Pervaporation Separation of Water/Isopropanol Mixtures through Crosslinked Carboxymethyl Chitosan/Polysulfone Hollow-Fiber Composite Membranes

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ABSTRACT: Carboxymethyl chitosan (CMCS)/polysulfone (PS) hollow-fiber composite membranes were prepared through glutaraldehyde (GA) as the crosslinking agent and PS hollow-fiber ultrafiltration membrane as the support. The permeation and separation characteristics for dehydration of isopropanol were investigated by the pervaporation method. Pure chitosan, carboxymethyl chitosan, and crosslinked carboxymethyl chitosan membranes were characterized by Fourier transform infrared (FT-IR) spectroscopy and X-ray diffraction (XRD) to study the crosslinking reaction mechanism and degree of crystallinity, respectively. The effects of feed composition, crosslinking agent, membrane thickness, and feed temperature on membrane performance were investigated. The results show that the crosslinked CMCS/PS hollow-fiber composite membranes possess high selectivity and promising permeability. The permeation flux and separation factor for isopropanol/water is 38.6 g/m^{2}h and 3238.5, using 87.5 wt % isopropanol concentration at 45°C, respectively. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1959–1965, 2007

Key words: pervaporation; water/isopropanol mixtures; carboxymethyl chitosan; membrane; crosslinking

INTRODUCTION

Pervaporation is a membrane separation process that can be applied to separate organic solvent–water mixtures, a great deal of research effort has been focused on the separation close azeotropic composition.[1–5] There are now more than 100 pervaporation plants in the world, most of which use plate-and-frame membrane modules for pervaporation dehydration of alcohols.[6] However, there are some disadvantages to the plate-and-frame module, such as its large size and low-packet density. Recently, compact hollow-fiber modules have been considered effective, and the development of such membrane modules for pervaporation depends on desirable membrane and anti-leakage encapsulation technology. To our knowledge, only a few publications have reported on the hollow-fiber module for pervaporation dehydration.[7–11] Chitosan is similar in chemical structure to cellulose and is the second abundant biopolymer after cellulose, which can be easily obtained in Nature, but its use and applications have not yet been realized to the extent of those for cellulose materials.

Because of its large number of reactive hydroxyl (—OH) and amine(—NH$_2$) groups, chitosan membrane and some of its modifications were recently investigated as membrane materials; the results showed that it is a more promising polymer material for application in pervaporation.[12–16] Modified chitosan and polysulfone are good materials for preparing composite membranes. However, the structural stability of this composite membrane is not acceptable to endure the long experimental conditions because they have opposite characteristics with respect to affinity for water. Huang et al.[17] introduced two methods for surface modification of polysulfone membrane to improve the membrane separation performance; we therefore also pretreated the surface of the PS hollow-fiber membranes, using dilute alkali solution in this study.

Isopropanol, a widely used solvent in the chemical, pharmaceutical industrials, and electronic industries, most of whose applications require high purity, is known to form an azeotropic at 12.5 mass % of water, a characteristic that creates difficulties in its recovery by conventional distillation.[18] The application of pervaporation as a means to achieve dehydration of isopropanol would be more advantageous than the conventional distillation.[18–20]

Selective separation of solute required strong adsorptions through interaction such as hydrogen bonding. It is expected that the carboxyl group might have

a strong interaction with water through hydrogen bonding and a membrane containing carbonyl groups might selectively permeate water. Y. M. Lee et al.[21] reported pervaporation separation of water–ethanol through some modified chitosan membranes; these investigators found that the carboxymethyl chitosan membrane showed maximum swelling and the ethanol flux at 10–30 wt % feed ethanol concentration due to the coupling effect and plasticizing. Uragami et al.[22] investigated the CMCS membrane crosslinked with glutaraldehyde for evapomeation of the aqueous alcoholic solutions; they found that a control in both chemical and physical structure is very important in permeation and separation through the membranes. In principle, crosslinking is one of the efficient strategies to control the permselectivity of the pervaporation. Crosslinking enhances the selectivity with sacrifice of the permeation flux because the membrane becomes more compact due to the crosslinking density increase and the polymer chains become more rigid.[17,23,24] Thus, penetrant molecules are less permeable due to the reduced free volume and increased penetration energy.

