

Properties and Pervaporation Characteristics of Chitosan–Poly(*N*-Vinyl-2-Pyrrolidone) Blend Membranes for MeOH–MTBE

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ABSTRACT: Clear blends of chitosan with poly(*N*-vinyl-2-pyrrolidone) (PVP) made from aqueous solutions appear to be miscible from visual appearance. Infrared (IR) spectra used to investigate the carbonyl–hydroxyl hydrogen bonding in the blends indicated compatibility of two polymers on a molecular level. The IR spectra were also used to determine the interaction change accessing with increasing temperature and indicated that a significant conformational change occurred. On the other hand, the blend membranes were evaluated for separation of methanol from methyl tert-butyl ether. The influences of the membrane and the feed compositions were investigated. Methanol preferentially permeates through all the tested membranes, and the partial flux of methanol significantly increase with the poly(*N*-vinyl-2-pyrrolidone) content increasing. The temperature dependence of pervaporation performance indicated that a significant conformational change occurred with increasing temperature. Combined with the IR results, the pervaporation properties are in agreement with characteristics of interaction between chain–chain within the blend membranes. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1452–1458, 1999

Key words: pervaporation; chitosan; poly(*N*-vinyl-2-pyrrolidone); blend; infrared spectra

INTRODUCTION

The use of pervaporation as a separation approach in multipurpose processes is becoming very attractive for its energy savings. It is widely used for dehydration of various solvents.¹ Up to now, the research is also done for the separation of organic mixtures, such as benzene–cyclohexane,² methanol methyl tert-butyl ether (MeOH–MTBE),³ and xylene isomers,⁴ wherein MeOH–MTBE mixture attracts much attention because MTBE is seeing increasing use as an oxygenate

for gasoline to meet the Clean Air Act requirements.⁵ MTBE is produced by reacting isobutene with excess MeOH, and the unreacted MeOH is subsequently distilled off and recovered. This distillation process is energy intensive because the excess MeOH can form an azeotropic mixture with MTBE.⁶

Previous results have been reported about the pervaporation separation of MeOH–MTBE or EtOH–ETBE using various membranes materials, such as CAB–CAP blend membrane,⁷ polysulfone,⁸ ceramics⁹ and PVA/PAA blend membranes.¹⁰ But, the performances of these membranes do not meet industrial requirements.

Chitosan is one of the most abundant natural polymers and has good properties for forming membranes. In the dehydration of solvents, the

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performances have been fully investigated, and the results showed it was an excellent membrane.¹¹ However, it has little permeability for MeOH–MTBE mixture, probably due to its rigid chain and close packing with the presence of several different types of intermolecular and intramolecular hydrogen bonding in the polymer matrix; thus, up to now, there is no report on this application.

In order to improve the industrial acceptance of the pervaporation process, research efforts are aimed to develop new membranes with better performance. In this study, structure characteristics of polyblends of chitosan and poly(*N*-vinyl-2-pyrrolidone), particularly, the hydrogen-bonding interaction between chain–chain in polyblends, were investigated on a molecular level by infrared (IR), and the various blend membranes were also evaluated for the separation of MeOH from MTBE by pervaporation. Further, the influences of both the blend composition and the structure properties on the permselectivity have been investigated. In addition, the effects of feed composition and operation temperature on the pervaporation properties were also studied.

EXPERIMENTAL

Materials

Chitosan with a degree of deacetylation of 78% and an average molecular weight of $3\text{--}4 \times 10^5$ as a membrane material was supplied by Koyo Chemical Co., Japan. Poly(*N*-vinyl-2-pyrrolidone) (PVP) with an average molecular weight of 4×10^5 was obtained from Aldrich Co. The other reagents and solvents were of analytical grade from commercial sources and used without further purification.

Membrane Preparation

The solution of poly(*N*-vinyl-2-pyrrolidone) (1.5 wt %) and chitosan solution (1.5 wt %) in 1.0 wt % aqueous acetic acid were mixed in different ratios. The casting solutions of both with different composition were poured on a glass plate that was prior brushed with cotton saturated by ethanol and evaporated at room temperature. The thickness of blend membrane is about 30 μm .

Pervaporation Experiments

Pervaporation experiments were carried out using an apparatus reported in earlier articles^{12,13}

in the following operation conditions: operation temperature, 50°C; pressure at the permeation side, less than 200 Pa; the effective membrane area, 25 cm². The compositions of feed and permeation solutions were determined by gas chromatography. The permeation flux was calculated from the permeation weight of the component in a defined period of time. The separation factor is defined as

$$\alpha = \frac{P_{\text{MeOH}}/P_{\text{MTBE}}}{F_{\text{MeOH}}/F_{\text{MTBE}}}$$

where P and F are the weight fraction of each component in permeates and feeds, respectively.

