

# NOTES

## Pervaporation Separation of Water–Ethanol Mixtures Through PVA–Sodium Alginate Blend Membranes

### INTRODUCTION

Poly(vinyl alcohol) (PVA) has been known as one of the widely used membrane materials for the separation of water–ethanol solution by pervaporation.<sup>1–5</sup> In general, PVA membranes show high permselectivities and relatively low permeabilities.<sup>6</sup> Their high water permselectivity is due to their good hydrophilicity and preferential attraction of water, whereas their low permeability is due to their close molecular packing and high degree of crystallinity.

To increase the water permeability of the PVA membrane without decrease in permselectivity or even with better permselectivity in water–ethanol separation, blending of PVA with sodium alginate was considered in this article. Sodium alginate was selected for blending with PVA because the rigidity and bulkiness of the membrane material is as important a factor as the hydrophilicity for the effective separation of water–ethanol with high flux. While the hydrophilicity is needed for the preferential attraction of water for high permselectivity, the high rigidity and bulkiness of the membrane materials are necessary for easy diffusion of permeants. On this basis, with excellent hydrophilicity and a rigid and bulky main chain, sodium alginate is a good material for this purpose.

In this work, sodium alginate was mixed with PVA to prepare blend membranes. The morphology and polymer structure of the membranes were characterized with scanning electron microscopy (SEM) and X-ray diffractometry. The pervaporation separation of water–ethanol mixtures was also carried out with the blend membranes.

### EXPERIMENTAL

#### Materials

Poly(vinyl alcohol) with 99% hydrolysis and  $M_n = 50,000$  g/mol was purchased from the Aldrich Chemical Co. Sodium alginate was purchased from the Tokyo Kasei, and high-performance liquid chromatography (HPLC) grade ethanol was purchased from the Merck Co. All three were used without purification.

#### Membrane preparation

Two grams of PVA and 2 g of sodium alginate were dissolved in 100 mL of distilled water in different flasks. Solutions with different polymer compositions (PVA/sodium alginate, 0/100, 25/75, 50/50, 75/25, and 100/0) were prepared from the two solutions. Each solution was cast on an acrylate plate and dried at room temperature. The dried films were 20  $\mu\text{m}$  in thickness. The blend membranes were in good conditions in terms of the mechanical properties and dimensional stability in feed solutions.

#### Characterizations

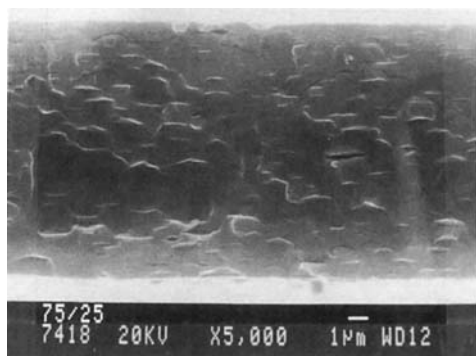
The crystallinity and polymer structure of the blend membranes were studied with an X-ray diffractometer (model D/MAX IIIB Rigaku) using nickel-filtered Cu-K $\alpha$  radiation with a wavelength of 1.54  $\text{\AA}$ . The morphology of the blend membranes was characterized by using scanning electron microscopy (SEM) (model JSM-80A, JEOL).

#### Pervaporation Measurements

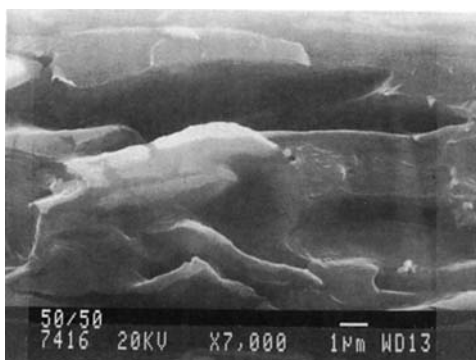
Pervaporation measurements were carried out by using a general pervaporation test cell, purchased from the Millipore Co. The membrane surface was 11.28  $\text{cm}^2$ , and downstream pressure was 0.3 mm Hg. The feed solution was 90 wt % of ethanol with a volume of 1 L. This ensures that the change of the feed composition is negligible during the time needed for a pervaporation experiment. The pervaporation measurements were carried out at various feed solution temperatures (30, 40, 50, and 60°C). The total flux through the membrane was measured by weighing the liquid mixture removed from a reservoir. The partial flux and permeate vapor composition were determined by analysis of the condensed permeate by a gas chromatograph (Perkin-Elmer 8500). The separation factor was defined as follows:

$$\alpha = (W_{\text{H}_2\text{O}}/W_{\text{ethanol}})_{\text{Permeate}} / (W_{\text{H}_2\text{O}}/W_{\text{ethanol}})_{\text{Feed}}$$

