Characterization of Sodium Alginate and Poly(vinyl alcohol) Blend Membranes in Pervaporation Separation

C. K. YEOM,[1] K.-H. LEE[2]

[1] Chemical Process and Engineering Center, Applied and Engineering Chemistry Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Daedeog-Danji, Taejon 305-606, South Korea

[2] Membranes and Separation Research Center, Applied and Engineering Chemistry Division, Korea Research Institute of Chemical Technology, P.O. Box 107, Daedeog-Danji, Taejon 305-606, South Korea

ABSTRACT: By blending a rigid polymer, sodium alginate (SA), and a flexible polymer, poly(vinyl alcohol) (PVA), SA/PVA blend membranes were prepared for the pervaporation separation of ethanol–water mixtures. The rigid SA membrane showed a serious decline in flux and a increase in separation factor due to the relaxation of polymeric chains, whereas the flexible PVA membrane kept consistent membrane performance during pervaporation. Compared with the nascent SA membrane, all of the blend membranes prepared could have an enhanced membrane mobility by which the relaxation during pervaporation operation could be reduced. From the pervaporation separation of the ethanol–water mixtures along with the temperature range of 50–80°C, the effects of operating temperature and PVA content in membrane were investigated on membrane performance, as well as the extent of the relaxation. The morphology of the blend membrane was observed with PVA content by a scanning electron microscopy. The relaxational phenomena during pervaporation were also elucidated through an analysis on experimental data of membrane performance measured by repeating the operation in the given temperature range. SA/PVA blend membrane with 10 wt % of PVA content was crosslinked with glutaraldehyde to enhance membrane stability in water, and the result of pervaporation separation of an ethanol–water mixture through the membrane was discussed. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci **67**: 949–959, 1998

Key words: pervaporation; sodium alginate/chitosan blend; glutaraldehyde; relaxation; ethanol–water mixture

INTRODUCTION

Usually, hydrophilic polymers are selected as a membrane material for the dehydration from various solvents in the pervaporation process because the water molecule is easily incorporated into the hydrophilic polymeric membrane. Among the hydrophilic membranes, sodium alginate (SA) membrane[1,2] is reported to present the most outstanding membrane performance for the dehydration of ethanol–water mixtures. In the previous work,[2] we found that the excellent pervaporation performance of the SA membrane was attributed mainly to the extraordinary permselectivity to water in the sorption step.

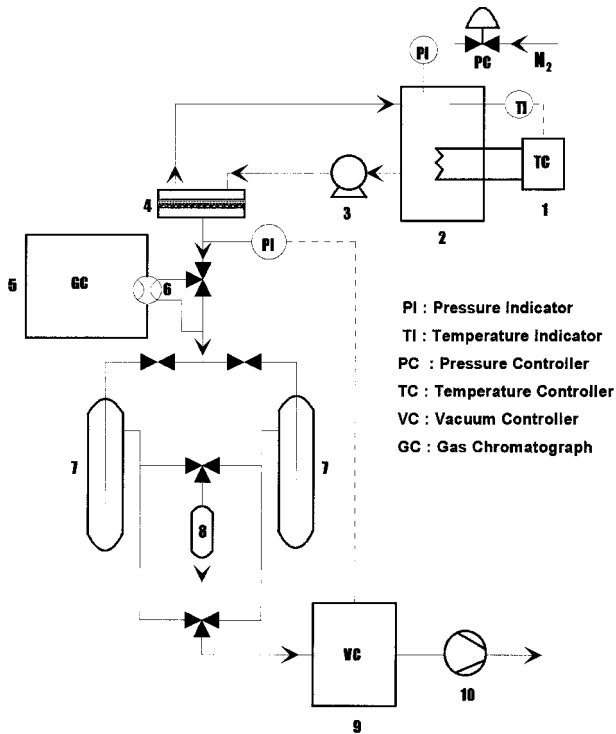However, the SA membrane was observed to

Figure 1 Schematic representation of pervaporation apparatus: 1, temperature controller; 2, feed tank; 3, pump; 4, membrane cell; 5, GC; 6, sample injector; 7, cold trap; 8, vent to atmosphere; 9, vacuum controller; and 10, vacuum pump.
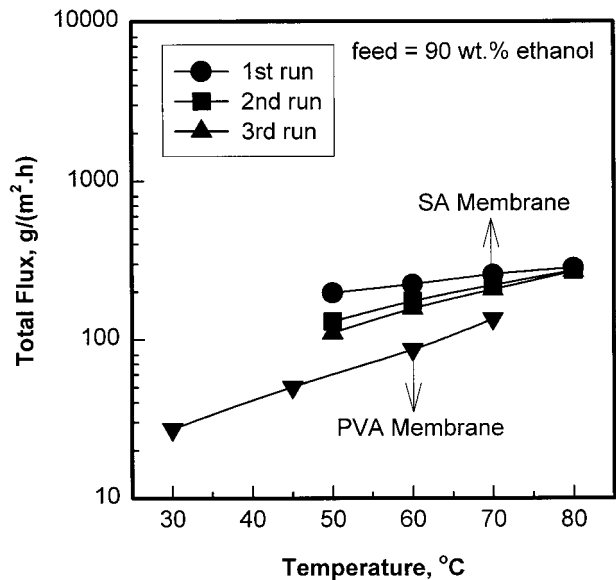

Figure 2 Comparison of total flux of nascent PVA and SA membranes against temperature in the separation of 90 wt % ethanol content of feed obtained in repeating the operation.

