Effect of Compatibility of Cellulose Acetate/Poly(vinyl butyral) Blends on Pervaporation Behavior of Their Membranes for Methanol/Methyl *tert*-Butyl Ether Mixture

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ABSTRACT: Binary blends and their blend membranes of cellulose acetate (CA) and poly(vinyl butyral) (PVB) are prepared by solution blending. The compatibility of the blends is studied by viscometry and Fourier transform IR. It is found that the incompatibility of the blends is markedly manifested when the weight fraction of PVB in the CA/PVB blends (W_{PVB}) is located at higher regions. On the other hand, compatibility is obtained for the CA/PVB blends with lower W_{PVB} values, especially at about 0.2. This compatibility is believed to play a key role in the good pervaporation behavior of CA/PVB blend membranes. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2434–2439, 2002

Key words: compatibility; polymer blend; pervaporation membrane; methanol; methyl *tert*-butyl ether

INTRODUCTION

Pervaporation separation represents one of the most effective and energy-saving means to a wide range of separation processes.[1] Searching for new polymeric materials for pervaporation membranes presents continuous research challenges.[2] Moreover, polymer blends are of great interest because they are the least expensive and most versatile way of achieving materials with new desirable properties.[3] Therefore, blend or composite membranes[4–11] in the pervaporation membrane field were used extensively for obtaining high-performance membranes, in spite of the dehydration of organic solvents, removal of volatile organic compounds from water, and separation of organic–organic mixtures. However, most polymer–polymer blends are immiscible thermodynamically or conditionally compatible.[3]

As is well known, cellulose acetate (CA) is one of the most important materials for membranes; poly(vinyl butyral) (PVB) is an alcohol-soluble polymer that is also used as a membrane material.[12] In the present study a trial was made to prepare a new CA/PVB blend system, examine their compatibility, and investigate the pervaporation behavior of their membranes for a methanol/methyl *tert*-butyl ether (MTBE) mixture, which is an important system for separation in industry. Much work was done on it recently.[13–16]

EXPERIMENTAL

Materials

CA {39.1 wt % acetyl content, intrinsic viscosity at 30°C with dioxane ($[\eta]_{dioxane}^{30°}$) = 117.4 mL/g, vis-

cosity-average molecular weight (M_η) = 3.30 $\times$ 10^4, according to the Mark–Houwink equation[17] $[\eta] = 0.1505M_\eta^{0.64}$} and PVB (69–77 wt % butyralization, $[\eta]_{dioxane}^{30°}$ = 118.6 mL/g) were purchased from Shanghai Chemical Reagent Supply Station. Dioxane and methanol were reagent grade and MTBE was industrial grade. All the products were used directly without further purification.

Intrinsic Viscosity Measurement

Solutions of CA, PVB, and their blends in dioxane were prepared at 45°C for 24 h and then filtered through G2 sintered glass filters. A viscosity measure was made with an Ubbelohde dilution viscometer at 30.00 $\pm$ 0.02°C. The flux times were recorded with an accuracy of $\pm$0.05 s. An extrapolation procedure from data obtained for five concentrations of solutions was used to evaluate the intrinsic viscosity.

FTIR Measurements

All the FTIR spectra of the CA/PVB blends were recorded on a Vector spectrometer at room temperature. Solution samples with a concentration of 3 g/mL were used, and the absorption of dioxane solvent was deducted by subtraction from the absorption of the solution. The resolution was 2 cm^{-1} with a repetition of 20 scans.

Membrane Preparation

The casting solutions of CA, PVB, and their blends at various compositions and a concentration of 8 g/100 mL were prepared by dissolving the polymers in dioxane for 3 days at 45°C, and then they were allowed to stand at room temperature. The symmetric membranes with about 20-μm thickness were prepared by pouring the polymer casting solutions onto a poly(tetrafluoroethylene) (PTFE) plate for swelling–releasing experiments, and the composite membranes for pervaporation experiments were obtained by casting the polymer solution on a poly(acrylonitrile) ultrafiltration asymmetric membrane ($\sim$ 60,000 cutoff molecular weight) as a support layer. All the membranes with about 23 μm thickness were prepared by the dry phase transform method. The evaporating temperature of the solvent is maintained at about 30°C.

