

Characterization of Sodium Alginate Membrane Crosslinked with Glutaraldehyde in Pervaporation Separation

C. K. YEOM,¹ K.-H. LEE²

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

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

Received 7 February 1997; accepted 8 July 1997

ABSTRACT: Dense sodium alginate (SA) membranes crosslinked with glutaraldehyde (GA) have been prepared by the solution method, wherein a nonsolvent of SA (acetone) was used in a reaction solution instead of an aqueous salt solution. Through infrared radiation, X-ray diffractometry, and the swelling measurement, the crosslinking reaction between the hydroxyl groups of SA and the aldehyde groups of GA was characterized. To investigate the selective sorption behavior of the crosslinked SA membranes, swelling measurements of the membranes in ethanol–water mixtures of 70–90 wt % ethanol contents were conducted by equipment that was able to measure precisely the concentration and amount of the liquid absorbed in the membranes. It was observed that the crosslinking could reduce both the solubility of water in the resulting membrane and the permselectivity of the membrane toward water at the expense of membrane stability against water. The pervaporation separation of an ethanol–water mixture was conducted with the membranes prepared at different GA contents in the reaction solution. When the membrane was prepared at a higher GA content, both flux and separation factor to water were found to be reduced, thus resulting from the more crosslinking structure in it. The pervaporation separations of ethanol–water mixtures were also performed at different feed compositions and temperatures ranging from 40 to 80°C. A decline in the pervaporative performance was observed due to the relaxation of polymeric chains taking place during pervaporation, depending on operating temperature and feed composition. The relaxational phenomena were also elucidated through an analysis on experimental data of the membrane performance measured by repeating the operation in the given temperature range. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 209–219, 1998

Key words: sodium alginate; glutaraldehyde; pervaporation; ethanol–water mixture; crosslinking reaction

INTRODUCTION

It is well known that hydrophilic polymers are selected as a membrane material for the dehydration from various solvents in pervaporation process because the water molecule is easily incorpo-

rated into the hydrophilic polymeric membrane. Among the hydrophilic membranes, alginate membranes^{1,2} are reported to present the most outstanding membrane performance for the dehydration of ethanol–water mixtures. In the previous work,² it appeared that the excellent pervaporation performance of the sodium alginate (SA) membrane is attributed mainly to the extraordinary permselectivity to water in the sorption step. However, excess hydrophilicity of membrane ma-

Correspondence to: C. K. Yeom (ckyeom@pado.kRICT.re.kr).

Journal of Applied Polymer Science, Vol. 67, 209–219 (1998)

© 1998 John Wiley & Sons, Inc.

CCC 0021-8995/98/020209-11

terial is not necessarily suitable for the dehydration process, because it can give a low selectivity and poor membrane stability against the aqueous solution at a cost of high flux. Usually, when a highly permeable polymer material is selected, selectivity and membrane stability can be enhanced by chemical modification or crosslinking with the corresponding sacrifice of flux. Therefore, the membrane material should be modified to have the optimal combination of flux and membrane stability or selectivity.

We developed a new solution technique for the crosslinking of poly(vinyl alcohol) (PVA) membrane.³ In the technique, a nonsolvent of PVA (acetone) was used as a reaction medium instead of aqueous salt solutions that had been used for the insolubilization of PVA in a reaction solution. Glutaraldehyde (GA) and hydrochloric acid (HCl) were used as a crosslinking agent and a catalyst for the reaction, respectively. When a dry PVA membrane was immersed in the reaction solution, the membrane could be reacted to a high extent without any deformation of their shape owing to the nonsolvent acetone; thus, a stable membrane could be prepared by the solution method. Herein, the crosslinking reaction took place between the hydroxyl groups of PVA and the aldehyde groups of GA. The SA also has hydroxyl groups, along with its chains. Thus, the new solution method can be used for the crosslinking reaction of the SA membrane.

It was investigated that relaxation of the polymeric chains during the pervaporation process can also influence membrane performance.² In particular, glassy polymers with rigid and bulky structures tend to be stressed or relaxed easily, depending on their thermal history. The relaxation process takes place significantly near the glass transition temperature (i.e., in the transition region of the polymer), and it can make the material structure more dense by the configurational rearrangement of polymeric chains so that flux can be decreased correspondingly.⁴ In the pervaporation process, wherein a glassy polymeric membrane is used for the dehydration of an aqueous mixture differently from other membrane processes, is a pronounced anisotropic swelling developed in the membrane, by which a phase gradient can be established across membrane thickness—a rubbery state at the feed-side membrane surface to a glassy state at the permeate-side surface.² In this case, relaxation phenomena can be complicated by a different relaxation process with location in the membrane, because relaxation can take place, depending on membrane mobility,

which may be a function of location in the membrane thickness direction.