In the present work, we report the preparation of glutaraldehyde crosslinked carboxymethyl chitosan hollow-fiber composite membranes; their pervaporation performance for aqueous isopropanol mixtures separation, the effects of GA, feed temperature, feed concentration, and membrane thickness are investigated. At the same time, the cause of the effects of GA on membrane pervaporation performance is discussed.

EXPERIMENTAL

Materials

Chitosan (CS) has a degree of deacetylation of 85% and a viscosity average molecular weight of 6.3×10^5.

Deionized water of conductivity was generated by electrodialysis in the laboratory itself. The PS hollow-fiber UF membrane [with a molecular weight cutoff (MWCO) of 30,000] was supplied by the National Engineering Research Center for Liquid Separation Membrane (People's Republic of China). Isopropanol was obtained from Shanghai Chemical Reagent and was used directly without further purification. Glyoxylate acid monohydrate was obtained from Fluka Co., Ltd. (Sweden). All other reagents and chemicals were of analytical grade.

Preparation of carboxymethyl chitosan and membrane

CMCS was prepared according to the modification methods described by Muzzarelli et al.[25] and Liu et al.[26] Figure 1 shows the preparation route of CMCS. As an example, chitosan (8.00 g) was suspended in 1100 mL deionized water. After 24 h, an aqueous suspension of chitosan was reacted with 1.25 g of glyoxylate acid monohydrate, and the pH was adjusted to ∼ 4.4 with 1 mol/L NaOH to cause dissolution. The resulting solution was then reduced with sodium borohydride (0.9 g) at ∼ pH 6.4 and was insolubilized for 24 h. The CMCS beads were filtered and air-dried. The newly formed beads of fully carboxymethylated CMCS were ground by using a laboratory jar mill to a consistent particle size (<150 μm) before use. The degree of substitution (DS) of CMCS, which was determined by potential titration, is 0.9. The casting solution was prepared by dissolving the CMCS in deionized water. The PS hollow-fiber ultrafiltration membranes were immersed in deionized water for 24 h and then immersed by 0.6 mol/L HCl for 40 min to remove the glycerol on the surface; the excess acid was neutralized by 0.5 mol/L NaOH solution. Finally, the membranes
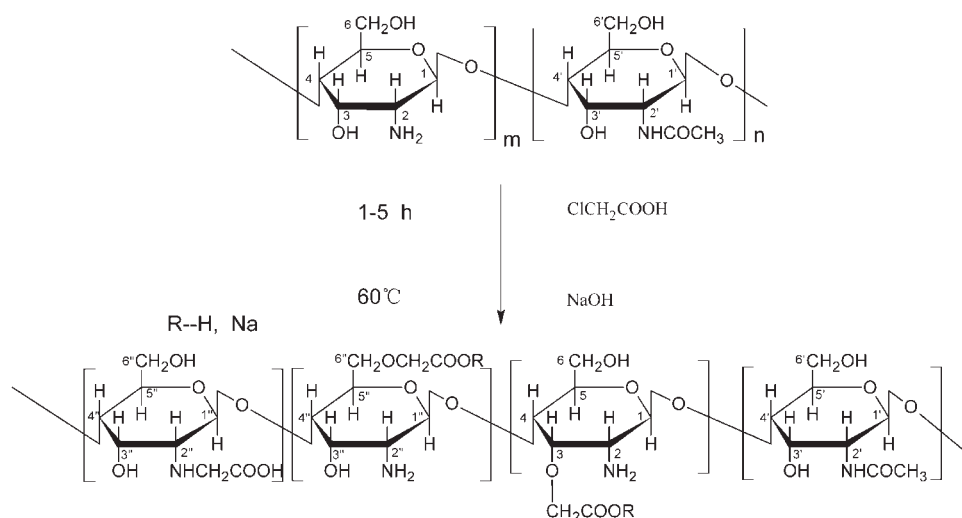