Swelling and Releasing Measurements

The degree of swelling (DS) and the degree of releasing (DR) of the membrane at a given time are defined by the following equations:

$$DS = \frac{m_t - m_0 (1 - W_{PVB})}{m_0 (1 - W_{PVB})} \times 100\% \qquad (1)$$

$$DR = \frac{m_{eq} - m_t}{m_{eq}} \times 100\% \qquad (2)$$

where m_0, m_t, and m_{eq} are the weights of the dry membrane, swollen membrane at any one time, and swollen membrane at equilibrium in methanol or MTBE, respectively; and W_{PVB} represents the weight fraction of PVB in the CA/PVB blends.

The experiments were carried out by weighting the membrane at room temperature. The free liquid on the surface of the swollen membrane must be removed carefully by using filter paper for the determination of the DS.

Pervaporation Measurements

The pervaporation experiments were conducted with equipment reported previously.[18] The vacuum system of the downstream side was maintained at about 150 $\pm$ 30 Pa. The experiments were carried out in a continuous steady state and constant temperatures of 25, 30, 35, 40, and 50°C for the methanol/MTBE mixture. The permeate was condensed by liquid nitrogen. The permeate flux (J) and separation factor (α) for all membranes were calculated according to a previous report.[19]

$$J = \frac{\Delta g}{s \times \Delta t} \qquad (3)$$

$$\alpha = \frac{y/_1 y_2}{x_1/x_2} \qquad (4)$$

where Δg, s, and Δt are the weight of the permeate, the membrane area, and the time of the experiment, respectively; and x and y represent the weight fractions in the feed and permeate, respectively. Indices 1 and 2 refer to the more permeable (methanol in this study) and the less permeable (MTBE) components, respectively.

RESULTS AND DISCUSSION

Compatibility Study of CA/PVB Blends

Viscometry

Theoretically, the intrinsic viscosity represents the effective hydrodynamic volume of a polymer

molecule in solution.[20] Therefore, its value is dependent on the expanding or shrinking of polymer chain coils in solutions: this chain expanding and chain shrinking will result in the increasing and decreasing of the $[\eta]$ of a polymer in solution, respectively. Figure 1 shows the variation of $[\eta]$ of CA/PVB blends with the composition in dioxane at 30°C. It can be observed that the $[\eta]$ values of the most of the CA/PVB blends deviate from the additive rule of the blends. A positive deviation is demonstrated at the lower weight fraction region of PVB ($W_{PVB} < 0.4$), which reflects the expanding of both coil dimensions of CA and PVB because of strong intermolecular interaction or compatibility between them; negative deviation is displayed at the higher weight fraction region of PVB ($W_{PVB} > 0.4$), which means the shrinking of both coil dimensions of CA and PVB that is due to incompatibility between them.[21–28] In other words, low $[\eta]$ values of the blends are connected with a low degree of overlapping of unlike polymer molecules, indicating that repulsive interactions between the two polymers prevail over attractive interactions. The increase of the repulsive interaction between CA and PVB chains in their blends with high W_{PVB} is probably due to the decreasing of hydroxy and the increasing of side butyl with the increasing W_{PVB} in the blends.