membrane is used for the dehydration of an aqueous mixture, is a pronounced anisotropic swelling developed in the membrane by which a phase gradient can be established across the membrane,
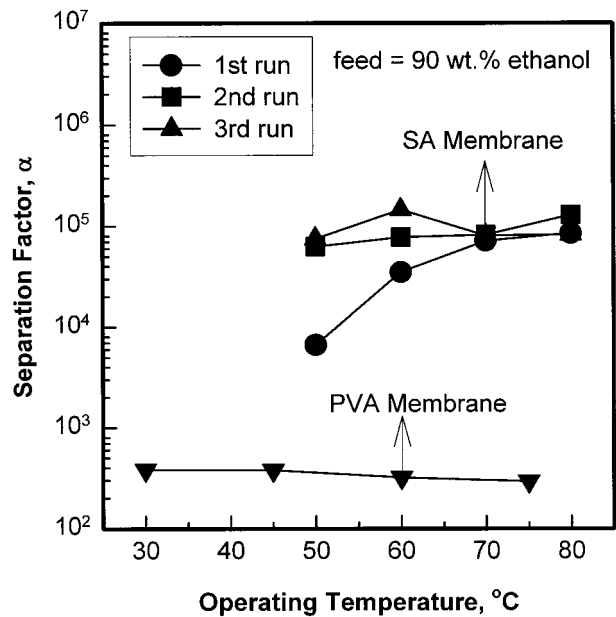
be subjected to a serious decline in flux by a relaxation of polymeric chains during pervaporation process. In particular, glassy polymers with rigid and bulky structure tend to be stressed or relaxed, depending on their thermal condition. A polymer backbone is considered to be in a frozen state below glass transition temperature (T_g), and thus segmental chain motions are drastically reduced, compared with the rubbery state, often causing a serious relaxation of the polymer chains with time. In this case, permeant transport through the glassy membrane is not only dependent on polymer chain motion, but also on the relaxation of the polymeric chains. In other words, relaxation during the pervaporation process may influence membrane performance.[2] The relaxation process takes place significantly near the glass transition region of the polymeric membrane and makes the material structure more dense by the configurational rearrangement of polymeric chains so that flux can be decreased correspondingly.[3] In the pervaporation process, where a glassy polymeric

Figure 3 Comparison of separation factor of nascent PVA and SA membranes against temperature in pervaporation of 90 wt % ethanol content of feed obtained in repeating the operation.
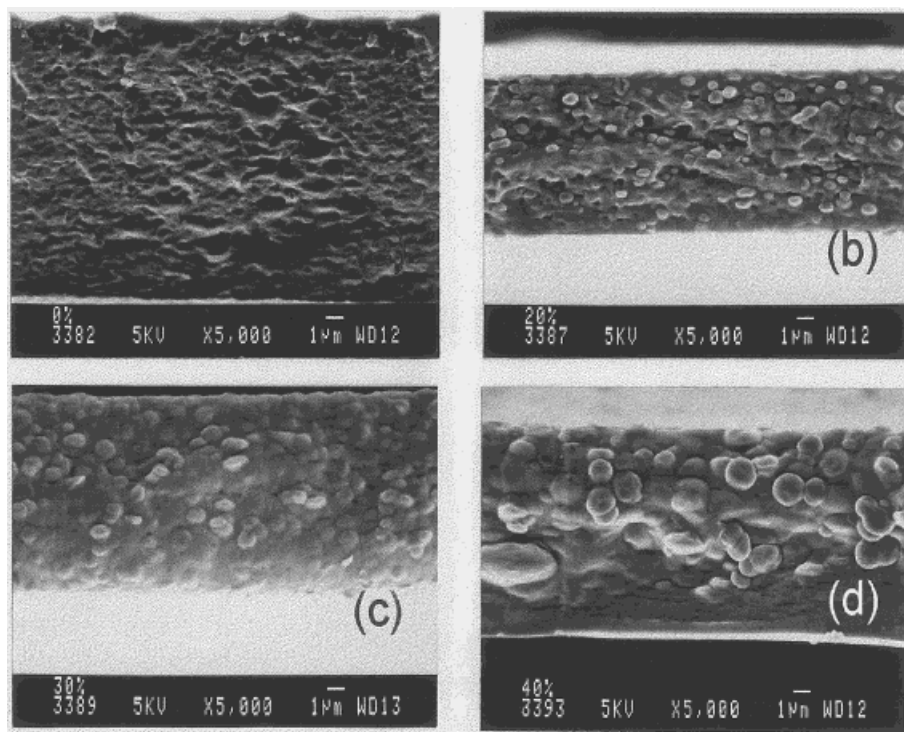
Figure 4 Scanning electron microscopic pictures of the cross sections of SA/PVA blend membranes with different PVA content: (a) 0 wt % PVA, (b) 20 wt % PVA, (c) 30 wt % PVA, and (d) 40 wt % PVA.

from a rubbery state at the feed-side surface to a glassy state at the permeate-side surface.[2] In this case, relaxation phenomena will be complicated by a different extent of relaxation with location across the membrane, because relaxation takes place, depending on membrane mobility, which may be a function of location in the membrane.

It is reported[4] that flexible polymers have an efficiently packed polymer matrix in the glassy state, resulting in limited segmental mobility after packing polymer matrix. Thus, the flexible polymers will be able to achieve a narrow size distribution of free volumes, whereas rigid polymers will lack this possibility, because these polymers are limited in achieving the same variety of conformations, resulting in a broader free volume distribution, through which the number of larger free volumes is substantially increased. The existence of free volume distributions has been shown experimentally.[5-8] A rigid polymer can have a large free volume, allowing increased segmental mobility in the glassy state, and higher glass transition temperature or an increased stiffness can be characterized in terms of a larger free volume or a broader free volume distribution. The

changes in relaxation time during physical aging are presented as a function of the reciprocal free volume at a temperature by positron annihilation lifetime spectroscopy.[8] During relaxation by physical aging, the free volume distribution changes; specifically, larger free volume elements preferentially disappear. From energy and entropy considerations, it follows that a polymer matrix will also strive after a narrow free volume distribution shifted into small size range through relaxation. That is why the rigid polymer with high T_g can experience a great deal of extent of relaxation at a temperature below T_g. On the other hand, when polymers are more flexible or of higher mobility, they will be more packed and have smaller free volumes and narrower free volume distribution, resulting from being in a more stable glass from the thermodynamic point of view. Thus, they will be subjected to less relaxation process.

