Polymer Bulletin 29, 423–429 (1992)

**Polymer Bulletin**

# Pervaporation of water-ethanol through poly(vinyl alcohol)/ chitosan blend membrane

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## SUMMARY

Blend membrane consisting of poly(vinyl alcohol)(PVA) and chitosan was prepared from solvent casting technique for effective separation of ethanol-water mixture by pervaporation. Selectivity toward water and the flux through the blend membrane, crosslinked with glutaraldehyde at the concention of 4 x $10^{-6}$ mol/g, were ~450 and 0.47 kg/$m^2$.hr, respectively.

## INTRODUCTION

We have previously reported on the pervaporation performance of the modified chitosan membranes(1-5) and modified polyacrylonitrile membranes(6-7) to separate water from aqueous ethanol mixtures. A basic assumption behind conducting these studies was that good selectivities for water could be obtained using ionic or hydrophilic groups or by the inclusion of these groups in the base membrane structure.

Blending the membrane is another technique to enhance the pervaporation performance in membrane application. Cabasso et al. used cellulose acetate-polyphosphonate blend membrane for separating benzene-cyclohexane(8). Suzuki et al. intended to increase the selectivity in water-ethanol separation using cellulose nitrate-poly(methyl methacrylate) membrane(9).

Several studies on the poly(vinyl alcohol)(PVA)/chitosan blend membrane have been reported(10-14). We have already reported on the properties, swelling kinetics and the controlled release of drugs through crosslinked PVA/chitosan blend membranes(10-11). According to Miya et al.(12-13) chitosan forms a clear homogeneous blend with PVA, and the tensile strength of blend is greater than the component values. Also Uragami et al.(14) prepared crosslinked PVA/chitosan blend with a fixed amount of crosslinking agent and studied for active transport of halogen ion through PVA/chitosan blend membrane. Reinhart and Peppas(15) reported the diffusion of bovine serum albumin in highly crosslinked PVA membrane.

In this study blend membrane was prepared from chitosan and PVA, and crosslinked with glutaraldehyde in varying concentration. The pervaporation performance of the blend membrane to separate water-ethanol mixture will be reported here.

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## EXPERIMENTAL

### Materials

Chitosan, whose degree of deacetylation was calculated to be 76% from the amino content, was purchased from Tokyo Kasei Co.(Japan), and was used after passage through 200 mesh sieve. PVA was purchased from Kuraray Co. (Japan). The degree of polymerization of PVA was 1570±50 and the saponification degree was 98.5%. Glutaraldehyde was purchased from Kokusan Chemical Work (Japan).

### Preparation of membrane

Casting solution was prepared by blending PVA:chitosan(=60:40). PVA(1.5g) was first dissolved in 50 ml of deionized water at 90°C. One gram of chitosan was added into the PVA solution. After 30 minutes, 50 ml of 1.5 wt% aqueous acetic acid solution was poured into the PVA/chitosan solution, followed by the addition of the known amount of glutaraldehyde (0.3 ~ 30 mol/g). Before gelation occurs, membrane was prepared by pouring casting solution onto a rimmed acryl plate and allowing the water to evaporate at 40 °C in a convective oven for a day. After immersing the membrane in 1*N* NaOH for a day, it was washed repeatedly with water to eliminate any unreacted glutaraldehyde and kept in deionized water(25 °C). The thickness of the membrane used in this work was 100±10 μm. PVA and chitosan homopolymer membranes were also obtained by the same methods as described above.

### Measurements

Infraed spectra were measured by Nicolet 5DX FT-IR spectrometer. Wide angle X-ray diffraction (WAXD) patterns were recorded with a flat-film camera using nikel-filtered Cu-Kα radiation produced by Phillips X-ray. Mechanical properties were measured by Instron Type universal testing machine (Tensilon/UTM-4-100, Japan), using samples of 5mm width cut from blend and homopolymers under dry and wet state. The test was carried out using a crosshead speed of 4mm/min and a gauge length of 20 mm. The tensile strength and elongation at break of samples were calculated. Thermal properties of materials were measured using differential scanning calorimeter(DSC, DuPont Model 910) with a heating rate of 20 °C/min. Thermogravimetric analyzer(TGA, DuPont Model 951) was used to investigate the thermal stability of blends.