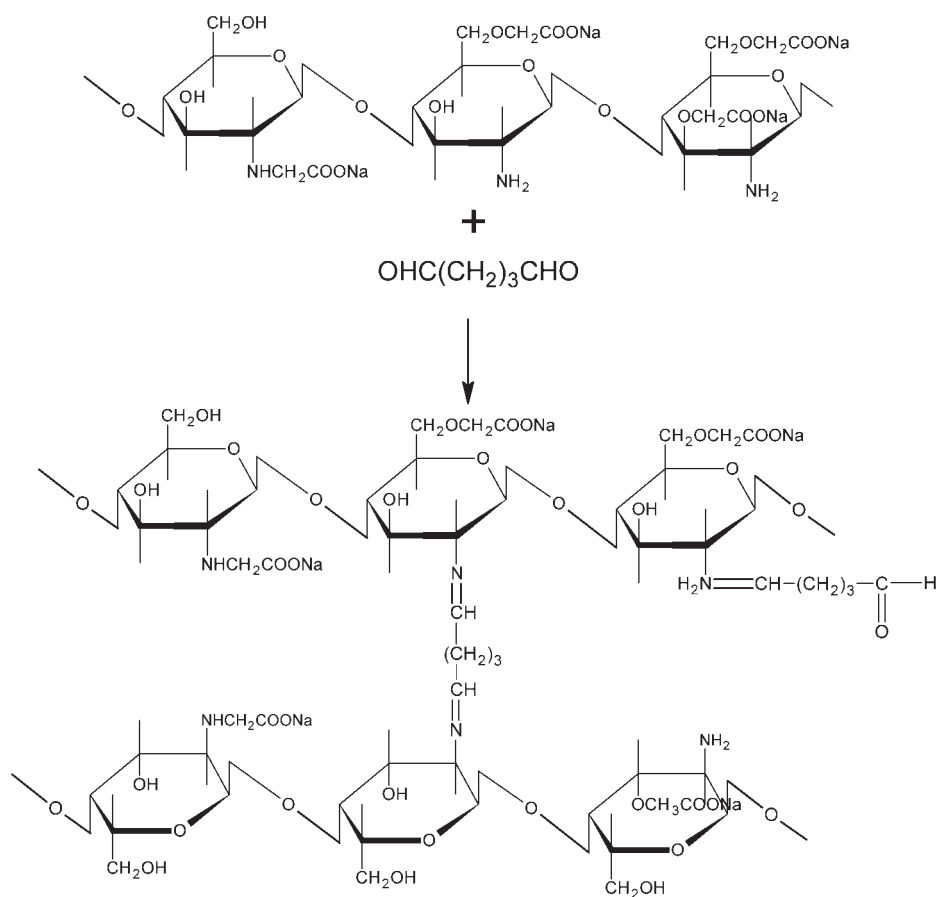**Figure 1** Preparation process of carbonxymethyl chitosan.

Figure 2 Crosslinking mechanisms of carbonxymethyl chitosan with glutaraldehyde.

were rinsed by deionized water repeatedly until the membrane surface was neutral. The hollow-fiber composite membranes were prepared by immersing PS hollow-fiber ultrafiltration membrane support in the casting solution; they were then taken up and dried at room temperature in a dust-free atmosphere. Next, the dry membranes were immersed in a reaction solution containing different concentration glutaraldehyde and 0.05 wt % sulfuric acid in 85% ethanol solution for some time, the crosslinking reaction mechanisms is shown in Figure 2. They were then removed from the solution and washed in ethanol thoroughly to remove any possible residual crosslinking agent. The thickness of the membranes was measured by SEM and screw micrometer about from 24 μm to 100 μm, respectively.