The purpose of this study is to prepare SA membranes crosslinked with GA by using the new solution technique to enhance the membrane stability against water. The crosslinking reaction will be characterized by infrared radiation (IR) spectroscopy, X-ray diffractometry, and swelling measurement. Selective sorption and permeation performance of the crosslinked SA membranes will be investigated. Pervaporation separations of the ethanol–water mixtures through the membrane will be investigated at different feed compositions and temperatures. Relaxational phenomena in the membrane will also be discussed from an analysis on experimental data of membrane performance measured by repeating the operation in the given temperature range.

EXPERIMENTAL

Materials

SA (extra pure grade) was purchased from Showa Chemical, Inc. (Tokyo, Japan). Ethanol (guaranteed reagent) was supplied by Merck (Darmstadt, Germany). GA (25% content in water, extra pure grade), HCl (35% content, extra pure grade), 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 (2.5 wt %) casting solution was prepared by dissolving SA in water. The casting solution was casted 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 membranes with a uniform crosslinking structure, the dry SA membrane was peeled off the glass plate and immersed at 40°C for 48 h in a reaction solution that contained a certain content of GA and 0.05 vol % of HCl in acetone. The GA content used in this study ranged from 0 to 20 vol %. 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 a vacuum for 24 h. Membranes prepared were 15–16 μm thick.

Infrared Measurement of Prepared SA Membranes

Infrared spectra of crosslinked SA membranes were measured with a Fourier transform infrared spectroscope (Digilab FTS-80; Bio-Rad, Richmond, CA). Membranes used were 7–8 μm in thickness.

X-ray Diffractometry

To investigate a change in membrane structure with crosslinking density, a wide-angle X-ray diffractometer (model D/MAX IIIB; Rigaku) with a scintillation counter detector using $\text{CuK } \alpha$ -radiation as a source was used. Angles (2θ) ranged from 2° to 50° . All samples were films with thicknesses of 11–13 μm .

Measurements of Swelling Ratio and Preferential Sorption

In an isotropic material, because a change in length due to swelling is the same in all directions, the ratio of the swollen length to the dry length of the membrane can be given by

$$R_L = \frac{L_x}{L_{x0}} = \frac{L_y}{L_{y0}} = \frac{L_z}{L_{z0}} = \frac{L}{L_0} \quad (1)$$

where L_x , L_y , and L_z are the dimensions of the swollen membrane in x , y , and z directions, respectively, and subscript o denotes the dry membrane. Therefore, the volume fraction of the solvent in the swollen membrane can be expressed in the following form⁵:

$$\phi = \frac{R_L^3 - 1}{R_L^3} \left(= \frac{L_x L_y L_z - L_{x0} L_{y0} L_{z0}}{L_x L_y L_z} \right) \quad (2)$$

The dense membranes were cut into a shape of slab with a dimension of 10×70 (mm). The slabs were soaked in the 70–90 wt % ethanol content of aqueous solutions for 2 days for an equilibrium swelling. For the measurement of preferential sorption, each swollen slab was taken out of the solution after equilibrium swelling, wiped off with tissue paper as quickly as possible, and then it was placed into the glass tube X which, subsequently, was fitted to the device as shown in Fig-

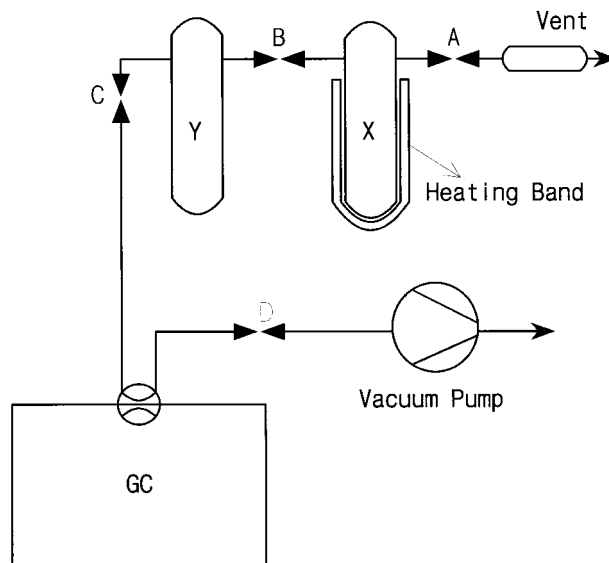


Figure 1 Schematic representation of desorption apparatus.

