Pervaporation Separation of Water–Isopropanol Mixture Using Carboxymethylated Poly(vinyl alcohol) Composite Membranes

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ABSTRACT: The pervaporation separation of water–isopropanol mixtures was carried out using carboxymethylated poly(vinyl alcohol) (CMPVA) composite membranes. Carboxymethylated PVA (CMPVA) was synthesized by reacting PVA with various concentrations of monochloroacetic acid. Substitution efficiency of the CMPVA ranged from 12–32%. The cross-sectional structure of the composite membrane for pervaporation was confirmed by scanning electron microscopy (SEM) exhibiting a 20-μm active skin layer. Glass transition temperature of the CMPVA was in the range of 74–84°C, and decreased with increasing substitution efficiency. Degree of swelling and permeation flux for water–isopropanol in pervaporation increased with the substitution degree of carboxymethylation. CMPVA composite membrane, having 16% substitution efficiency, showed the following pervaporation performance; permeation flux of 831 g/m^2 h and separation factor of 362 measured at 80°C and 85 wt % feed isopropanol concentration. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 241–249, 1999

Key words: pervaporation separation; water–isopropanol mixtures; CMPVA composite membranes

INTRODUCTION

Pervaporation is a process for the separation of organic mixtures having an azeotropic point, similar physical and chemical properties, and aqueous organic mixtures. Pervaporation is especially useful for the dehydration of aqueous alcohol mixtures. This is due to the energy-saving effeciency of pervaporation compared with conventional azeotropic distillation. GFT has commercialized PVA composite membranes for the separation of water–ethanol mixtures.[1] In the case of using polymeric membranes in pervaporation, semicrystalline polymers are more selective toward water than elastomers. Therefore, semicrystalline polymers can be used as composite membranes by casting a selective skin layer onto a porous reinforcing support.[2] Composite membranes are composed of three layers; a selective dense layer, a microporous layer (ultrafiltration membrane), and a substrate (nonwoven fabrics). The selective dense layer should have a defect free surface and very low thickness. Ultrafiltration (UF) membranes are used for supporting selective thin layers, and sometimes can have some resistance for permeation.[3] In the resistance model for pervapo-

ration of composite membranes, the selective dense layer has a higher resistance to permeation than porous ultrafiltration support membranes, and UF membrane resistance to permeation depends on their pore size and porosity.[4]

Isopropanol has been widely used in semiconductor and liquid crystal display industries as a water-removing agent. Used isopropanol can be recycled by several methods, including pervaporation processes. Water and isopropanol form an azeotrope at 85.3 wt % isopropanol concentration. We have investigated pervaporation performances of water–isopropanol mixtures using modified chitosan composite membranes and the possibility of the hybrid system consisting of pervaporation and distillation.[5,6] It was confirmed that a hybrid process consisting of pervaporation and distillation was superior to the conventional azeotropic distillation column and the benzene recovery column, whereas the former process was regarded as an energy-saving processes. Zhang et al.[7] reported that a chitosan/PAN composite membrane with specific interfacial bonding between substrate and active layer exhibited a high separation factor of more than 8000 and flux of around 981 g/m^2 h using 80 wt % isopropanol concentration at 60°C. Huang et al.[8,9] also reported a study on pervaporation of water/isopropanol mixtures through asymmetric polyetherimide and chitosan membranes. They showed effects of membrane-casting parameters on the pervaporation. Their membranes had a separation factor of about 200 and flux of 60 g/m^2 h using 0.32 mol fraction (87.6 wt %) isopropanol aqueous solution at 25°C. Chitosan membrane crosslinked with 1,6-hexamethylene diisocyanate showed an improved separation factor via crosslinking, and the advantage of a composite membrane over homogeneous membranes at above 70 wt % feed isopropanol concentrations.

Poly(acrylic acid) (PAAc)-based membranes exhibited good pervaporation performances for water–ethanol mixtures, resulting from high affinity of carboxyl groups toward water molecules.[10,11] PAAc has a high charge density based on the dissociated carboxyl groups. However, when the feed solution to be separated has a low concentration of ethanol, PAAc is dissolved or significantly swollen, followed by a remarkable decline of selectivity.[12] Because of this drawback of poly(acrylic acid) for dehydration, several researchers have modified membranes to introduce PAAc through chemical reaction and graft reaction onto the membrane surface. We investigated cross-linked blends of the poly(vinyl alcohol) with chitosan and substituted anions.[13–16] Kang et al.[17] reported pervaporation of water–ethanol mixtures through crosslinked and surface-modified poly(vinyl alcohol) membranes using monochloroacetic acid. They reported that crosslinked and surface-modified membranes exhibited permselectivity toward water that was enhanced by a factor of nearly two, compared to that for the only crosslinked membrane. Meanwhile, carboxyl groups in PVA affected anticoagulation activity of heparin, and could possibly influence the pervaporation performances of water–isopropanol mixtures.