Membrane characterization

Pure CS, CMCS and crosslinked CMCS membrane samples were scanned within the range 400–4000 cm^{-1} wavenumber, using a Perkin-Elmer 283B FTIR spectrophotometer. Scanning electron microscopy (SEM) was used to measure the thickness of the membranes. Cryogenic fracturing of the mem-

brane was done after freezing the samples in liquid nitrogen. All specimens were coated with a conductive layer of sputtered gold. X-ray scattering experiments were carried out to study the dry CS, CMCS, and crosslinked CMCS. The angle of diffraction (2θ) was varied from 0° to 65°.

Pervaporation process of isopropanol/water separation

A schematic diagram of the pervaporation apparatus and a detailed procedure for performing the pervaporation experiment can be found in our previous publications.[27,28]

RESULTS AND DISCUSSION

Fourier transform infrared spectra data analysis

Figure 3 shows the FTIR spectra for membranes of original chitosan, carboxymethyl chitosan, and crosslinked carboxymethyl chitosan. Figure 3 (a) shows the basic characteristics of chitosan at: 3455 cm^{-1} (O—H stretch), 2867 cm^{-1} (C—H stretch), 1598 cm^{-1} (N—H bend), 1154 cm^{-1} (bridge-O stretch), and 1094 cm^{-1} (C—O stretch). Figure 3 (b) shows the IR spectrum
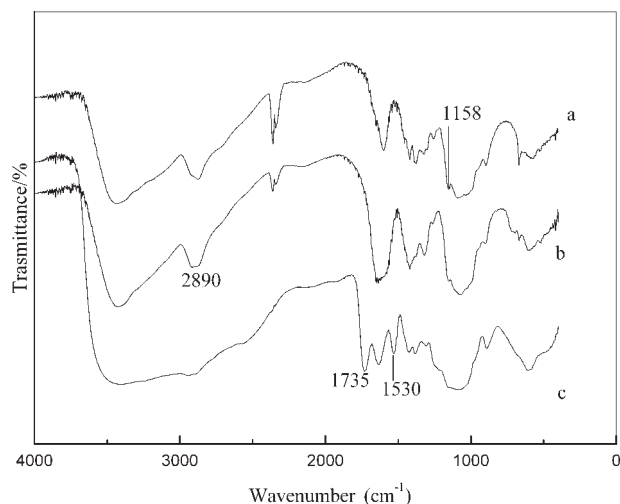
Figure 3 FT-IR of CS, CMCS, and crosslinked CMCS.

of CM chitosan in Na salt. The peak of —COONa (1598 cm^{-1}), 1070—1136 cm^{-1} (—C—O—), the —NH$_2$(1592 cm^{-1}). The bands at 1650 and 1560 cm^{-1} represent amino I and amino II functional groups in chitosan. Figure 3 (c) shows the IR spectrum of crosslinked CMCS at: —CHO(1735 cm^{-1}), =CH(2890 cm^{-1}). FT-IR analysis confirms the crosslinking of CM chitosan by the reaction of hydroxyl and amine groups of CS with the aldehyde group of glutaraldehyde.

XRD analysis

The X-ray diffraction (XRD) patterns of original chitosan, pure CMCS, and crosslinked CMCS samples are shown in Figure 4. It is observed that XRD patterns of both pure chitosan and CMCS membrane appear to be semicrystalline. The diffraction peaks of original chitosan around 10° of 2θ indicate the average intermolecular distance of the amorphous part and relatively sharp semicrystalline peaks are centered at ∼ 20° of 2θ. CMCS were more amorphous than the original chitosan because of the introduction of the carboxylate group destroying the secondary structure of the original chitosan. The ordered arrangement in CMCS molecules resulting from the crosslinking between GA and CMCS (which destroys the crystallization structure) leads to decrease in the crystallinity of crosslinked CMCS; thus, crosslinked CMCS was more amorphous than CMCS.