FTIR Measurements

Infrared spectra of pure polymers and blends were recorded on Bruker Fourier Transform Infrared (FTIR) Vector 22 spectrophotometer. The spectra were recorded with a resolution of 2 cm⁻¹.

RESULTS AND DISCUSSION

Chain–Chain Interaction in the Blending Membranes

Chitosan is practically insoluble in water and organic solvents due to its micelle structure, the close packing, and the presence of several different types of hydrogen bonds. Chitosan gives water-soluble salts with acetic acid (Fig. 1) and, thus, blends with PVP to form clear films. Their transparency is dependent on the polyblend composition. The IR spectra of pure PVP and chitosan have been obtained.^{14–16} The main characteristic bands are the following: 3480 cm⁻¹, C₆–OH stretching band of chitosan; 3447 cm⁻¹, C₃–OH stretching band of chitosan; 3375 cm⁻¹, hydrogen bonding of amide; 3264 cm⁻¹, N–H stretching band; 1681 cm⁻¹, C=O stretching of PVP; 1652 cm⁻¹, amide I band of chitosan; 1558 cm⁻¹, amide II band of chitosan overlaps with NH₃⁺ band, and 1550 cm⁻¹, a symmetric NH₃⁺ deformation peak, overlapping with amide II band of chitosan.

The identification of these peaks and relative intensities allow us to investigate the influence of chain–chain interaction between the polyblend. The chain–chain interaction between two polymers can be deduced from the shifts of the vibration frequencies of the group involved in the hydrogen bonding, for example, the frequencies of

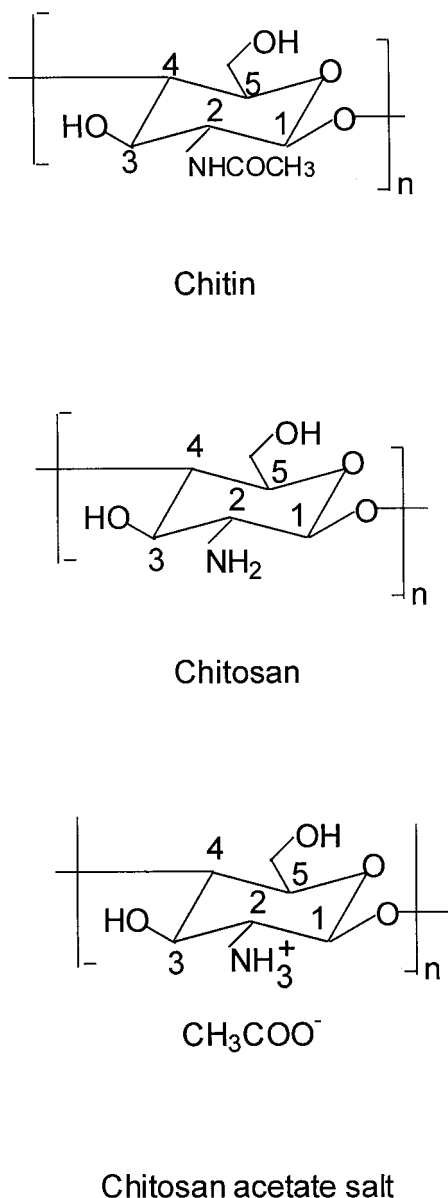


Figure 1 The chemical structure of chitin and chitosan.

the PVP carbonyl (Fig. 2) and those of the O—H bands of chitosan (Fig. 3). When the PVP content increases, the carbonyl band shifts towards lower frequencies and finally overlaps with the amide I band, indicating that carbonyl of PVP takes part in hydrogen bonding with chitosan. With increasing the PVP content, the strong NH_3^+ band, overlapping with amide II band at 1558 cm^{-1} , exists in polyblends and has no obvious shift, indicating that the NH_3^+ does not participate in the intermolecular bonding between chitosan and PVP, so it could be regarded that the carbonyl of PVP should

