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Development of Polymeric Hybrid Gel Membranes for the Separation of Organic Mixtures

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1. Introduction

In recent studies, the hydrophilic zeolite membranes are successful in removing water from mixture with methanol or ethanol by using pervaporation and vapor permeation because of molecular-sized pores and their adsorption properties [1-5], while the effective polymeric membranes for the dehydration in methanol aqueous solution are not yet. Hence the objective of the current study was to prepare the effective polymeric membranes for the separation of methanol/water mixtures in vapor permeation process. We have announced that the annealed polyelectrolyte complex gel (PECG) membranes, based on an ionic polysaccharide such as sodium alginate (SA) and carrageenan (CG) in previous works, exhibited the excellent separation performance for the dehydration of methanol-water mixtures [6]. To separate methanol-water mixtures by vapor permeation process, an annealing method was used to modify the morphology of PECG membranes that were composed of SA and CG, and complexed with divalent calcium ions. It was showed that water components almost penetrated through the membrane to the permeate side, and the membrane performance enhanced gradually as the operating temperature increased. This phenomenon was due to the change of morphology, induced by rearranging the polymer chains, having a deformation of the chelate structure. From this result, we have also deduced that the annealing of complex membranes acts as a molecular sieve, which can be modulated by shrinking the free volume between the polymer chains in the structural viewpoint. However, the resulting membranes exhibited lower permeability than the non-annealed membranes. Accordingly, we attempted to prepare the annealed PECG composite membranes, based on two anionic polysaccharides, composed to sodium alginate and carrageenan, inducting divalent calcium ions, in order to develop of the effective membrane for removing water from methanol mixtures..

2. Experiments

2.1. Membrane Preparation

Polyetherimide (Ultem1000, PEI) was dissolved in N-methyl-2-pyrrolidone (NMP) solution stirring for 12h at 80℃ to make 25 wt% PEI homogeneous solution. A known amount of Alumina with 0.1㎛ particle size was added into the PEI solution which was stirred for 12h then was kept

in an ultrasonic bath for about 1 h. The PEI solution with alumina loading of 10 wt% (the ratio of alumina weight to weight of PEI plus alumina) were cast onto a glass plate with the aid of a casting knife and then dried at room temperature for 24h. Sodium Alginate (SA) and carrageenan (CG) was dissolved in deionized water to form a homogeneous solution of 2wt% polymer. The mixtures of SA/CG solution with weight ratios of 95/05, respectively, were stirred at room temperature for 12hr. To prepare the polyelectrolyte complex gel (PECG) composite membranes, the mixed solutions were cast on the skin layer side of the prepared PEI support membranes and dried them at room temperature for 24 h in a dust free, environmentally controlled chamber. The dried films immersed in 5wt% $CaCl_2$ aqueous solution for 12 hr, and washed several times with pure water to eliminate any possible residual calcium ions, and dried at room temperature. The annealed PECG membranes have been prepared by heating the complex membranes in convection oven at 90~110°C during 4h.

2.2. Membrane Characterization

The chemical structures of the prepared membranes were characterized with a fourier transform infrared spectroscopy (Digilab FTS-80; Bio-Rad, Richmoned, CA). The change of membrane morphology was investigated with a wide-angle X-ray diffractometry (model D/MAX IIIB; Rigaku) with a scintillation counter detector using CuK - radiation as a source. Angles (2) ranged from 2° to 50°. The thermal properties of the prepared membranes were measured with a thermogravimetric Analysis (Model: 2950). TGA thermograms were obtained with a DuPont 951 thermogravimetric analyzer with a heating rate of 10℃/min in the temperature range from 30 to 800℃ under a continuous nitrogen flow of 50ml/min. The surface morphologies and internal structures of the PECG membranes were examined using a JEOL JSM-80A scanning electron microscope. For the study with a SEM, membrane samples were fractured in liquid nitrogen and coated with gold.

2.3. Permeation Test

A schematic permeation test apparatus used in this study has been described elsewhere. [2] The membrane cell was designed to produce the saturated vapor of a feed liquid at a feed temperature. The effective membrane area was 19.6 cm^2. The feed mixture was circulated from the feed tank, having a capacity of 2.5L, through the membrane cell. The feed mixture enters the cell through the lower opening, leaves the cell through the higher opening with enough flow rate for the liquid level not to exceed the position of the higher opening. During circulating the feed mixture through the membrane cell, the saturated vapor in equilibrium with feed mixture at feed temperature could be produced in the cell. The cell was placed in a heating oven. By the heating oven, the temperature of the produced vapor could be controlled 5 ℃or higher above the feed temperature to prevent the vapor from condensing in the cell. The feed tank was wrapped with the heating tape to heat the feed mixture, and controlled by using PID temperature controller with an accuracy of 0.5℃. The composition of permeation vapor was collected in a cold trap by liquid nitrogen with a given time interval, heated up to room temperature, and weighed to determine the flux. Separation analysis was carried out by gas chromatograph (Model Shimadzu GC 14B) equipped with a column packed with Porapak-Q and with a thermal conductivity detector. The separation factor ($\alpha_{water\ /methanol}$) was calculated by the following Eq.(1)

$$\alpha_{water/methanol} = (Y_{water}/Y_{methanol})/(X_{water}/X_{methanol}) \quad (1)$$

where X and Y are the weight fractions of each component in feed and permeate, respectively.