PERVAPORATION PERFORMANCE OF ISOPROPANOL AQUEOUS SOLUTIONS DEHYDRATION

Effect of feed concentration

The effect of feed concentration on the crosslinked CMCS hollow-fiber composite membrane perform-

ance was investigated at temperature of 45°C, the results are shown in Figure 5. The permeation flux decreases but the selectivity increases with increasing isopropanol composition in the feed. CMCS membrane may experience two phenomena during the pervaporation process. One is the swelling, which depends on the feed concentration; the other is the intrinsic relaxation behavior, which was studied mainly in alginate membrane, as well as the potential for the polysaccharides, such as modified chitosan.[29]The extent of water sorption correspondingly decreases with an increase in feed isopropanol concentration, resulting in decreased flux. The separation factor depends on the partition of two components between the feed solution and the upstream layer of the membrane, as well as on the difference in their diffusivities across the membrane. The membrane swelling caused by water decreases with increasing the isopropanol concentration in the feed, the water permeation flux decreases, though the isopropanol permeation flux increases slightly (the permeation flux of the isopropanol is not shown in the present study), the extent of the former is larger than the latter, so the separation factor increases.

Effect of temperature

The temperature dependence of pervaporation performance of CM-CS is shown in Figure 6. The permeation flux increases and the selectivity decreases as temperature increases. In general, the effect of temperature on flux is positive. One is due to the increased thermal motion of the chain with increasing temperature that improves the diffusion of the permeants. In contrast, during the solution process, it was suggested by Huang and Lee[20,21] that the interactions among the permeates, such as those between water–water, water–ethanol, and ethanol–
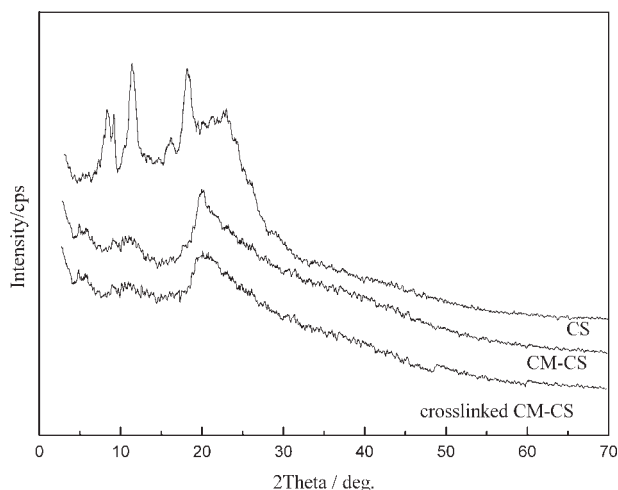

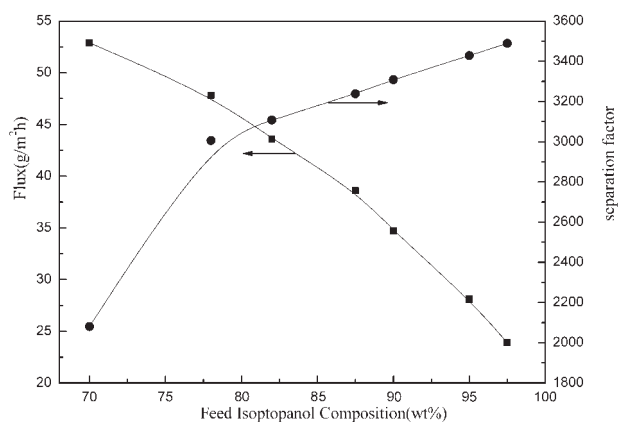**Figure 4** XRD of CS, CMCS, and crosslinked CMCS.