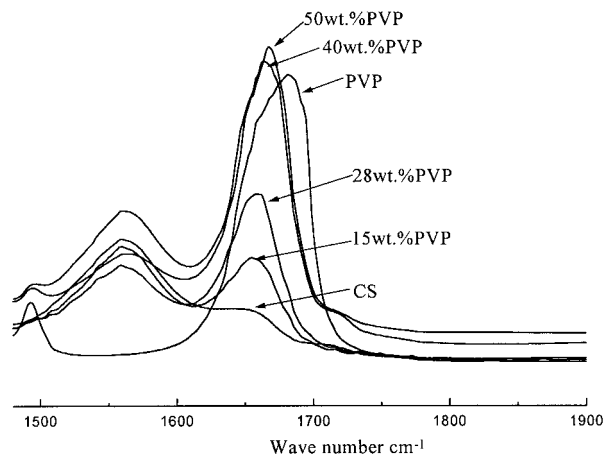


Figure 2 IR spectra of chitosan–PVP blends in region of $1300\text{--}1900\text{ cm}^{-1}$.

form hydrogen bonding with hydroxyl of chitosan. This result also proves that there is miscibility at a molecular level between two polymers, at least in some regions. The C—O stretching band of chitosan near 1100 cm^{-1} shifts steadily towards higher frequencies when the PVP content is increased (Fig. 4). The possible explanation could be that the C—O—H groups in the pure chitosan film are involved in different types of self-associations and/or that the C—O stretching frequency is lower than the frequency of a free C—O—H group. With the incorporation of PVP into chitosan, many hydroxyl groups are involved in hydroxyl—carbonyl hydrogen bonding at the expense of hydroxyl—hydroxyl hydrogen bonding. As a result many oxygen atoms of C—OH are freed from hydrogen bonding. Meanwhile, a similar phenomenon may happen with the OH

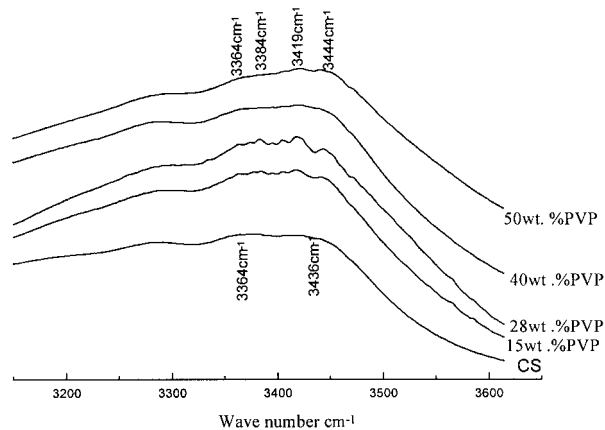


Figure 3 IR spectra of chitosan–PVP blends in region of $3150\text{--}3600\text{ cm}^{-1}$.

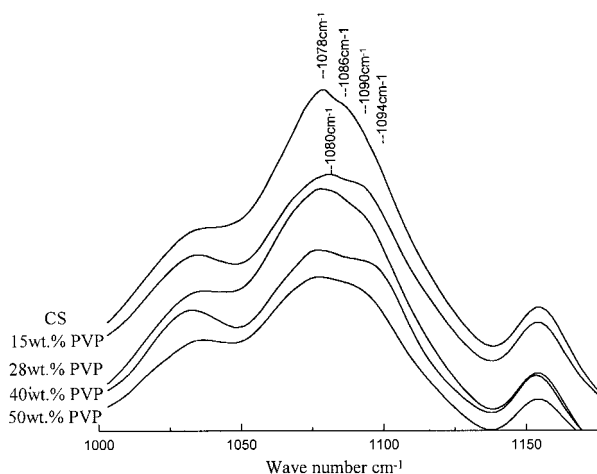


Figure 4 IR spectra of chitosan–PVP blends in region of 1000–1200 cm^{-1} .

stretching band (Fig. 3). This band is usually assigned to the hydrogen-bonded hydroxyl. The splitting of the hydroxyl band of chitosan upon blending with PVP supports this interaction in the system. With the blend composition changing, the relative intensities of the split bands change, and these bands indicate the interactions changing within the system.