ure 1. While the glass tube was heated up by the heating band, the liquid absorbed in the slab was evaporated and collected in the glass tube Y by liquid nitrogen under vacuum with valves B and C opened. Collected liquid was vaporized by applying heat on the glass tube Y, with the valves B and D closed so that the region between the tubes could be filled with a vapor of the liquid. Vapor was analyzed by a gas chromatograph (Shimadzu, model GC-14B; Shimadzu Scientific Instruments, Columbia, MD), that was equipped with an integrator (Shimadzu, model C-R6A), two auto sample injectors, a thermal conductivity detector, a flame ionization detector, and two packed columns. Each sample injector was actuated by compressed air. Columns were 5 ft long with a $\frac{1}{8}$ -in. inside diameter packed with a Poropak Q. Vapor was automatically injected into the gas chromatograph by the injector. Ultrapure helium was used as carrier. For measurement of the swelling ratio, the swollen slab was taken out and put on a paper wetted by the same solution, and then both ends of the slab were marked on the paper with a pen as quickly as possible. The distance L between the marks was measured with Vernier Caliper, with an accuracy of $\pm 10 \mu\text{m}$. After drying, the length L_0 of the dry slab was measured. The solubility of the liquid in the swollen membrane ϕ was calculated eq. (2). All measurements were repeated four or five times, and the resulting data had a standard deviation of $\pm 8\%$.

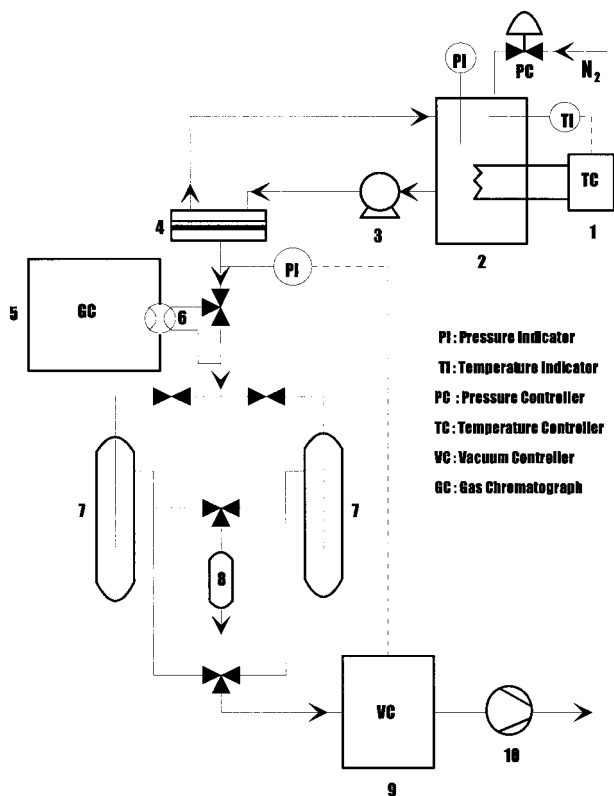


Figure 2 Schematic representation of pervaporation apparatus: 1, temperature controller; 2, feed tank; 3, pump; 4, membrane cell; 5, gas chromatograph; 6, sample injector; 7, cold trap; 8, vent to atmosphere; 9, vacuum controller; 10, vacuum pump.

Pervaporation

A schematic pervaporation apparatus used in this study is illustrated in Figure 2. 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.⁶ The effective membrane area was 19.6 cm². 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. Gas chromatography was the same as used in the preferential sorption 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:

$$\alpha_{\text{water/ethanol}} = \frac{Y_{\text{water}}/Y_{\text{ethanol}}}{X_{\text{water}}/X_{\text{ethanol}}} \quad (3)$$

where X and Y are the weight fractions of each components in feed and permeate, respectively. To investigate the flux change with repeating the operation, the pervaporation run was repeated at different feed compositions in the temperature range of 40–80°C until the flux was not changed. Each run was composed of isothermal operations made every 10°C in the temperature range of 40–80°C: after measuring both flux and separation factor in the isothermal process at a temperature, the feed mixture was heated to the next temperature step with a certain rate and then after reaching it to the new temperature; feed mixture was applied to the isothermal pervaporation experiment, and the sample collection began 2 hr later when the isothermal process started for the steady state. Between the consecutive runs, the membrane was maintained at 40°C in the membrane cell with the permeate side vented to the atmosphere for 12 h. The heating rates used were 1–0.7°C/min.