The objective of this article is to report on the separation of water–isopropanol using several composite poly(vinyl alcohol) membranes with different contents of carboxymethyl group.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (Elvanol 71-30, M_n = 52,000, Du Pont) was used after drying under reduced pressure. Extra pure grade glutaraldehyde (Junsei Chemical Co.) was used as a crosslinking agent. All the other chemicals used in this work were extra pure grade from Junsei Chemical Co. Ultrafiltration (UF) membrane for preparing the composite membrane was purchased from Fluid Systems Co. and had a pore size of 30–70 Å and a molecular weight cutoff of 7000–10,000 reported by the supplier. The UF membrane is composed of a polyethersulfone porous layer and a poly(ethylene terephthalate) nonwoven fabric substrate.

Membrane Preparation and Characterizations

The detailed procedure for preparation of CMPVA is described elsewhere.[14,18,19] Briefly, PVA was dissolved in 6 wt % NaOH aq. solution and then stirred intensely overnight to introduce alkoxide groups into the PVA chain. Monochloroacetic acid was added the PVA solution with a concentration ranging from 2 to 12 wt %. These solutions were stirred followed by neutralization with NaOH solution, consecutively washing with ethanol and acetone. The substitution efficiency of CMPVA was determined by the acid-base titration method and confirmed by elemental analysis. A small amount of CMPVA without neutralization was

Figure 1   Ideal structure of crosslinked CMPVA.

precipitated in ethanol and then dissolved in hot water for titration of NaOH solution.

CMPVA composite membranes were formed by casting the CMPVA solution on a polyethersulfone UF membrane. CMPVA solution was prepared by dissolving CMPVA powder into hot water (90°C) and crosslinked with aq. glutaraldehyde solutions. Ideal structures of crosslinked CMPVA are illustrated in Figure 1. Then they were cast onto the UF membrane before gelation using a tailor-made casting machine and dried at 60°C in a convection oven over 24 h. CMPVA solution can be easily gelled because of the self-crosslinking between carboxyl and hydroxyl groups in the CMPVA chain in an acidic condition.

Morphology of the cross-section of the CMPVA composite membranes was characterized with scanning electron microscope (SEM, JEOL Model JSM-35CF). The instrument was operated at an accelerating voltage of 15 keV. FTIR spectra were performed on the Nicolet Model Magna 550 FTIR spectrometer. X-ray diffraction patterns were performed on a Rigaku Denki RAD-C X-ray diffractometer. The substitution efficiency of CMPVA was confirmed by elemental analysis (EA 1110 CE Instrument).

Pervaporation

The equipment used to conduct the pervaporation experiments is described elsewhere.[20] The effective membrane area in contact with the feed liquid is about 25.98 cm². The volume of the feed chamber is 5 L. Downstream pressure was maintained below 3 Torr. Permeate after equilibrium

was collected at constant time intervals. The values reported here are an average of at least three experiments, and the standard deviation from the mean value is within ±5%.

Separation analysis was carried out by Shimadzu GC-14B equipped with a 3 m-long column packed with Porapak-Q and a thermal conductivity detector. Separation factor (α) and permeate flux (J) are defined as follows.

$$\alpha = \frac{Y_w/Y_s}{X_w/X_s} \tag{1}$$

$$J = \frac{Q}{A \times t} \tag{2}$$

where Y_i is the weight fraction of component i in permeate, and X_i is that in feed. w and s denote water and isopropanol in the water–isopropanol mixture. Q, A, and t represent the weight of permeant (g), effective membrane area (m²), and operating time (t), respectively.

RESULTS AND DISCUSSION

The structure of CMPVA was confirmed by FTIR spectroscopy. The FTIR spectra of CMPVA membranes are revealed in Figure 2. A characteristic peak of the carboxylate salt resulting from neutralizing reaction is shown at around 1600 cm^{-1}. The acid carbonyl absorption at 1725 cm^{-1} vanishes as the carboxymethylate salt is formed.

Figure 2   FTIR spectra pf CMPVA membranes. (a) PVA, (b) CMPVA12, (c) CMPVA16, (d) CMPVA21, (e) CMPVA23, and (f) CMPVA32.

Figure 3 Substitution efficiency of CMPVA membranes.

Substitution efficiency of CMPVA membranes is shown in Figure 3. Substitution efficiency of the CMPVA increased with the concentration of monochloroacetic acid. The sample designation of the CMPVA membranes used in pervaporation is described in Table I. The sample number increases with the concentration of the monochloroacetic acid.