Additionally, it is also found that the blend membrane is sensitive to the temperature (Fig. 5). When the temperature is increased from 30 to 60°C, it is the carbonyl band of the PVP, not the amide I band of chitosan, because the amide II band and the amide hydrogen bonding (3375 cm^{-1}) have no shift, which shifts to higher frequencies. This phenomenon indicates that the hydrogen–carbonyl hydrogen bonding is reduced by improving the chain motion. In fact, with the temperature increasing, the change of the peaks

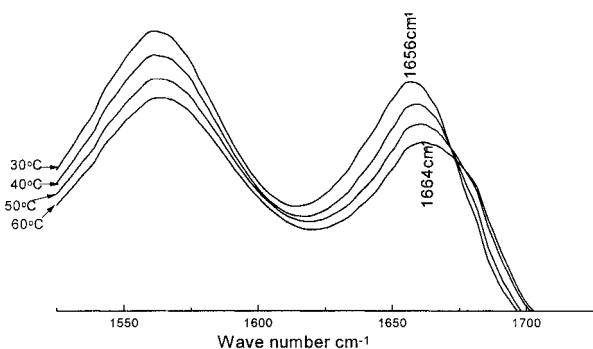


Figure 5 Influence of temperature on IR spectra of blend membrane with 28 wt % PVP content in region of 1450–1700 cm^{-1} .

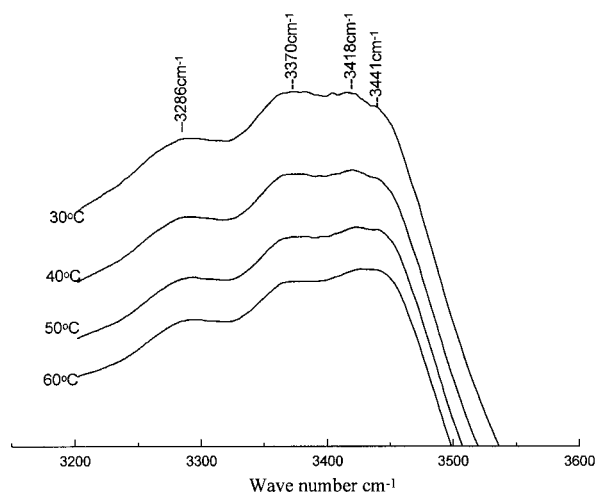


Figure 6 Influence of temperature on IR spectra of blend with 28 wt % PVP content in region of 3250–3500 cm^{-1} .

in 3000–3600 cm^{-1} region also supports the above conclusion (Fig. 6). The peaks at 3264 and 3375 cm^{-1} don't obviously change, but the relative intensities of peaks at 3447 and 3480 cm^{-1} change. Generally, these bands are assigned to hydroxyl groups associated by multiple hydrogen bonds with hydroxyl groups and carbonyl groups.¹³ So this temperature dependence is indicative of bands that reflect conformational sensitivity and suggests that a significant rearrangement of bond structure may be taking place within the blended membranes.

Pervaporation through Chitosan–PVP Blend Membranes

Membranes made of polyblends of PVP and chitosan were evaluated for the separation of methanol from MTBE. The partial flux of MeOH and MTBE are given in Figure 7 as a function of the PVP content in the blend, and the separation factor is listed in Table I. For the feed mixtures containing 14.45, 20.75, and 38.78 wt % methanol, the blend membranes, particularly, compared with a pure chitosan membrane, which exhibits almost no permeability (about 0.08 $\text{g m}^{-2} \text{h}^{-1}$ for the feed with 14.45 wt % methanol), showed better separation properties, as shown in Figure 7. Maybe owing to its rigid chain and close packing with the presence of several different types of hydrogen bonding in polymer matrix, the pure chitosan membrane has little permeability. But for the polyblend, the PVP, as a proton-acceptor

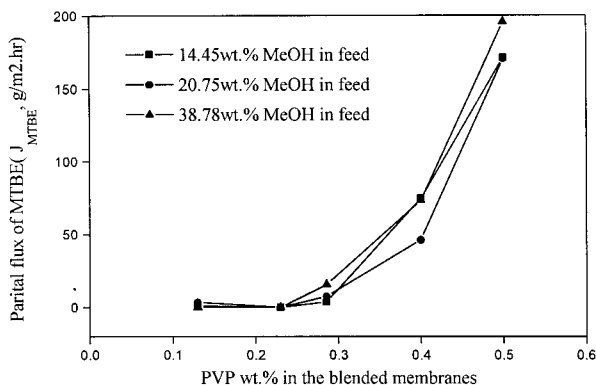
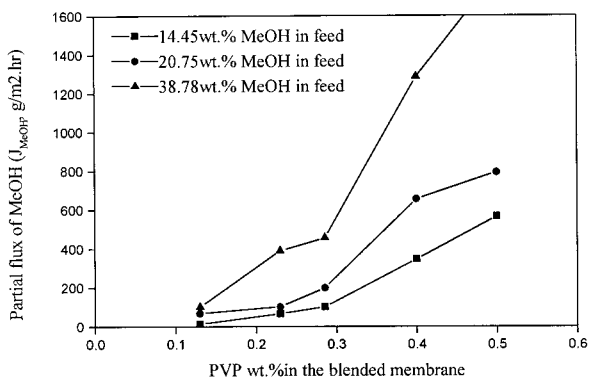