Figure 5 Effect of feed composition on pervaporation performance of crosslinked CMCS membranes. Membrane thickness, 40.1 μm; feed temperature, 45°C; crosslinking agent content, 4.5%.

ethanol, might have an enhancing effect on the energy of solution. As the temperature increases, the interaction between the permeates becomes weaker and the interaction between the permeate and membrane is strengthened. The dependence of the permeation flux on the temperature can be related by an Arrhenius-type expression of the form:[30,31]

$$J = J_0 \exp(-E_J/RT), \qquad (1)$$

where J_0 is constant, E_J has been considered the activation energy for permeation, T is the absolute temperature, and R is the gas constant. E_J can be obtained from the $\ln J$ vs $1/T$ plot. Figure 7 shows the Arrhenius plot of water and isopropanol flux versus temperature. The average activation energy of water and isopropanol permeation across CMCS/PS

hollow-fiber composite membrane (for feed isopropanol, concentration 87.5%) are 28.52 kJ/mol and 81.49 kJ/mol, respectively. These values indicate that a higher energy is needed for isopropanol permeation through the composite membrane than water.

The effect of temperature on the separation factor of membrane was explained by considering two parallel effects of temperature on the membrane. One effect is increasing polymer chain mobility and the free volume and facilitating the diffusion of both components. The activation energy for transport of water is lower than that of isopropanol, indicating that water molecules require less energy than isopropanol molecules to facilitate permeation through the membrane. This difference in the activation energy for water and isopropanol could allow us to speculate that isopropanol permeates by a random molecular diffusion within the amorphous matrix and water permeates by a selective transport through hydrophilic moiety in the polymer. The difference in the activation energy for each component may arise from several material factors such as the molecular size and the affinity between permeates and membrane. As a consequence, water molecules are preferentially absorbs and permeates more easily as compared with isopropanol due to the smaller molecular size as well as the higher affinity for the membrane. Moreover, Guo et al.[32] reported that the diffusion coefficient of water is always higher than that of ethanol; it might be that the effect of the temperature on the alcohol diffusion coefficient is larger than that of water, so diffusion selectivity of water and isopropanol decrease with increasing the feed temperature. In contrast, the solution of water in the CMCS membrane is caused mainly by interaction between water and hydrophilic groups in the CMCS membrane.
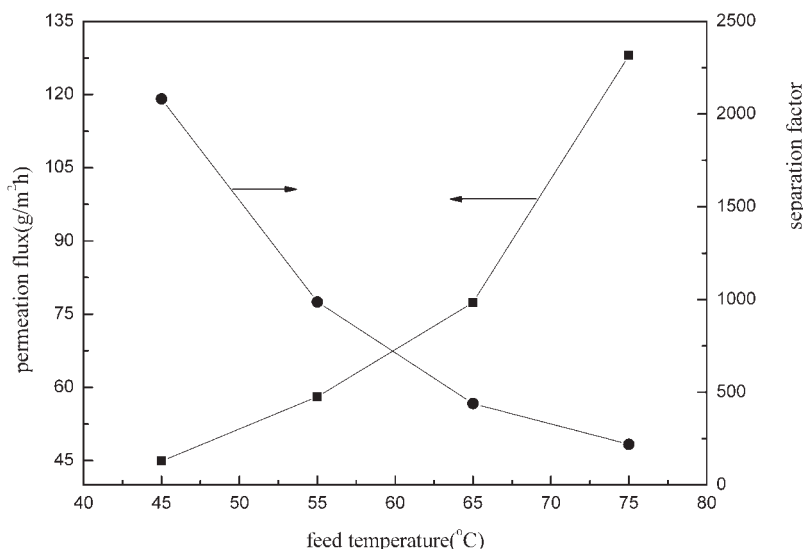