The purpose of this study is to prepare SA membranes blended with a flexible polymer to reduce the relaxation taking place during pervaporation. In this study, the rigid polymer, SA, was blended with a flexible polymer, poly(vinyl alcohol)(PVA) to enhance the membrane mobility by
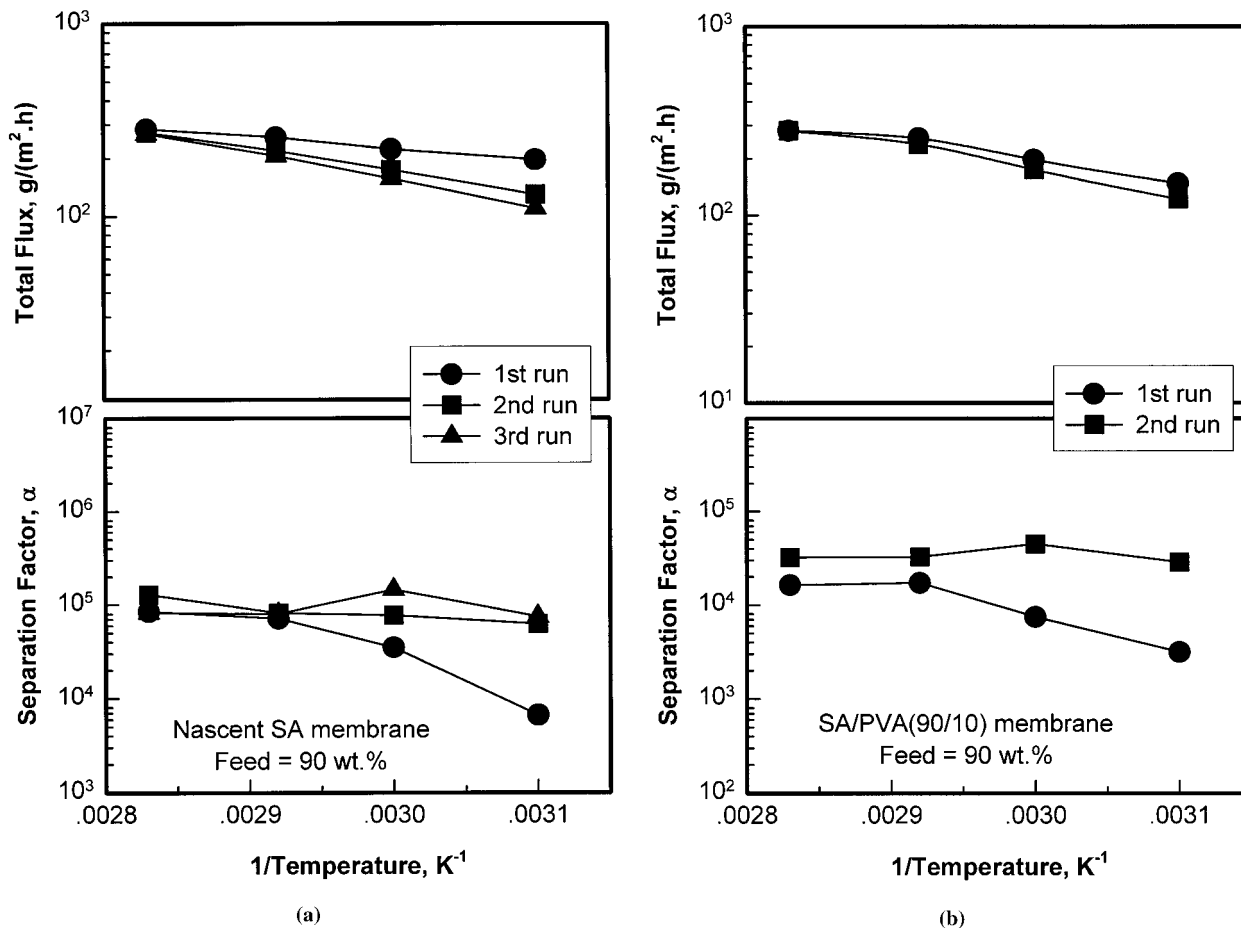
Figure 5 Arrhenius plots of flux and separation factor against inverse temperature in repeating operation in pervaporation of 90 wt % ethanol content of feed through various membranes: (a) nascent SA, (b) SA/PVA (90/10), (c) SA/PVA (80/20), (d) SA/PVA (70/30), and (e) SA/PVA (60/40).

which the relaxation during pervaporation operation would be reduced. The pervaporation separations of the ethanol–water mixtures through the SA/PVA blend membranes prepared at different composition were conducted with feed composition at different temperatures ranging from 50 to 80°C. The relaxational phenomena during pervaporation will also be discussed through an analysis on the experimental data of membrane performance measured by repeating the operation in the given temperature range.

EXPERIMENTAL

Materials

PVA was purchased from Aldrich Chemical Co. (Milwaukee, WI). The average molecular weight and saponification of PVA were 50,000 and 99%, respectively. SA (extrapure grade) was purchased from Showa Chemical, Inc. (Japan). Ethanol (guaranteed reagent) was supplied by Merck (Darmstadt, Germany). Glutaraldehyde (GA) (25% content in water, extrapure grade, which is called GA hereafter), hydrochloric acid (35% content, extrapure grade, called HCl hereafter), and acetone (guaranteed reagent) were purchased from Junsei Chemical Co. (Tokyo, Japan). Ultrapure deionized water was used. All chemicals were used without any further purification.