### Degree of swelling

The weight of completely dried sample was measured directly, and the sample was dipped into the petri dish filled with a different pH buffer solution where temperature was measured at 37 °C in an incubator. The degree of swelling of these samples was calculated with the following equation,

$$\text{Degree of Swelling } (Q_w) = \frac{X_2 - X_1}{X_1} \qquad (1)$$

where $X_1$ and $X_2$ are the weight of dry and swollen samples measured at a different time period, respectively.

### Pervaporation experiment

A detailed procedure for performing the pervaporation experiment can be found elsewhere(16).

## RESULTS AND DISSUSION

Crosslinked PVA/chitosan membrane showed a reasonable mechanical strength as discussed in the references(10-11). Mechanical properties of the blend are greater than each component value. Crosslinking makes a contribution to enhance the tensile strength in both dry and wet states and the thermal stability of the blend. The swelling study indicates that the crosslinking reduces the swelling capacity of the membrane due mainly to the growing crosslinking density and also to the discounted ability of hydrogen bonding between water molecules and hydroxyls and amino groups in the PVA and chitosan blend.

Infrared spectra for PVA, blend and chitosan (Fig. 1) revealed that the crystallization - sensitive band of PVA at 1140cm$^{-1}$ is observed with a similar intensity without a significant

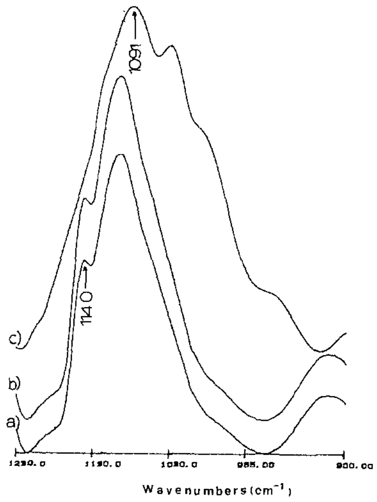

Figure 1. FTIR spectra for a)PVA, b) uncrosslinked PVA/chitosan(60/40) blend membrane and c)chitosan.

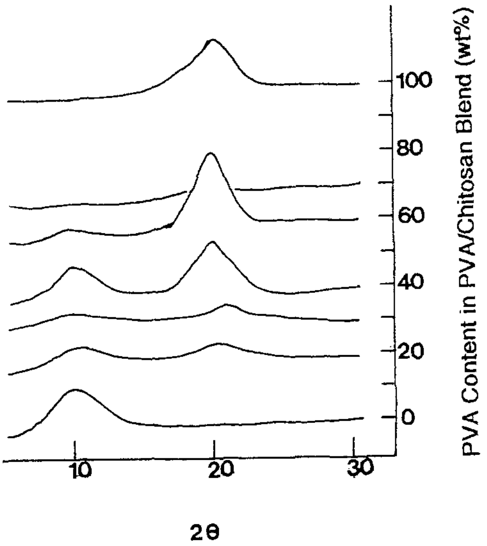

Figure 2. X-ray diffraction patterns of uncrosslinked PVA/chitosan blend membranes. Numbers represent the blend ratio of PVA:chitosan.

change in frequency. The most intensive band at 1091cm$^{-1}$ appears clearly for pure chitosan only. According to Miya et al.(12-13), disappearance of this peak means that an intermolecular interaction between PVA and chitosan disturbs a crystallization of chitosan in a blend state. In the IR spectra of crosslinked blends prepared from different concentration of crosslinking agent, a characteristic peak for the crystalline region in PVA appears at 1140 cm$^{-1}$, and the band intensity decreases with increasing the concentration of crosslinking agents.