FTIR Spectroscopy

FTIR spectroscopy has proved to be a useful technique for characterization of specific intermolecular interactions between groups on polymer molecules.[29] These intermolecular interactions mainly refer to hydrogen-bonding and dipole–di-
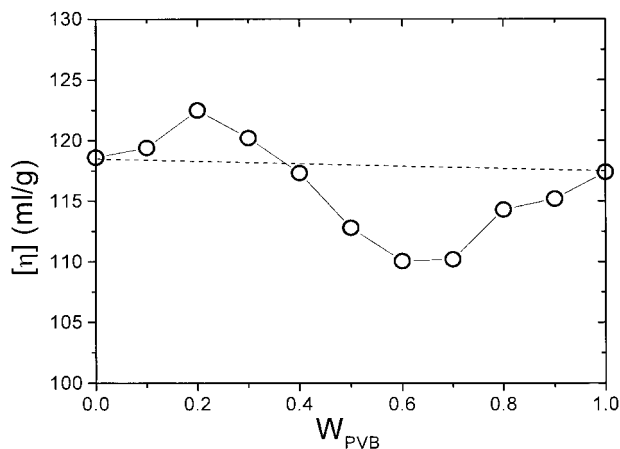
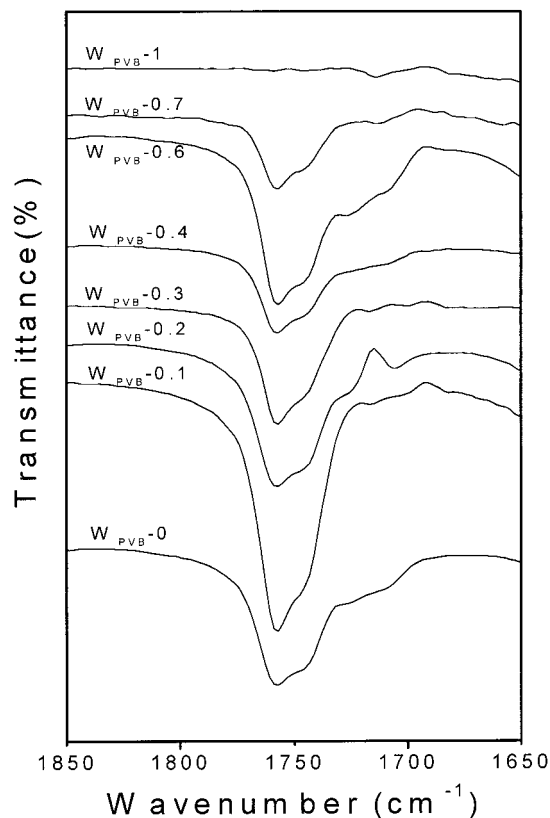**Figure 2** FTIR spectra in the carbonyl absorption region for CA/PVB blends with W_{PVB} = 0, 0.1, 0.2, 0.3, 0.4, 0.6, 0.7, and 1.0.

Figure 1 A plot of the intrinsic viscosity and composition for CA/PVB blends in dioxane at 30°C.

pole interactions and result in the compatibility of polymer blends. Besides frequency shifts or bank broadening,[30] the new peak occurring from the polymer blend also indicates that significant intermolecular interaction is present such as the peak of the hydrogen-bonded carbonyl group.[31] Figure 2 shows the —C=O stretching frequency region of pure CA and its blends with PVB in various compositions. The —C=O main peaks of pure CA and its blend with various compositions are strictly at 1756 cm^{-1}, but a new peak occurs at 1704 cm^{-1} for the CA/PVB blend with W_{PVB} = 0.2, which is attributed to the intermolecular interaction between CA and PVB. Some changing of the spectra of the CA/PVB blends with W_{PVB} = 0.1 and 0.3 also occurs compared to the spectra of the CA/PVB blends with W_{PVB} = 0 and 0.4. Therefore, it is supposed that some intermolecular interaction between CA and PVB in CA/PVB blends with $W_{PVB} < 0.4$ is demonstrated. This is in good agreement with the $[\eta]$ result from the viscometry.