Membrane Preparation

SA and PVA solutions were prepared by dissolving SA and PVA in distilled water, respectively.
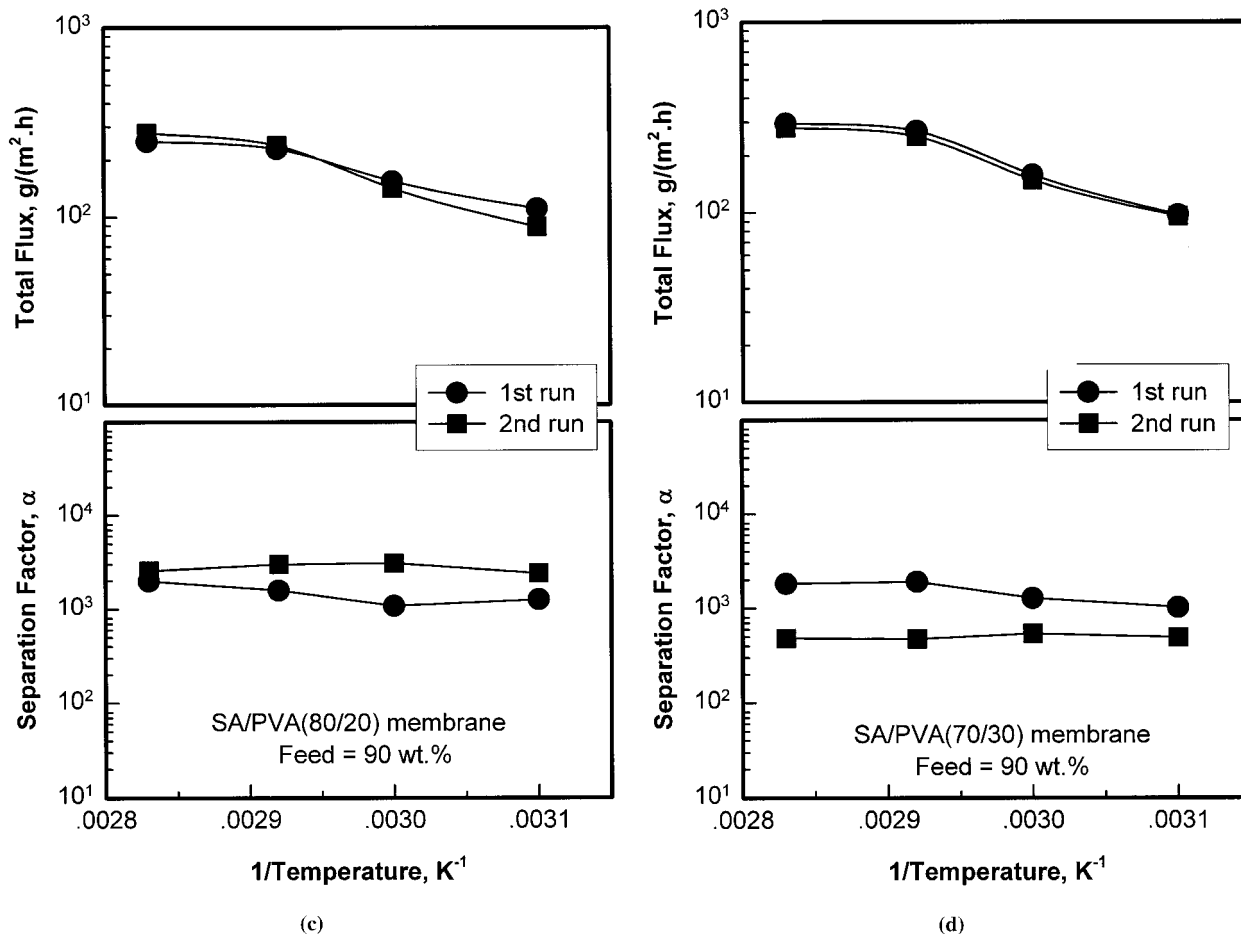
Figure 5 (*Continued from the previous page*)

Both of the solutions have 2.5 wt % of polymer content. The casting solution was prepared by uniformly mixing together the two solutions with a given ratio. The casting solution was cast onto a glass plate with the aid of a Gardner casting knife and dried at room temperature in a fume hood for 1 day. Further drying was conducted in a heating oven at 100°C for 4 h. For the preparation of a membrane with a uniform crosslinking structure, the dry blend membranes were peeled off the glass plate and immersed at 40°C for 48 h in a reaction solution that contained 10 vol % of GA and 0.05 vol % of HCl in acetone. After the crosslinking reaction, the membrane was taken out of the reaction solution, washed out several times with pure methanol, immersed in methanol for 24 h at 40°C to eliminate any possible residual HCl and GA, and then dried under vacuum for 24 h. A detail on the crosslinking reaction is described elsewhere.[9] Membrane thickness prepared was 15−16 μm.