Swelling behavior of CMPVA membranes is shown in Figure 4. The degree of swelling is defined as,

$$\text{Degree of swelling } (\%) = \frac{W_w - W_d}{W_d} \times 100 \quad (3)$$

where W_w and W_d are the weight of wet and dry samples, respectively.

Figure 4 Effect of (a) substitution efficiency and (b) feed IPA concentration on degree of swelling for CMPVA membranes.

With increasing the substitution efficiency of the membrane, the degree of swelling increased. However, notice that carboxymethylated membranes exhibit lower swelling values than that of the PVA

Table I   Sample Designation of the Carboxymethylated Membranes

Designation	Concentration of Monochloroacetic acid (wt %)	Substitution Efficiency (%)	Crosslinking Agent Content (mg/g Polymer)
PVAX3	0	0	37.5
CMPVA12	2	12	—
CMPVA16	4	16	—
CMPVA21	6	21	—
CMPVA23	8	23	—
CMPVA32	10	32	—
CMPVA16X1	4	16	12.5
CMPVA16X2	4	16	25.0
CMPVA16X3	4	16	37.5
CMPVA16X4	4	16	50.0
CMPVA16X5	4	16	62.5

Figure 5   Membrane microphotographs of CMPVA16X3.

membrane. Usually, carboxymethylation of polysaccharides provides solubility in water. For example, carboxymethyl cellulose and carboxymethyl chitin or chitosan are all soluble in water. Interestingly, CMPVA does not dissolve in water, and moreover, its degree of swelling gradually decreases as the carboxymethylation proceeds further. A possible reason for this phenomenon can be assumed to be that gelation from self-crosslinking between carboxyl and hydroxyl groups in CMPVA chains decreases the affinity of CMPVA to water more than that of PVA. For CMPVA membranes, an increase of the degree of swelling with the substitution efficiency of the membrane can be explained by the fact that an affinity of the membranes to water molecules can be improved by increasing the content of carboxylic acid groups, which have higher ability of hydrogen bonding with water molecules than do hydroxyl groups.

Swelling behavior of various feed isopropanol mixtures was investigated for predicting the pervaporation performance at various feed isopropanol concentrations. The degree of swelling decreased with decreasing feed water concentrations. This is understandable, because most hydrophilic polymer membranes show an enhanced degree of swelling at high water concentrations.

A cross-section of CMPVA composite membrane is shown in Figure 5. A composite membrane consists of three layers; a hydrophilic active layer, a supported ultrafiltration membrane layer, and a nonwoven fabric. Commercial membranes and highly selective membranes for pervaporation are prepared as composite type membranes to achieve high permeate flux. In the present study, thickness of active layer of the composite membrane was about 20 μm.

Dielectric thermal analysis of CMPVA membranes is illustrated in Figure 6. In comparison with the PVA membrane, CMPVA membranes exhibit lower T_g values. Flexible pendant groups in some classes of polymers reduce the glass transition of the polymer by acting as internal diluents, and lowering the frictional interaction between chains. The net effect is to reduce rotational energy requirements of the backbone.[21] Shen et al.[22] also showed a decline in glass transition as aliphatic side groups were introduced in the polymer.

X-ray diffraction patterns of the membranes are revealed in Figure 7. PVA exhibited a typical peak that appeared at $2\theta = 20$ degree. This peak was assigned to be a mixture of (101) and (200).[23] X-ray diffraction patterns show that the carboxymethylation serves to decrease the peak intensity at around $2\theta = 20°$. Accordingly, we can see that the relative crystallinity in PVA decreases upon carboxymethylation.

The effect of crosslinking and carboxymethylation on pervaporation performance of water–isopropanol mixtures through CMPVA composite membranes is shown in Figures 8 and 9. Figure 8 shows that PVA has higher flux and lower separation factors than those of CMPVA membranes. The lower permeation flux of CMPVA membranes than PVA can be explained by similar trends in swelling behavior. Incorporation of carboxymethyl groups in CMPVA enhanced the affinity to water molecules, resulting in an increase of sorption of water. In CMPVA membranes, with increasing carboxymethylation, selectivity of the membrane toward water decreased and the permeate flux increased. Note

Figure 6   Dielectric thermograms of CMPVA membranes.

Figure 7 Wide-angle X-ray diffraction patterns of CMPVA membranes.

that the degree of swelling increases upon carboxymethylation, causing a reduction of relative crystallinity of CMPVA membranes. In fact, a decrease of relative crystallinity and an increase of the carboxymethyl group content both affected the swelling of the membrane.