Figure 6 Effect of solution temperature on pervaporation performance of crosslinked CMCS/PS hollow-fiber composite membrane. Membrane thickness, 40.1 μm; crosslinking agent content, 4.5%.
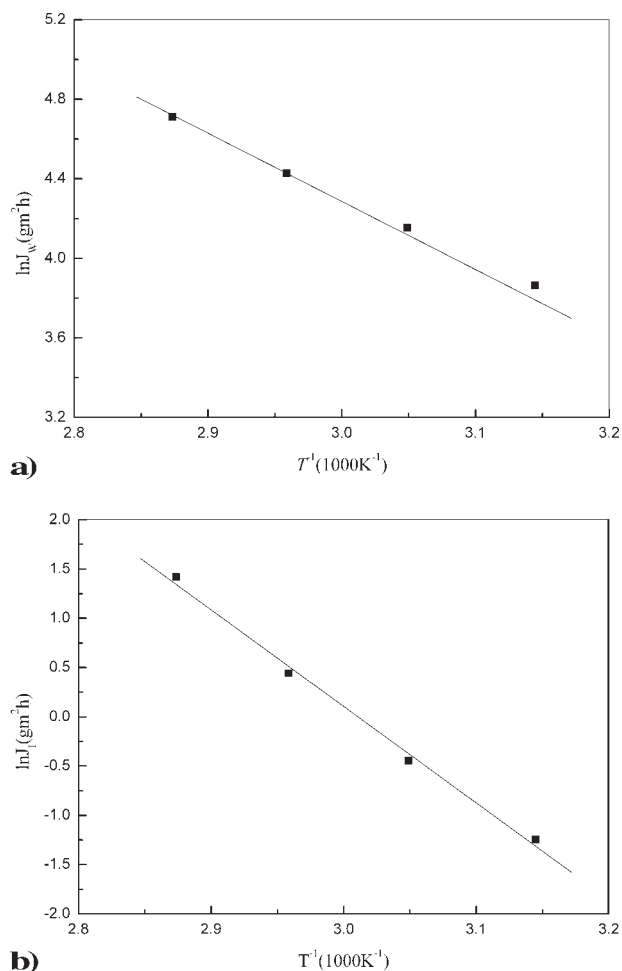
Figure 7 Arrhenius plot of water flux vs temperature at 87.5% feed isopropanol composition for pervaporation permeation of isopropanol-water solution through composite membrane. (a) Water. (b) Isopropanol.

According to Huang and Lee,[20,21] the interaction between water and hydrophilic groups in the CMCS membrane is strengthened with increasing the temperature but reduces the solubility of water, whereas that of isopropanol is caused mainly by random molecular solution within the amorphous network of the CMCS matrix, the solubility of isopropanol is improved with increasing the temperature. The solubility of water and isopropanol increases with increasing the temperature, but the solution selectivity decreases. The separation factor of membrane decreases by considering two parallel effects of temperature on the membrane.

Effect of crosslinking agent content

Crosslinking is an efficient strategy to control excessive swelling of membranes. In principle, a polymer material with higher crosslinking density has lower membrane mobility and a more compact network structure, resulting in less flux and less liquid solu-

bility.[33] In this study, glutaraldehyde was used as the crosslinking agent for the CMCS membrane, and pervaporation dehydration of the crosslinked CMCS membrane was carried out for aqueous solutions with 87.5 wt % isopropanol. Figure 8 shows that the permeation flux decreases and separation factor increases with increasing glutaraldehyde content. The decrease in permeation flux is explained as follows: the many reactions between GA and CMCS result in an increase in the crosslinking density of the CMCS top layer of the CMCS/PS hollow-fiber composite membrane. Therefore, the chain mobility and swelling ability of CMCS decreases. The thermal mobility of polymeric chains apparently drops and the absolute free volume to diffuse the permeants through the membrane decreases due to the crosslinking. However, water molecules with relatively small molecular size can diffuse through the crosslinked membrane easily rather than isopropanol molecules with large molecular size. The chemical crosslinking changed not only the physical density but also the chemical nature such as hydrophilicity of the membrane. This might result in a decrease in the separation factor. The crosslinked membrane is a good pervaporation membrane for the separation of isopropanol-water mixtures. The permeation flux and separation factor for isopropanol/water is 38.6 g/$m^2 \cdot$h and 3238.5 using 87.5 wt % isopropanol concentration at 45°C respectively.