Swelling Measurements

Swelling measurements of the crosslinked membranes were performed to see if the crosslinking reaction was done sufficiently. Dry membrane strips were immersed in water thermostated at 40°C for 48 h to allow the strips to reach equilibrium sorption. The dimension of a strip was 7 × 1.5 (cm). After measuring the swollen length, l, of a strip at equilibrium sorption, the strip was dried for 30 h at room temperature under a vacuum and the dry length, l_o, was measured. The swelling ratio, R, for an isotropic material is defined as

$$R = \frac{l - l_o}{l_o} . \tag{1}$$

All measurements were repeated four or five times, and the resulting data had a standard deviation of ±8%.
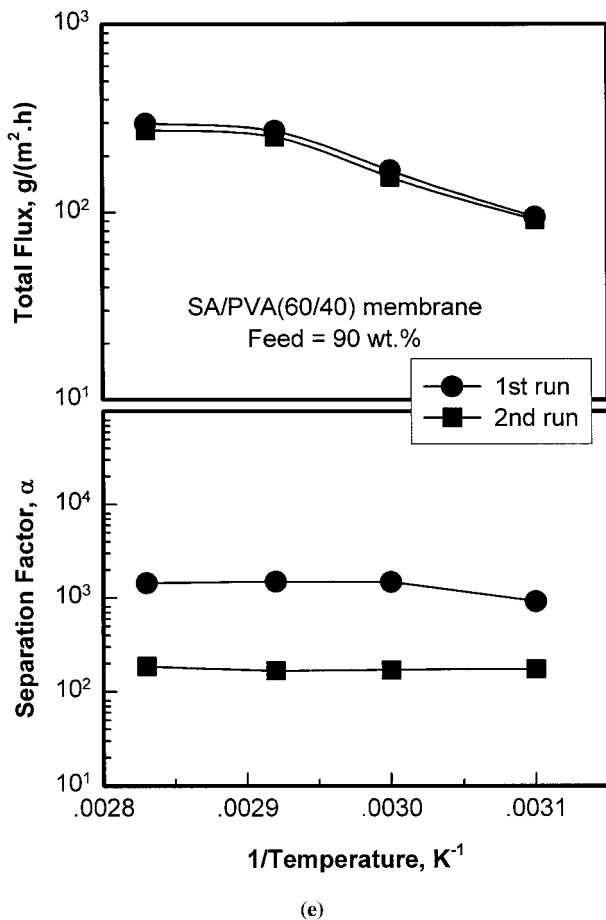
(e)

Figure 5 *(Continued from the previous page)*

Scanning Electron Microscopy

The morphologies of the SA/PVA blend membrane were observed with PVA content by a scanning electron microscope (JEOL model JSM-840). In preparing the specimens, the fracture surface of the cross section of the membranes was obtained by breaking the membranes in liquid nitrogen.

Pervaporation

A schematic pervaporation apparatus used in this study is illustrated in Figure 1. The membrane cell is made of a stainless steel. A feed mixture enters the cell through the center opening, flows radially through the thin channel, and leaves the cell through the side opening, which allows relatively high fluid velocity parallel to a membrane surface. Cell structure is depicted elsewhere.[9] The effective membrane area was 19.6 cm^2. The feed mixture was circulated from the feed tank having a capacity of 2.5 L through the membrane cell. The feed tank was wrapped with the heating tape to heat the feed mixture. The feed mixture temperature was controlled by the temperature controller. The permeate pressure was controlled by the proportional–integral–derivative (PID) controller. The composition of permeate vapor was determined by on-line gas chromatography analysis. The gas chromatography was the same as used in preferential sorption measurement. Thus, the permeate vapor could be injected directly into one of the columns by the injector in on-line measurement. The permeate vapor was collected in the cold trap by liquid nitrogen with a given time interval, heated up to room temperature, and weighed to determine the flux. Separation factor was calculated by the following equation:
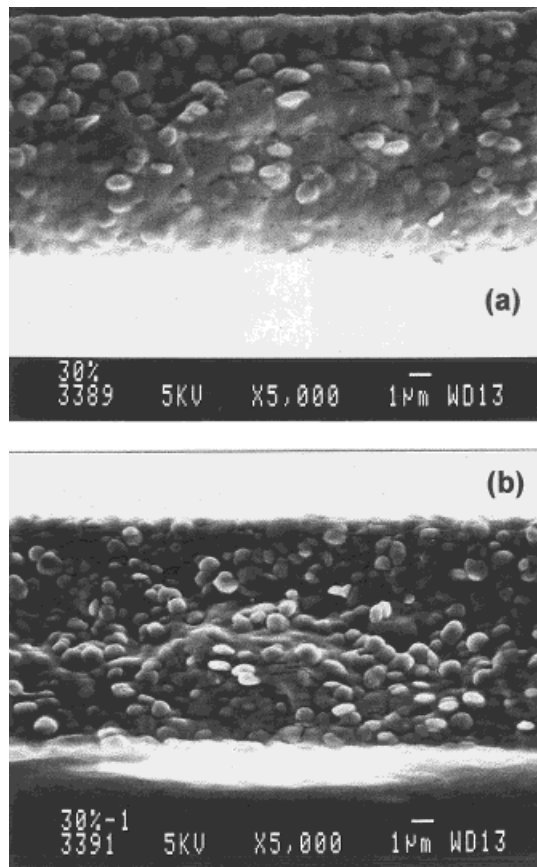