In Figure 2 wide angle X-ray diffraction patterns (WAXD) of PVA, chitosan and the blend membranes are shown. PVA exhibited a typical peak that appeared at $2\theta = 20°$. This peak was assigned to be a mixture of (101) and (200). Typical pattern for chitosan appeared at around $2\theta = 10°$. According to Sakurai et al.'s analysis of X-ray patterns in chitosan film(17), peaks appeared at around $2\theta = 10°$ are assigned to be (001) and (100). WAXD patterns show that the blending serves to decrease the peak intensity except those of blend films having PVA content of 40 and 60 %. When we crosslinked the typical 60:40(PVA:chitosan) blend membrane, the peak intensity decreases with increasing the concentration of the crosslinking agent.

Fig. 3 illustrates the swelling behavior of the blend membrane in 90 wt% aqueous ethanol mixture tested at 37 °C.

The pervaporation performance of the blend membrane was shown in Fig. 4 as a function of blend ratio in PVA/chitosan. Flux generally shows a bell-type curve. Selectivity was greater for the blend membranes having 40:60 and 60:40 blend ratio than the rest of the membranes. Particularly, $\alpha$ was about 350 for a 60:40 PVA/chitosan blend membrane. The reason why the selectivity was greater at 40:60 and 60:40 blend ratio can be related with the X-ray diffraction data, where the crystalline character appeared at these blend ratio. It is not

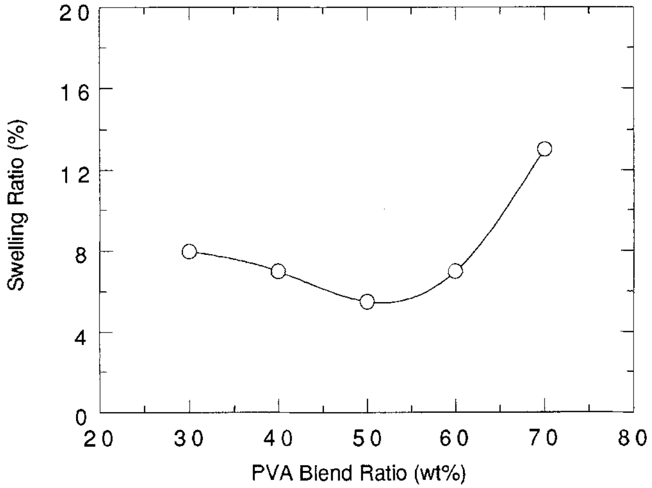

Figure 3. Swelling of crosslinked PVA/chitosan blend membranes in 90 wt% ethanol solution measured at 40 °C.

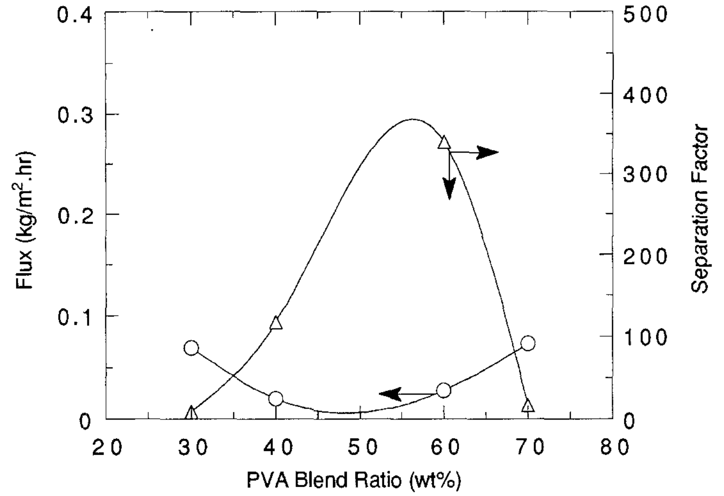

Figure 4. Effect of blend ratio on the flux ( O ) and separation factor (Δ) of crosslinked PVA/chitosan blend membrane measured at 90 °C and using 90 wt% feed ethanol solution.