In Figure 9, when the content of crosslinking agent is increased, the selectivity of the mem-

Figure 9 Effect of crosslinking and carboxymethylation on pervaporation performance of water–isopropanol mixtures through CMPVA membranes (85 wt % feed isopropanol concentration, 80°C operating temperature).

brane is enhanced, while the membrane blocks the permeation flux. In general, with increasing crosslinking degree, free volumes and hydrophilicity of the polar membrane decreases while mechanical properties of the membrane are enhanced. Therefore, crosslinking controls the hydrophilic–hydrophobic balance and increases solubility selectivity.[24]

The effect of feed isopropanol concentration on pervaporation performance of water–isopropanol mixtures through CMPVA composite membranes (CMPVA16X3) is illustrated in Figure 10. It demonstrates that the selectivity towards water decreases and the permeate flux increases with increasing water content in the feed solution. The tendency for the permeate flux to increase with feed concentrations is similar to the swelling behavior of membranes. Higher swelling of the

Figure 8 Effect of substitution efficiency on pervaporation performance of water–isopropanol mixtures through CMPVA membranes with 37.5 mg/g polymer crosslinking agent content (85 wt % feed isopropanol concentration, 80°C operating temperature).

membrane made permeate easily penetrate through the membrane. However, extensive swelling of water molecules loosens and plasticizes the polymer chains in the membrane and then also assists the penetration of isopropanol molecules as well. Swollen water molecules at high water concentration act as plasticizing agents in this case.

The effect of operating temperatures on pervaporation performance of water–isopropanol mixtures through CMPVA composite membranes (PCX043) is shown in Figure 11. Permeation flux increases and separation factor decreases with temperature. With increasing operating temperature, free volume of CMPVA molecules and the diffusion of permeating molecules increase due to thermal expansion of polymer chains. At low temperature, only a small size water molecule can move through polymer chains. At higher temperature, however, permeation fluxes of both water and isopropanol increase because of expanding free volumes of polymer molecules and plasticizing effects of water molecules in the membrane. The temperature dependence of the permeate flux can be expressed by an Arrhenius-type relationship

$$J_p = A_p \exp\left(\frac{-E_p}{RT}\right) \qquad (4)$$

where A_p and E_p are the preexponential factor and the overall activation energy of the permeation, respectively. The activation energy of permeation increases from 46.4 to 50.3 kJ/mol · K with increasing isopropanol concentration of the

Figure 10 Effect of feed isopropanol concentration on (a) separation factor and (b) flux of water–isopropanol mixtures through CMPVA16X3 membranes at an 80°C operating temperature.

Figure 11 Effect of operating temperature on (a) flux and (b) ln(flux) of water–isopropanol mixtures through CMPVA16X3 membranes in a 85 wt % feed isopropanol concentration.

feed mixtures. This phenomenon can be explained by the fact that an enhancement of isopropanol flux at higher isopropanol concentration is caused by the plasticizing effect of water molecules at high temperatures. Activation energies of the permeation for CMPVA membranes are summarized and compared with several membranes in Table II. Chitosan and cellulose membranes show lower activation energies than those of CMPVA membranes. This means that permeation flux of CMPVA membranes is more sensitive to operating temperature. Thus, it is advantageous to operate pervaporation with CMPVA membranes at high operating temperature.

CONCLUSIONS

CMPVA composite membranes were prepared for pervaporation of water–isopropanol mixtures.

Table II   Activation Energies for the Permeation of Water/IPA Mixture with Several Membranes

Membrane	Activation Energy (kJ/mol K)	Feed Concentration (wt %)	Reference
Cellulose acetate	36.5	—	29
Chitosan	28.0	90	9
Chitosan/PAN	22.8	80	7
β-chitosan	34.9	90	35
CMPVA16X3	46.4	60	This study
CMPVA16X3	49.4	70	This study
CMPVA16X3	51.6	85	This study
CMPVA16X3	50.3	95	This study

Carboxymethylation efficiency ranged between 12–32%, depending on monochloroacetic acid concentrations. Upon carboxymethylation, relative crystallinity of CMPVA decreased while chain mobility of the polymer increased, as characterized by X-ray diffraction patterns and dielectric thermal analysis. Pervaporation performance was conducted with various membranes and conditions. When crosslinking of membranes increased, selectivity toward water increased and permeation flux decreased. Degree of swelling and permeation flux for water–isopropanol in pervaporation showed a similar pattern, meaning that they increased with the substitution degree of carboxymethylation. A CMPVA composite membrane having 16% substitution efficiency showed the following pervaporation performance; a permeation flux of 831 g/m^2 h, a separation factor 362 at 80°C, an operating temperature, and 85 wt % feed isopropanol concentration.

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