Pervaporation Study of CA/PVB Blend Membranes

DS and DR Study

Figure 3 gives a typical variation of the DS with the time of swelling of CA/PVB blend membranes in methanol and MTBE at 27°C. Figure 4 shows the variation of the equilibrium DS with the composition of CA/PVB blend membranes in methanol and MTBE at 27°C. In methanol the equilibrium DS of the blend membranes with high W_{PVB} (such as $W_{PVB} > 0.6$) is equal to -1 because $m_t = 0$ in eq. (1), which is attributed to the PVB component that is totally dissolved and the CA component that is thoroughly dispersed in the methanol. The equilibrium DS of the blend membranes with $W_{PVB} = 0.3–0.4$ is almost equal to zero; this means that m_t is about equal to $m_0(1 - W_{PVB})$ in eq. (1): the weight of methanol con-
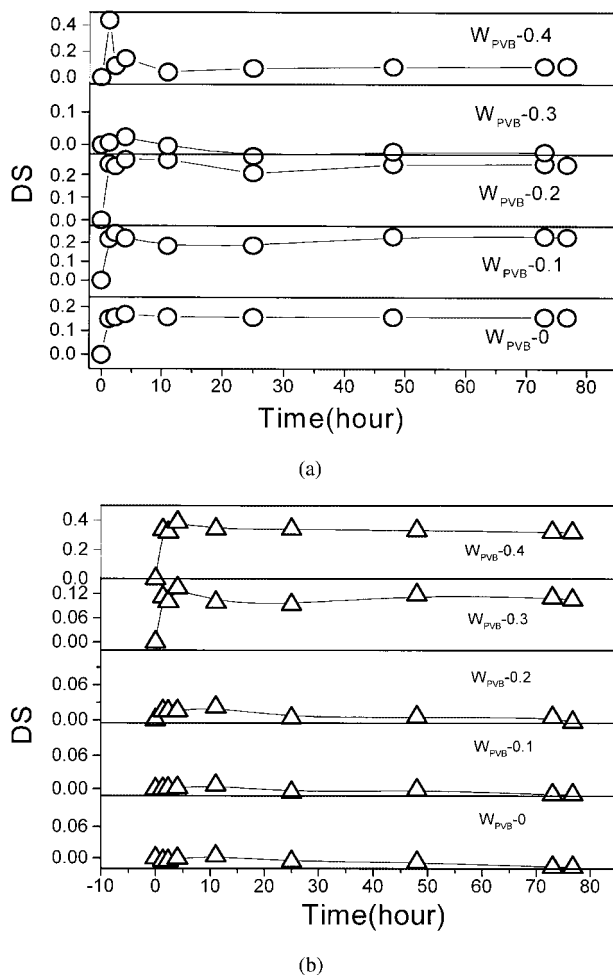
Figure 4 The equilibrium degree of swelling versus the composition for CA/PVB blend membranes in methanol and MTBE.

Figure 3 The degree of swelling versus the time for the CA/PVB blend membrane with $W_{PVB} = 0, 0.1, 0.2, 0.3,$ and 0.4 in (a) methanol and (b) MTBE.
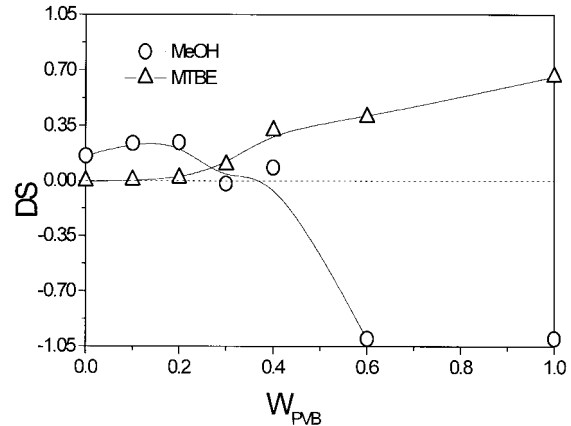
tained in the membrane due to swelling is almost equal to the weight of the PVB component in the membrane that is lost because it dissolves in methanol. Interestingly, the equilibrium DS of the blend membranes with $W_{PVB} = 0.1–0.2$ is larger than that of the pure CA membrane with $W_{PVB} = 0$. This means that the swelling of the PVB component occurs because of intermolecular interaction between the CA and PVB in their blends; in other words, this intermolecular interaction prevents the PVB component from dissolving in the methanol. However, in MTBE the swelling of CA/PVB blend membranes with various compositions is the opposite that in methanol; the equilibrium DS of the blend membranes are almost zero at $W_{PVB} = 0–0.3$, increase rapidly at $W_{PVB} = 0.3–0.6$, and then gradually increase after $W_{PVB} > 0.6$.