Figure 6 Scanning electron microscopic pictures of the cross sections of SA/PVA (70/30) membranes: (a) before run; (b) after run.
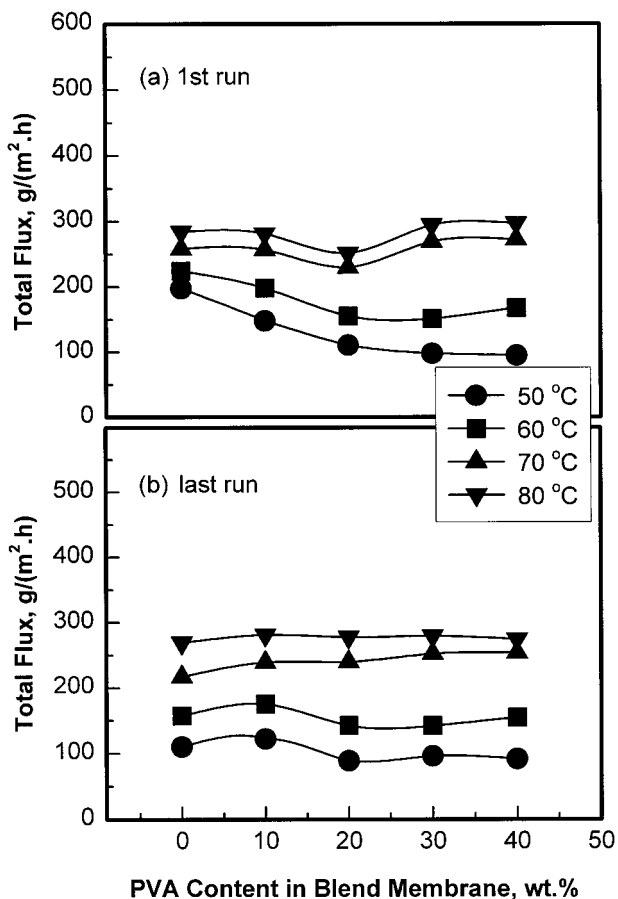
Figure 7 Total flux and separation factor of SA/PVA blend membrane with PVA content at different temperatures; feed composition: 90 wt % ethanol content. (a) First run; (b) last run.

$$\alpha_{\text{water/ethanol}} = \frac{Y_{\text{water}}/Y_{\text{ethanol}}}{X_{\text{water}}/X_{\text{ethanol}}} \qquad (2)$$

where X and Y are the weight fractions of each components in feed and permeate, respectively. To investigate the relaxation of the membrane with operating time, pervaporation run was repeated at different feed compositions in the temperature range of 30–80°C until the flux was not changed. In each run, the feed temperature was increased from 30 to 80°C in a sequence of temperature steps, and the measurements of flux and separation factor were made every 10°C: after measurement of membrane performance at a temperature step, the feed mixture was heated to the next temperature step with a certain rate; then, after reaching the new temperature, the feed mix-

ture was applied to the isothermal pervaporation experiment, and sample collection began 2 h later when the isothermal process is in a steady-state. Between the consecutive runs, the membrane was maintained at 40°C in the membrane cell with permeate side vented to atmosphere for 12 h. The heating rates used were 1–0.7°C/min.

RESULTS AND DISCUSSION

The rigid SA membrane with high T_g can have a higher specific volume in glassy state than that in thermodynamic equilibrium due to large free volumes that are frozen, not agitated by chain motion. Cooling of the polymer below its T_g arise
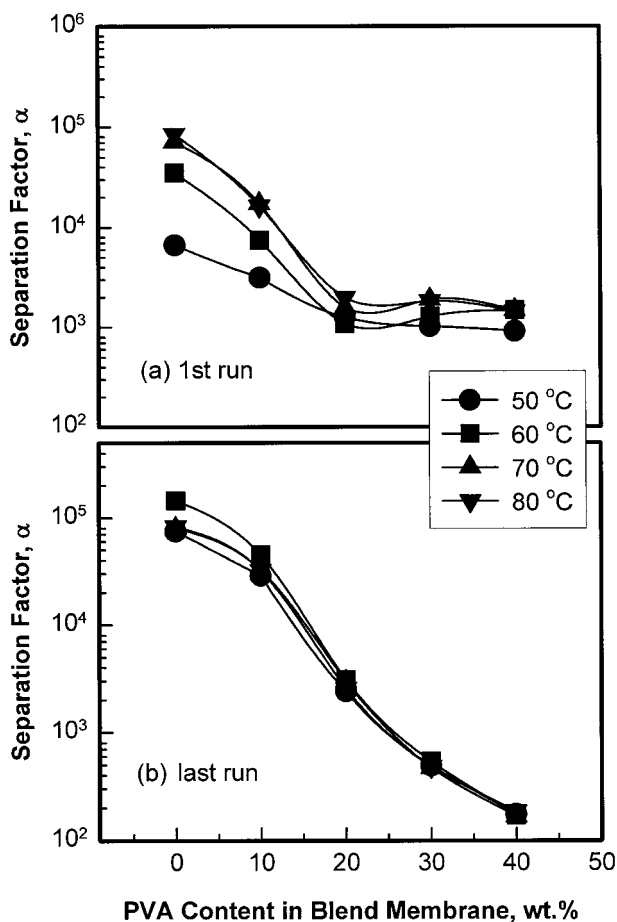

Figure 8 Separation factor of SA/PVA blend membrane with PVA content at different temperatures; feed composition: 90 wt % ethanol content. (a) First run; (b) last run.
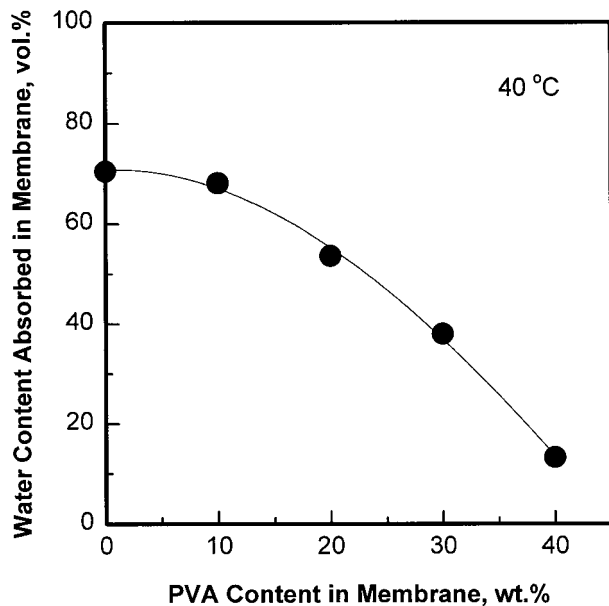
Figure 9 Water content of SA/PVA (90/10) crosslinked at 10 vol % of GA content in reaction solution absorbed in water at 40°C.