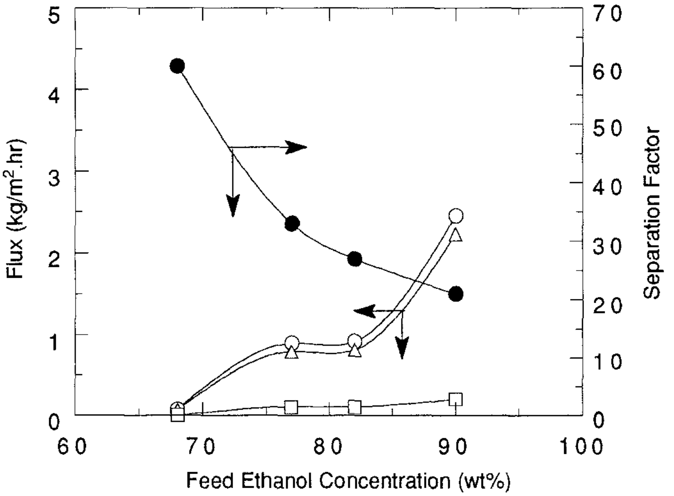

Figure 5. Effect of feed ethanol concentration on the total flux (O), water flux( Δ ), ethanol flux ( □ ) and separation factor ( ● ) of crosslinked PVA/chitosan (60/40) blend membrane measured at 60 wt%.

still clear why the crystalline character appears or disappears upon blending, but we speculate that there exists a specific interaction such as hydrogen bonding between hydroxyls and amino groups in PVA and chitosan in the blend.

Figure 5 shows the effect of feed ethanol concentration on the pervaporation performance of the membrane having the highest crystallinity. Feed ethanol concentration varies from 65 - 90 wt% maintaining at 60 °C. Flux generally increases and the selectivity decreases upon increasing the feed ethanol concentration. Note that the permeate ethanol concentration was only about less that 5 wt% over the whole feed ethanol concentration range. The pervaporation flux increases and the selectivity decreases drastically upon increasing the temperature.

Figure 6 illustrates the effect of crosslinking in 60:40 PVA/chitosan blend membrane on the pervaporation performance. Selectivity increases upon crosslinking while the flux was generally in the range of 0.8 - 1.0 kg/m$^2$.hr. The selectivity was about 450 with the flux value of 0.47 kg/m$^2$.hr, when the concentration of crosslinking agent was 4 x 10$^{-6}$mol/g.

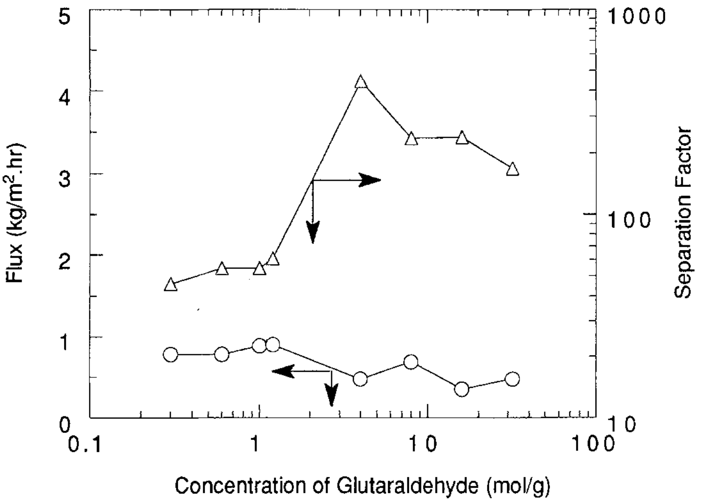

Figure 6. Effect of concentration of crosslinking agent on the separation factor(△) and flux(○) of blend membrane measured at 60 °C and using 90 wt% feed ethanol solution.

## CONCLUSION

Blend membrane consisting of PVA and chitosan was prepared from solvent casting technique. IR analysis showed that there existed an intermolecular interaction between PVA and chitosan. Pervaporation performance of the blend membrane showed that the selectivity was about 450 with the flux value of 0.47 kg/m$^2$.hr, when the concentration of crosslinking agent was 4 x 10$^{-6}$ mol/g.

## ACKNOWLEDGEMENTS

We are deeply indebted to the Korean Ministry of Education - 1991 Research Fund for Advanced Materials.

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Accepted July 29, 1992 S