Figure 5 gives a variation of the DR of methanol and MTBE with time at 27°C from blend membranes swollen to equilibrium. Figure 6 shows the variation of the equilibrium DR of CA/PVB blend membranes with the W_{PVB}. Clearly, the variation of the DR is very similar to the variation of their DS within the region of $W_{PVB} = 0–0.4$. Also, the equilibrium DR in methanol and in MTBE approach each other with the increasing W_{PVB} in the blend membranes.

Pervaporation Properties

According to the results in Figures 4 and 6, there was hardly any swelling of the CA membrane in MTBE compared to methanol, but there was dissolving and high swelling of the PVB membrane
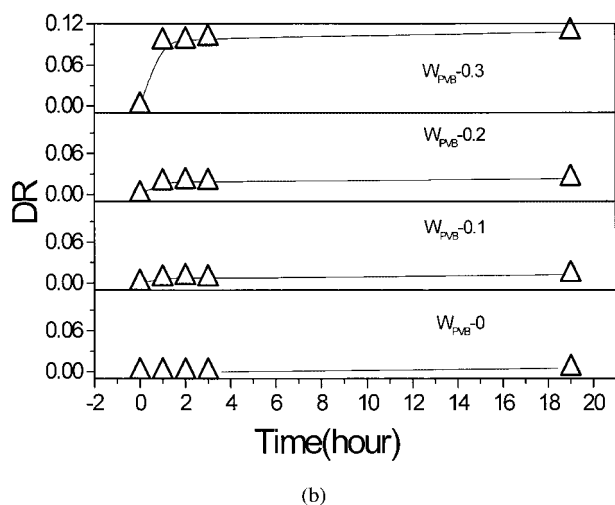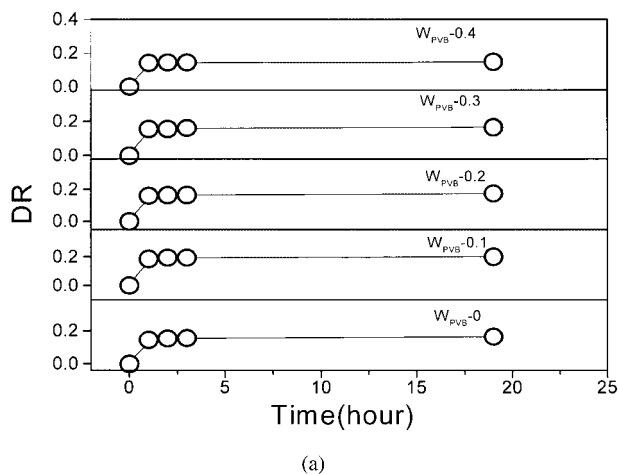
(a)

(b)

Figure 5 The degree of releasing versus the time for CA/PVB blend membranes with W_{PVB} = 0, 0.1, 0.2, 0.3, and 0.4 in (a) methanol and (b) MTBE.