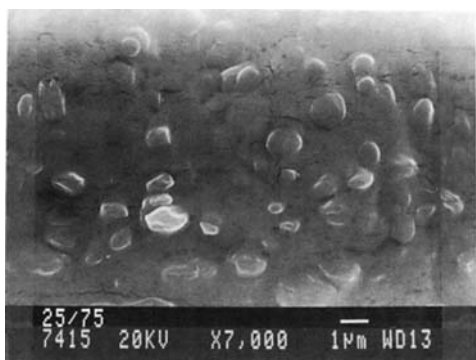
where  $W_{\text{H}_2\text{O}}$  is the weight fraction of water and  $W_{\text{ethanol}}$  is the weight fraction of ethanol.



(a)



(b)



(c)

**Figure 1** Scanning electron micrographs of the fracture of blend membranes for PVA/sodium alginate compositions (in weight percent): (a) 75/25, (b) 50/50, and (c) 25/75.

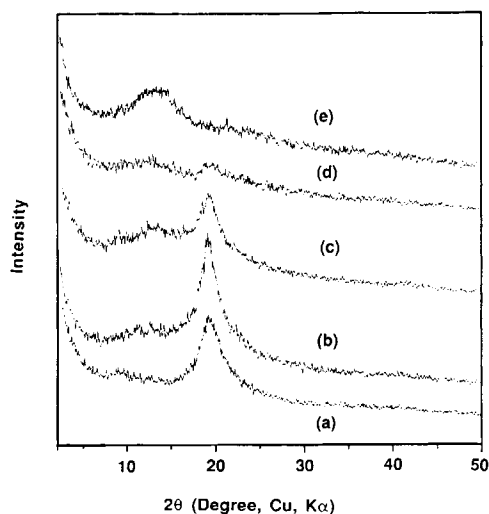
## RESULTS AND DISCUSSION

### Membrane Preparation

Figure 1 presents the SEM microphotographs of the fractures of the blend membranes. For membrane composi-

tions of 25/75 and 75/25 in PVA/sodium alginate, the membranes are phase separated: For the first membrane, PVA is the dispersed phase and sodium alginate the continuous phase. The shape of the PVA dispersed phase is round, and its size is about 1  $\mu\text{m}$ . For the second membrane, sodium alginate is the dispersed phase and PVA the continuous phase. The shape of the sodium alginate dispersed phase is almost rectangular, and its size is also about 1  $\mu\text{m}$ . However, the blend membrane containing equal amounts of PVA and sodium alginate shows no phase separation. For this membrane, the two components are in equal amount and form a cocontinuous phase. From these results, it is found that the two polymers, PVA and sodium alginate, are comparable enough for the formation of pervaporation membranes with good mechanical strengths.

Figure 2 shows the X-ray diffractograms of the blend membranes. The PVA membrane is semicrystalline with  $d$  spacing (4.43  $\text{\AA}$ ) of crystallites, and the sodium alginate membrane is totally amorphous with average intermolecular distance 6.55  $\text{\AA}$ . PVA has a flexible backbone, while sodium alginate has a bulky and rigid backbone structure. The flexible PVA backbone is favorable for the close molecular packing and crystallization, but the bulky and rigid backbone of the sodium alginate is unfavorable for the crystallization. The X-ray diffraction patterns of the blend membranes vary with their compositions. The crystallinity decreases with increasing sodium alginate content. The membrane containing 75 wt % of sodium alginate shows a small amount of crystallinity (from very weak PVA crystalline peak at  $2\theta$ ). From this result, it was found that the two polymers, PVA and sodium alginate, were mixed together in a certain range and affect each other in the crystallization