from excess free volumes that are frozen into the amorphous structure. The large free volumes can be easily relaxed to smaller size with asymptotically approaching thermodynamic equilibrium by the rearrangement of its polymeric chains, resulting in a more packed structure. When the rigid SA membrane is blended with the flexible polymer, PVA, the resulting membrane will have larger membrane mobility and a more packed polymer matrix than the nascent SA membrane. Therefore, it may have smaller free volumes and narrower free volume distribution, resulting from being in more stable glass from the thermodynamic point of view. Thus, the relaxation process occurring in a rigid membrane may be reduced by blending with a flexible polymer.

Figures 2 and 3 present the pervaporative performances of nascent SA and PVA membranes with operating temperature in the separation of a ethanol–water mixture with 90 wt % ethanol content. These figures exhibit that the SA membrane has a superior performance to the PVA membrane in the separation. The reason for that had been explained in terms of the outstanding preferential sorption of the SA membrane to water.[2] It is very interesting to note that the rigid SA membrane showed a decline in flux and an increase in separation factor with repeating the

operation. The change of membrane performance is more remarkable at lower operating temperature. This is a typical observation of the relaxation of polymeric chains during pervaporation, as demonstrated in the previous works.[2,10] However, the flexible membrane, PVA, has almost constant performance, regardless of repeating the operation.

In this study, SA/PVA blend membranes were prepared to enhance membrane mobility. The SA having better pervaporative performance was taken as a major component and the PVA as a minor component in preparing the blend membranes. PVA content in the membranes ranged from 0 to 50 wt %. Two components could be compatible in solution state, but phase separation was observed to happen as the cast film was drying, changing its color from transparent to opaque. When the PVA content was 50 wt %, the phase separation took place seriously, and the resulting membrane was too fragile to peel off a glass plate. Thus, further experiments could not be progressed any more with the membrane. Figure 4 shows the scanning electron microscopic photographs of the cross sections of SA/PVA blend membranes with different PVA contents. The nascent SA membrane had a uniform and dense structure, whereas a morphology of phase separation could be observed in all of the blend membranes. Obviously, the continuous matrix was composed mainly of SA, and the separated domains were composed of PVA. The PVA domain size increases with PVA content in the membrane, as a result of more significant phase separation.

Figure 5(a–e) demonstrates fluxes and separation factors through the blended membranes against operating temperature in repeating the operation run. In these figures, both flux and separation factor decreased with increasing PVA content, which might be attributed to a decrease in the content of SA having a high affinity to water. Flux was decreased until the third run and then kept almost constant with repeating the run in the nascent membrane, whereas the blend membranes yielded a constant flux from the second run and the decrease of flux with repeating the run was less significant at higher PVA content. It was investigated in the previous work[2] that the decrease of flux with repeating the run occurred as a result of the relaxation of polymeric chains in the transition region and glassy layer among the phase gradient that was developed across the glassy membrane during
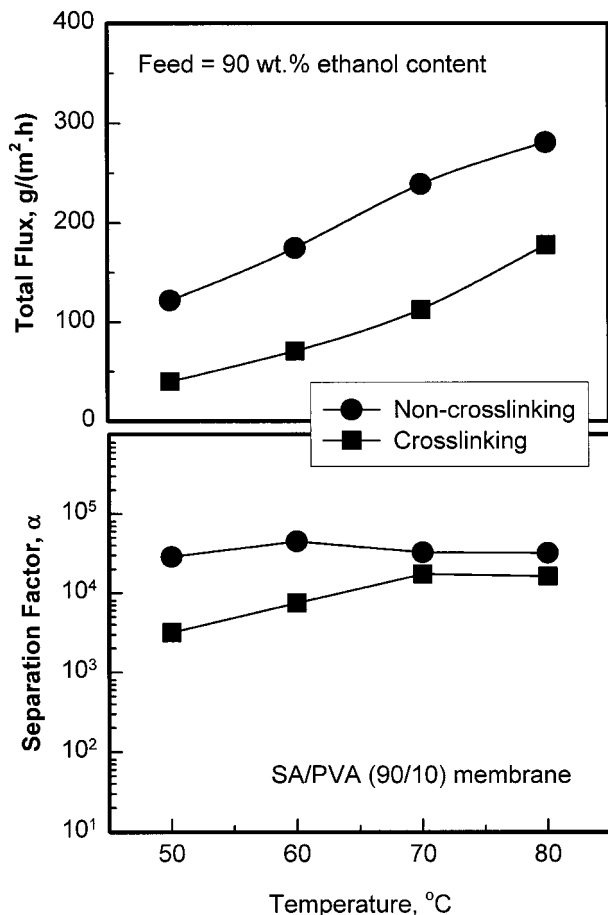
Figure 10 Plots of flux and separation factor through noncrosslinked and crosslinked SA/PVA (90/10) membranes; feed: 90 wt % ethanol content.