Figure 7 Partial flux of MeOH and MTBE for blend membranes as a function of blend composition.

in membranes, participates in the hydrogen bonding with hydroxyl of chitosan, and, thus, loosens the chitosan network, decreasing the chain-chain interaction within the chitosan. On the other hand, it also provides a proton-acceptor for par-

Table I The Separation Factor of Blend Membranes for Three Different Feeds

Separation Factor	Blend Membrane with PVP Wt %				
	0.13	0.23	0.285	0.40	0.50
α_1	68.67	∞	155.69	26.61	18.95
α_2	72.43	∞	100.64	54.30	16.73
α_3	∞	∞	45.69	26.87	16.22

α_1 , α_2 , and α_3 are the separation factor of feeds with 14.45, 20.75, and 38.78 wt % methanol, respectively.

∞ indicates that no methanol was detected in permeate by gas chromatography.

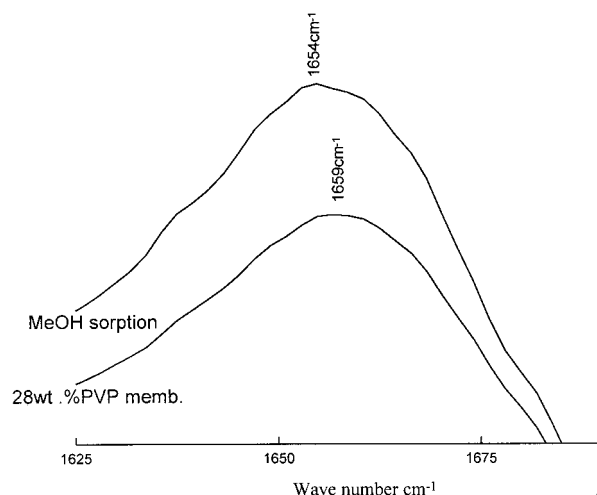


Figure 8 IR spectra of blend membrane with 28 wt % PVP content swollen in methanol.

ticipating in the hydrogen bonding with methanol in the feeds. As a result, the PVP act as a carrier for pervaporation separation of MeOH from MTBE, and, thus, the partial flux of methanol increased with the PVP content increasing. The IR spectrum of the blend membrane swollen in methanol shows that the carbonyl band shifts to lower frequency, indicating that the carbonyl functions as an interaction site during pervaporation permeation process (Fig. 8). For the polyblend-MeOH-MTBE system, it could be inferred that the MeOH molecules have more opportunity to be dissolved in the blend membrane than that for the MTBE molecules. As a result, MeOH molecules occupy many carbonyl groups and much more hydrophilic groups of the membrane polyblend with increasing MeOH content in feed. Generally, the distribution of the dissolved molecules in the polymer is dependent on the affinity between the small molecules and the polymer, just like the orientation of surfactant molecules on water surface. The dissolved methanol molecules left few hydrophilic groups for MTBE molecules and also created obstacles for MTBE transport through the membrane. So MeOH molecules preferentially permeate the blend membranes, and the partial flux of MeOH is much higher than that of MTBE for the same feed and blend membrane compositions.

Additionally, the increasing magnitude of partial flux of MeOH for the feed mixture with 38.78 wt % methanol content is stronger than those for the other two feeds in Figure 7. This phenomenon can be explained in the terms of the plasticization

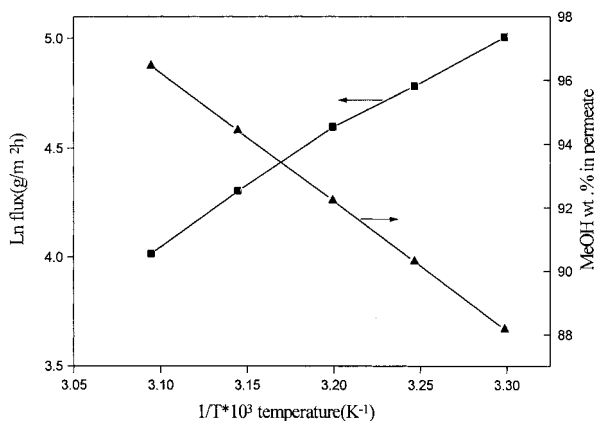


Figure 9 Influence of the operation temperature on total flux and methanol content in permeate of blend membrane with 28 wt % PVP content for feed with 14.45 wt % methanol.

effect exhibited by the permeating molecules, and the plasticization effect is greater for the higher methanol content in the feed. The more methanol in the feed, the more hydroxyl-carbonyl hydrogen bonding in the polyblend as the PVP contents increasing.