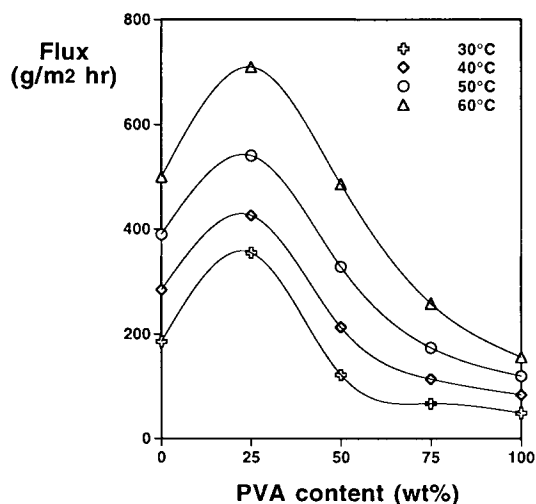
**Figure 2** Wide-angle X-ray diffractograms of the blend membranes for PVA/sodium alginate compositions (in weight percent): (a) 100/0, (b) 75/25, (c) 50/50, (d) 25/75, and (e) 0/100.

during the membrane formation. By blending of PVA with sodium alginate, the close packing of the PVA molecules for the formation of crystallites was hindered by the sodium alginate molecules, and blend membranes with less crystallinities were formed.

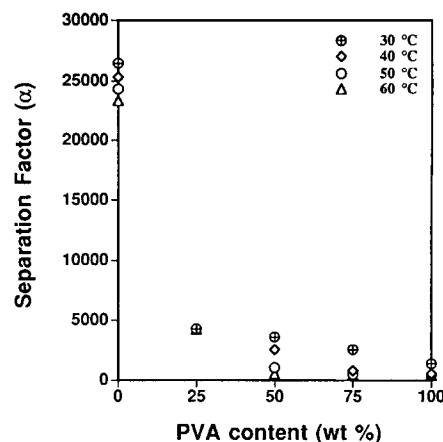
### Effect of Composition

Figure 3 shows that the total fluxes depend strongly on the composition of the blend membranes and increase with increasing content of the sodium alginate, up to 75 wt % of sodium alginate. The increase in total flux maybe due to the bulkiness of the sodium alginate, which has a rigid six-membered ring structure in its backbone that is unfavorable for the close molecular packing and even for the crystallization. The blending of sodium alginate with poly(vinyl alcohol) definitely brings a loose molecular packing, which is favorable for easy diffusion of permeants. Consequently, the total flux through the blend membranes containing higher content of sodium alginate is higher.

Figure 4 shows that the separation factors of blend membranes increases gradually with increasing content of sodium alginate. The pure sodium alginate membrane shows a separation factor higher than 25,000 at 30°C, while pure PVA membrane shows only about 2000. The big difference in separation factors between the two membranes (PVA membrane and sodium alginate membrane) and the variation in the separation factors as a function of the composition of blend membranes are probably due to the hydrophilicity difference. Sodium alginate is a polyanionic polymer containing anionic groups on the polymer main chain, while poly(vinyl



**Figure 3** Total fluxes of the PVA/sodium alginate blend membranes in the pervaporation separation of water/ethanol mixture (10/90 in weight percents) as a function of PVA content.



**Figure 4** Separation factors of the PVA/sodium alginate blend membranes in the pervaporation separation of water/ethanol mixture (10/90 in weight percents) as a function of PVA content.

alcohol) is a nonionic polymer that does not have any ionic group. It is very well known that ionic groups are more polar and more hydrophilic than nonionic groups. Consequently, sodium alginate membrane is much more hydrophilic and absorbs water molecules more selectively than poly(vinyl alcohol). This selective absorption of water molecules of sodium alginate is the reason for the increase in the separation factors of the blend membranes with increasing content of sodium alginate.

### Effects of Temperature

Figures 3 and 4 also show the temperature dependence of the total fluxes and separation factors of the blend membranes, respectively. The total fluxes increase gradually with increasing operating temperature (as in the case of the other membrane). With increasing temperature from 30°C to 60°C, the total fluxes increase almost three times. On the other hand, the behavior of separation factors with increasing temperature is a function of membrane composition, as shown in Figure 4. For the sodium alginate membrane and blend membrane containing 75 wt % of sodium alginate, the variation of the separation factor with increasing operating temperature was minor. However, for the blend membranes composed of 50 wt % or 25 wt % of sodium alginate, the separation factors gradually decrease with the increasing temperatures.

For an explanation of these results, the flexibility of the membrane materials should be considered: Poly(vinyl alcohol) (PVA) has flexible main chains, while sodium alginate has a very rigid six-membered ring structure on the backbone. The blend membranes composed of higher contents of PVA are relatively easier

for local movement of the molecules of the membrane materials and will make larger sizes of free volume. Eventually, the blend membranes with higher content of PVA will show lower separation factors with increasing operating temperature.

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