pervaporation. It reveals that the relaxation process is reduced by an increase in the mobility of the resulting membrane through blending SA with PVA. It can be seen that the blend membranes have a discontinuity at 70°C in the flux curve. Above 70°C, all of the fluxes and the slopes of the curves were almost identical, regardless of PVA content in the membranes; below 70°C, the slope of the flux curve tended to increase with PVA content (i.e., the permeation of permeants was more sensitive to temperature at higher PVA content). The reason for that is not clear, but may be postulated as follows. Usually, when a glassy membrane is used, the phase gradient can be developed across the membrane from rubbery phase at the feed-side surface of the membrane to the glassy phase at the permeate-side surface due to the anisotropic swelling occurring during

pervaporation process.[2] Among them, a glassy phase of layer has the lowest membrane mobility and the lowest diffusivity of permeants through it, and it thus can be a rate-determining layer. The PVA has a T_g adjacent to 70°C, whereas the SA has a very high T_g higher than 250°C. In principle, a polymer in a rubbery phase has a higher thermal expansion coefficient than that in the glassy phase. At a operating temperature below 70°C, since both of the components in the layer will be in glassy state, the permeation behavior of permeants can be more dependent on the their intrinsic characteristics. According to the publications,[2,11] the permeation activation energy is higher through the PVA membrane than the SA membrane, resulting in the permeation behavior of permeants more sensitive to temperature at higher PVA content below 70°C. However, at a temperature above 70°C, the PVA will be rubbery and SA be glassy in the membrane. As can be seen in the scanning electron microscopic pictures, because SA is a continuous phase, most of the rubbery PVA domains can be surrounded by the glassy SA matrix to such an extent that the expansion of the rubbery PVA can be restricted by the glassy continuous matrix. Thus, above 70°C, the rubbery PVA seems to be depressed by the glassy SA and hardly responds commensurate with temperature change. Therefore, the permeation behavior could be determined mainly by SA characteristics.

In the PVA content range of 0–20 wt %, the separation factor was increased with repeating the operation run until twice or three times, and then kept constant, which must be a result of the densification of the SA phase by the relaxation of polymeric chains. At PVA content above 30 wt %, the separation factor decreased with repeating the run and the decrease was found more significant at a higher PVA content. In addition, when the operation was repeated more than three times, the flux was often increased and the separation factor kept decreasing rapidly; finally, the membrane was broken in repeating the operation run. From the scanning electron microscopic pictures in Figure 4, microcracks were found in the membrane with PVA content higher than 30 wt %. As the operation was repeated, these microcracks grew bigger (as shown in Fig. 6). Figure 6(a) was of the membrane with 30 wt % PVA content before operating, and Figure 6(b) was of the same membrane after repeating the run three times. It is clear that flux can be large and separation factor

be reduced in the permeation of permeants through the membrane having large microcracks.

In Figures 7 and 8, the membrane performances of the blend membranes in the first and last runs were plotted with PVA content at various temperatures, respectively. The membrane performance in the second run was taken as that of the last run for the membrane with PVA content above 30 wt %, because of membrane breakage in repeating the operation run more than twice. As operating temperature increases or PVA content is higher, the membrane mobility would be higher, so that the extent of relaxation occurring could be smaller. Thus, the flux was less decreased and separation factor also less increased. In the beginning of the operation, the membrane was not much relaxed and flux decreased with PVA content but, after sufficient relaxation, flux through the membrane relaxed sufficiently has a similar value, regardless of PVA content. It is because the less packed part of SA in the membranes with higher PVA content could be densified to the same extent by relaxation. At PVA content above 30 wt %, the relaxed membrane showed a more remarkable decline in separation factor with increasing PVA content, because of permeation through larger microcracks as discussed previously.

The blend membranes were crosslinked with GA to enhance membrane stability against water. The swelling measurements of the crosslinked membranes were performed at 40°C to see if the membranes are stable enough in water or not. All of the crosslinked membranes were stable, and the result was depicted in Figure 9. The crosslinked membrane with 10 wt % PVA content, which has the highest water solubility, was chosen. The pervaporation separation of 90 wt % ethanol content of an ethanol–water mixture with the crosslinked membrane was conducted at various temperatures. Figure 10 shows the result of the pervaporation separation, compared with the uncrosslinked membrane. Usually, when a membrane is crosslinked, a membrane mobility, as well as liquid solubility, is decreased as well. Compared with the uncrosslinked membrane, because a smaller amount of water was absorbed from the feed into the crosslinked membrane, sodium salt ions in the SA part could be ionized to a less extent and the plasticization action of the absorbed liquid could be reduced, so that the crosslinked membrane would have less preferential sorption of water and less diffusivity. As a result, the crosslinked membrane should have inferior membrane performance to the uncrosslinked membrane, although it has better membrane stability.

CONCLUSIONS

SA/PVA blend membranes were prepared by blending the rigid polymer, SA, and the flexible polymer, PVA. In this study, the SA having better pervaporative performance was taken as a major component and the PVA as a minor component in preparing the blend membranes. By repeating the pervaporation run, the rigid SA membrane showed a serious decline in flux and an increase in separation factor due to the relaxation of polymeric chains, whereas the flexible PVA membrane kept consistent membrane performance during the pervaporation separation of an ethanol–water mixture. The morphologies of the blend membranes with different PVA content were observed by a scanning electron microscope. The continuous matrix was composed mainly of SA, and the separated domains were composed of PVA. The PVA domain size was bigger, with increasing PVA content in the membrane as a result of more significant phase separation. From the pervaporation separations of the ethanol–water mixtures, it was found that all of the blend membranes prepared could have an enhanced membrane mobility by which the relaxation during pervaporation operation would be reduced, compared with the nascent SA membrane. The effects of operating temperature and PVA content in membrane were investigated on membrane performance, as well as the extent of relaxation manifested as the change of membrane performance. The relaxational phenomena during pervaporation were also elucidated through an analysis on experimental data of membrane performance measured by repeating the operation run in the given temperature range. SA/PVA blend membrane was crosslinked with GA to enhance membrane stability in water, but the crosslinked membrane was observed to have an inferior membrane performance to the uncrosslinked membrane because of less membrane mobility and less preferential sorption of water.

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