Effect of membrane thickness

The effect of membrane thickness on water flux and separation factor was evaluated at constant feed composition(azeotropic) and permeate pressure (2 mmHg) by casting membranes of thickness ranging from 24 μm to 100 μm. With the membrane thickness increasing, a gradual reduction in flux
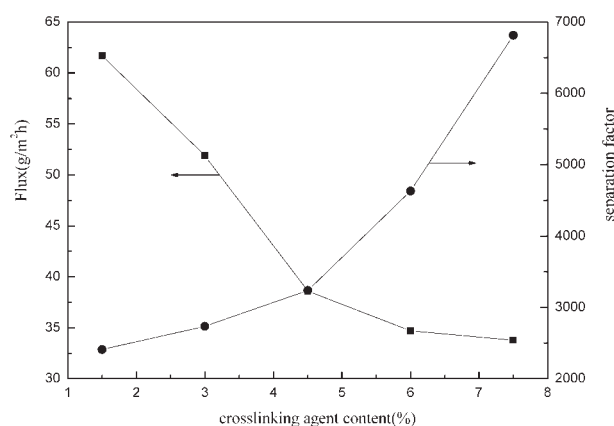

Figure 8 Effect of crosslinking agent content on the pervaporation performance of crosslinked CMCS/PS hollow-fiber composite membrane. Feed temperature, 45°C; membrane thickness, 40.1 μm; feed isopropanol composition, 87.5%.
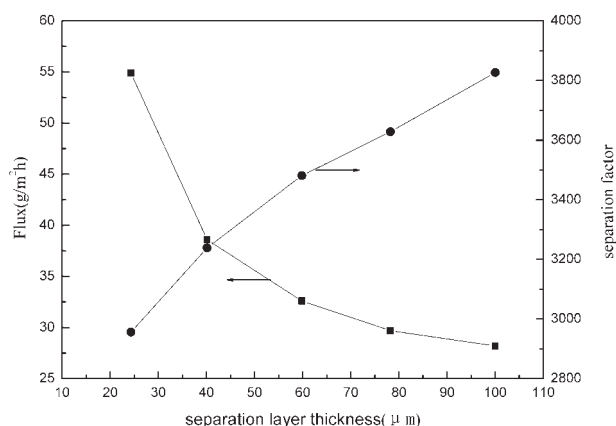
Figure 9 Effect of separation layer thickness on the pervaporation performance of crosslinked CMCS/PS hollow-fiber composite membrane. Feed temperature, 40°C; crosslinking agent content, 4.5%; feed isopropanol composition, 87.5%.

from 28.2 to 54.9 g/m$^2 \cdot$h and increase in separation factor from 2956 to 3827 can be clearly observed from Figure 9. Even though the availability of polar groups enhances with an increase in membrane thickness, the flux decreases since diffusion of feed is retarded due to the increased resistance to mass transfer. In the pervaporation experiment, upstream layer of the membrane is swollen and plasticized due to sorption of feed liquid, thus allowing the unrestricted transport of feed components.[34,35] In contrast, the downstream layer is virtually dry due to continuous evaporation in the permeate side; therefore, this layer forms the restrictive barrier, which allows only the interacting and smaller molecules such as water to pass through. It is expected that the thickness of the dry layer would increase with an increase in the overall membrane thickness, thereby resulting in an improved selectivity, as observed in the present case.

CONCLUSIONS

Crosslinked carboxymethyl chitosan/PS hollow-fiber composite membranes have been prepared for the separation of isopropanol/water mixture. The crosslinking nature of glutaraldehyde has been studied using FT-IR spectra and XRD. With an increase in feed isopropanol concentration, the membrane performance was found to be affected substantially due to a decrease in the extent of swelling of the polymer, thereby resulting in an decrease of flux, but the separation factor increased. The flux decreased with increasing the separation layer thickness, but improved the separation selectivity. Water–isopropanol mixtures can be effectively separated by pervaporation through crosslinked carboxymethyl chitosan/PS hollow-fiber composite membranes.

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