in methanol and MTBE. Therefore, the CA membrane should be very selective for separating methanol from a methanol/MTBE mixture, and the PVB membrane should have very high permeate but small selective fluxes. As expected, the pervaporation behaviors of the CA/PVB blend membranes tend toward those of the pure CA membrane with the decreasing of the W_{PVB} in the CA/PVB blend membranes (i.e., high separation factor and low permeate flux) and vice versa as the increasing of W_{PVB} in the CA/PVB blend membranes. Interestingly, the permeate flux of the CA/PVB blend membrane was changed rapidly at about W_{PVB} = 0.4; in other words, the values of the permeate flux are lower and higher than those from the additive law before and after about W_{PVB} = 0.4. The permeate flux curve of the CA/PVB blend membranes (Fig. 7) is the opposite
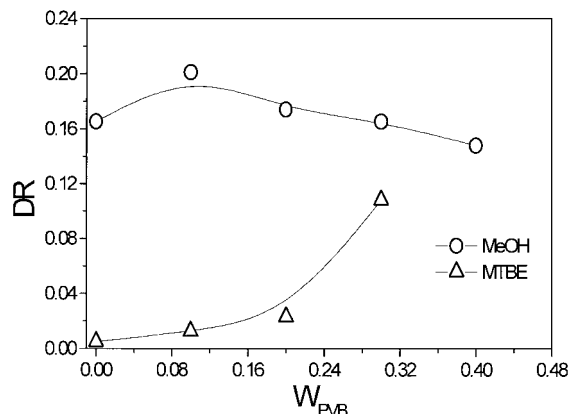

Figure 6 The equilibrium degree of releasing versus the composition for CA/PVB blend membranes swelled to equilibrium in methanol and MTBE.

of the [η] curve of the CA/PVB blends mentioned in Figure 1. Therefore, the negative additive law of the permeate flux of the blend membrane with lower W_{PVB} is assigned to the strong intermolecular interaction or compatibility between CA and PVB molecules in the CA/PVB blends with lower W_{PVB}. By contrast, the positive additive law of the permeate flux of the blend membrane with higher W_{PVB} is due to the lack of intermolecular interaction or incompatibility between CA and PVB molecules in the CA/PVB blends with higher W_{PVB}, which results in the dissolving of the PVB component in the CA/PVB blend membranes in methanol (negative DS, Fig. 4). Extremely low separa-
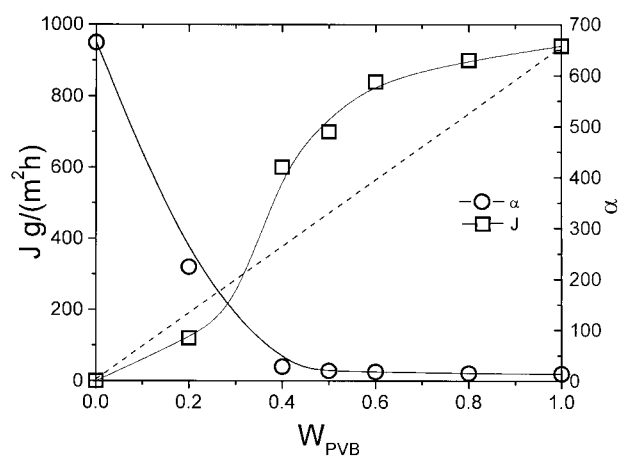

Figure 7 The permeate flux and separation factor versus the composition for CA/PVB blend membranes with a methanol concentration of 3 wt % in the feed of a methanol/MTBE mixture at 30°C (P_{dw} = 150 ± 30 Pa).

tion factors also occur for the CA/PVB blend membranes with $W_{PVB} > 0.4$. These results are similar to those of gas separation membranes (i.e., the permeability of the membrane from immiscible blends is larger than that of the membrane from miscible blends).[32]

CONCLUSIONS

The following conclusions can be drawn from the present study:

1. The CA/PVB blends with a lower weight fraction of PVB ($W_{PVB} < 0.4$) are compatible according to the $[\eta]$ and FTIR of the blends.
2. The high separation and low permeate fluxes of the CA/PVB blend membrane for the methanol/MTBE mixture are related to the compatibility of the CA/PVB blends and vice versa for the incompatibility of the CA/PVB blends.
3. The compatibility of CA/PVB is favorable to resistance to methanol for PVB because of the intermolecular interaction between CA and PVB molecules.

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