3. Results and discussion

To estimate the effective coating layer for the separation of methanol/water mixture, a series of annealed polyelectrolyte complex gel (PECG) composite membrane with different number of deposited layers were prepared and characterized by using SEM and permeation test for the methanol solution containing 50 mol% of water. As can be seen in Figure 1 and 2, the resulting membranes showed that both the permeation rates and methanol concentrations in the permeate side decrease gradually with an increase of the coating times. From this result, it was concluded that the active layer of annealed composite membranes needs more than 2 μm thickness as shown in Figure 2., in order to prepare the successful composite membranes for the separation of methanol/water mixtures.

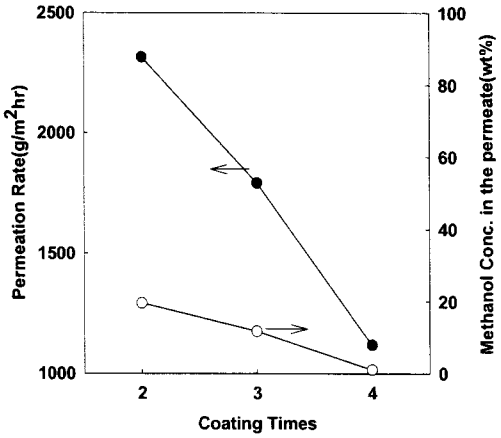

Figure 1. Permeation results of the annealed polyelectrolyte complex gel composite membranes for the 50/50 mol% methanol-water mixture as a function of the coating time at 70℃

Figure 2. Cross-sectional SEM photographs for the annealed polyelectrolyte complex gel composite membranes as a function of the coating time; (a) 2 times, (b) 3 times, (c) 4 times.

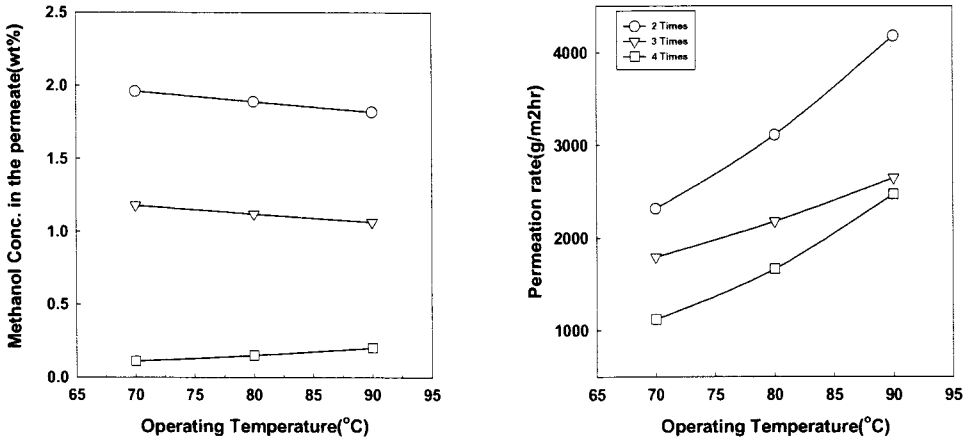

Figure 3. Permeation results of the annealed polyelectrolyte complex gel composite membranes for the 50/50 mol% methanol-water mixture as a function of the operating temperature.

On the other hand, when the operating temperature is raised, the permeation rate of annealed complex membranes is gradually improving without decreasing of a permselectivity as a whole, as shown in Figure 3. Generally, when the operating temperature increases, according to the free volume theory, the thermal motion of polymer chain can increase and generate more free volume in the polymer matrix to facilitate sorption and diffusion of permeants in the membrane. As a result, the overall permeation behaviors are trending toward the increase in the permeation rate and the decrease of the permselectivity. However, the permeation behaviors of the annealed composite membranes showed that the permeation of water component increases highly, but that of methanol remains constant generally. Therefore, it should be concluded that the annealed gel composite membranes, prepared with over 2m thickness, has the effect of molecular sieving for the separation of methanol and water mixtures by thermal annealing, due to shrinking a free volume between the polymer chains involving the chelate segments.

4. Acknowledgements

This work was supported by a grant from the Regional Technology Innovation Program of the Ministry of Commerce, Industry, and Energy (MOCIE), and a grant from the Basic Research Program of the Korea Research Institute of Chemical technology

5. References

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