Figure 7 also shows the partial flux of MTBE increases with increasing the PVP content in blend membranes. The PVP, as a proton-acceptor in the membranes, will take part in hydrogen bonding with hydroxyl of chitosan and, thus, liberates some hydroxyl groups of chitosan from the complicated inter- and intramolecular interaction within pure chitosan. As a result, the liberated hydroxyl groups have opportunity to form hydrogen bonding with MTBE molecules, particularly for the blend membrane with higher PVP content. For the membranes with higher PVP contents, there are more interactions between liberated hydroxyl groups and MTBE, and, thus, the partial flux of MTBE starts to increase. As a result, the separation factor of three feeds correspondingly decreases with increasing PVP content in blend membrane, as listed in Table I, owing to the partial flux of MTBE increasing.

Influence of the Operation Temperature on the Pervaporation Properties

The temperature dependence of pervaporation has been investigated over a temperature range of 30–50°C for the blend membrane with 28 wt % PVP contents. Figure 9 illustrate the total flux and the methanol content in permeate as a func-

tion of temperature for feed with 14.45 wt % methanol.

Generally, the temperature dependence of the permeation flux is described by an Arrhenius-type exponential relation with the apparent energy for permeation. In Figure 9, the methanol content in permeate gradually increases with the feed temperature increasing, but the pervaporation flux gradually decreases with the feed temperature, holding the reverse changing trend compared with the general results.¹⁷ According to the above FTIR results of membrane with 28 wt % PVP as the temperature increases, the carbonyl—hydroxyl hydrogen bonding decreases, and, thus, there are relatively more carbonyl groups participating in hydrogen bonding with methanol. As a result, the methanol concentration in permeate increased with increasing the temperature. On the other hand, maybe the inside structure trend to be the pure chitosan after the carbonyl groups free from the carbonyl—hydroxyl hydrogen bonding with chitosan during the temperature changing, and, thus, the permeation flux decreased.

According to Figure 9, the corresponding total apparent activation energy is -19.96 KJ/mol. The activation energy is only an empirical parameter that relates temperature dependence of membrane matrix, and it is a combination of enthalpy of permeant sorption in the membrane and the activation energy of permeant diffusion in the membrane. While the activation energy of diffusion is normally positive, the enthalpy of sorption can be either positive or negative, depending on whether the sorption process is endothermic or exothermic. Kakizaki et al.¹⁸ found the magnitude and the sign of sorption enthalpy can change when the polymer undergoes the glass transition. Admittedly, it is not clear at present time whether the temperature dependence of pervaporation properties of chitosan-PVP blend membrane is caused by the glassy transition or the second transition of membrane materials. The glassy transition temperature of a wet chitosan membrane is regarded to be substantially lowered because of the strong plasticization effect of MeOH molecules in feed. This is supported by the experimental observation that the dense homogeneous membrane become soft and elastic in feed but becomes quite rigid when completely dried. Moreover, the IR spectra of chitosan-PVP polyblend showed that there seemed to have a conformational change with the increasing temperature, and this change on the chain-chain interaction may also affect the sorption enthalpy,

accounting for the flux changing with the temperature increasing.

CONCLUSION

Blend membranes of chitosan with poly(*N*-vinyl-2-pyrrolidone) (PVP) are made from aqueous solutions, as supported by the IR spectra investigation of the carbonyl—hydroxyl hydrogen bonding in the blends, which provides evidence that the compatibility of two polymers is on a molecular level. Meanwhile, the IR spectra also explored the interaction changing during increasing temperature and indicated that a significant conformational change took place. Furthermore, the blend membranes were tested for separation of methanol from MTBE. The influences of the membrane composition and the feed composition were investigated. Methanol preferentially permeates through all the tested membranes, and the partial flux of methanol significantly increases with the PVP content increasing. The temperature dependence of pervaporation performance indicated that there seemed to have a significant conformational change with increasing the operation temperature. Combined with IR results, the pervaporation properties are in agreement with the structure characteristics that were evaluated, that is, the characteristics of hydrogen bonding between PVP and chitosan in polyblend and the interaction changing during increasing temperature.

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