture through SA composite membrane at an operating temperature of 70°C. In the pervaporation experiments, as the feed ethanol concentration increases, the permeation flux decreases. In Figure 6, permeation flux decreased and feed ethanol concentration increased with operating time, respectively. In order to investigate long-term stability of SA composite membrane, pervaporation experiments of each membranes are done with 3 times. At every run, pervaporation performance
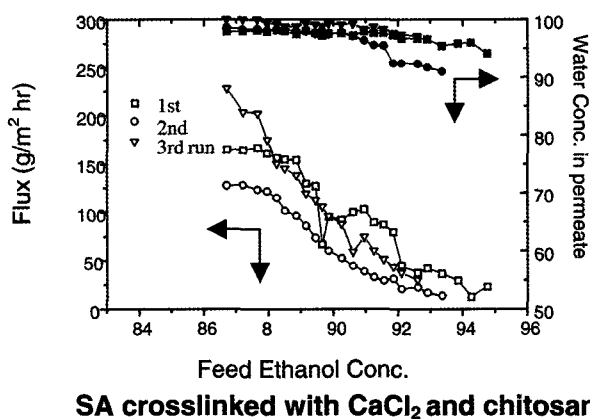

SA crosslinked with CaCl₂   SA crosslinked with CaCl₂ and chitosan
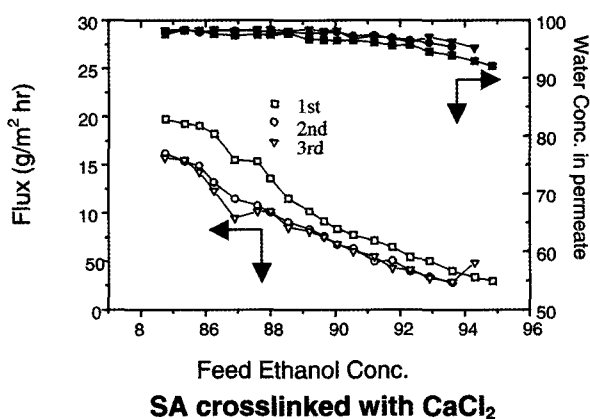
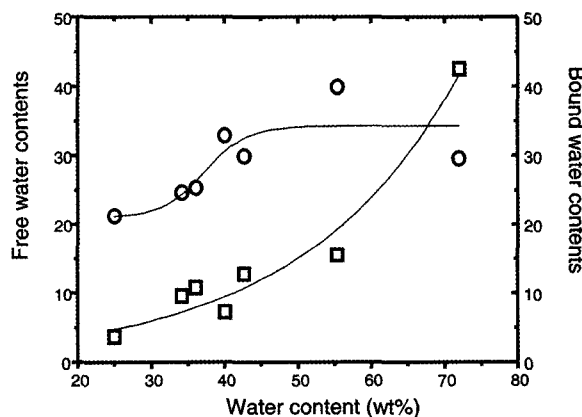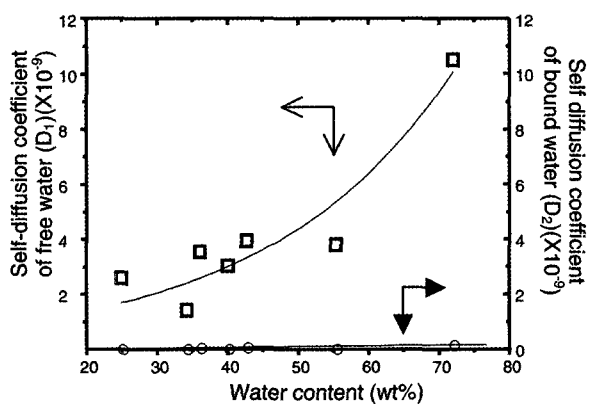Fig. 6. Pervaporation performance of SA and SA coated with chitosan membranes.

Fig. 7. Self diffusion characteristics of the SA membranes.

of the membranes showed similar trends of permeation flux.

In order to selective peremation of water molecule through SA membrane using pervaporation, self diffusion coefficient was calculated using NMR. Sodium alginate membrane crosslinked with glutaraldehyde has two different diffusion channels with different self-diffusion coefficients which represents free water and bound water state in the membranes. Free water has a restricted site bound to specific groups in the sodium alginate chains and free water showed similar trends to that of total swelling of water molecules. Figure 7 shows the self diffusion characteristics of the SA membranes. Self diffusion coefficient of the water molecules in the aqueous ethanol solution increased with increasing water content and free water content also increased with increaing water content. It means that self diffusion coefficient of the water molecules is affected by free water content in the membrane.

4. Conclusions

Sodium alginate composite membrane crosslinked with CaCl$_2$ and chitosan to separate water molecules from organic solvent was prepared. The membrane showed good dehydration performance for the separation of water/ethanol mixture and chitosan layer on active layer protects sweeping out of calcium ions from the membrane. Eventually, sodium alginate composite membrane crosslinked with chitosan enhanced long term stability of pervaporation experiments.

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