RESULTS AND DISCUSSION

IR Measurement

In the previous study,³ the crosslinking reaction between the hydroxyl groups of PVA and the aldehyde groups of GA had been characterized in the new solution technique. SA has also hydroxyl groups along with the polymeric chains, so that the same technique could be applied for the crosslinking of the polymeric chains by GA molecules. Thus, in this study, the solution technique was used for the crosslinking reaction of the SA membrane: a nonsolvent of SA (acetone) was also used as reaction medium, and HCl was used as a catalyst for the reaction. The content of HCl in the preparation of all membranes was kept as low as possible to minimize the acidification of the sodium salt groups of SA by the catalyst. From IR measurement, it was confirmed that 0.05 vol % of HCl content could be enough for the crosslinking reaction without causing significant acidification of the sodium salt groups. SA membranes were crosslinked at different GA contents in the reaction solution. Stable membranes could be pre-

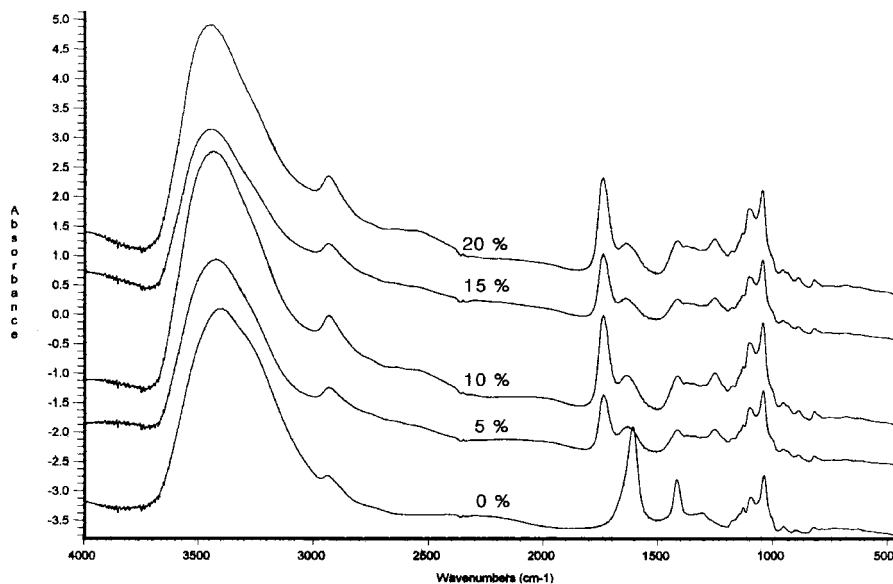


Figure 3 IR spectra of the SA membranes crosslinked at a different GA content in the reaction solution.

pared with GA content above 5 vol % of GA content. Figure 3 illustrates the IR spectra of the SA membranes crosslinked at different GA contents. The IR spectra show the following two sets of significant changes, with increasing GA content to confirm the crosslinking reactions:

- an increase in the absorbance of peaks at $1734, 2700\text{ cm}^{-1}$, which were attributable to the characteristics of the aldehyde, and
- an increase in the absorbance of a peak 1250 cm^{-1} , which could be assigned to the formation of an acetal ring and ether linkage as a result of the reaction between the hydroxyl groups of SA and the aldehydes of GA.

From the previous spectral changes, it can be seen that, as the GA content in the reaction solution increases, more acetal rings and ether linkages are formed as a result of the reaction between SA and GA. The significant aldehyde peaks are also found as observed in the reaction of PVA and GA.³ There is little possibility of any residual GA in the membrane, because it was removed from the membrane by thoroughly washing and drying under vacuum. Therefore, this set of aldehyde peaks can only be evidence for unreacted aldehyde pendent to the SA chains, created by the monofunctional reaction of GA. Of the two aldehyde groups in a GA molecule, only one group participates in the reaction and is connected with a SA chain, whereas the other remains unreacted and pen-

dent to the SA chain. Therefore, from the previous spectral changes, it can be seen that monofunctional reaction, as well as bifunctional reaction of GA, takes place in the reaction system of SA and GA.

X-ray Diffractometry

Figure 4 demonstrates the diffraction pattern of the SA membranes crosslinked at different GA contents in the reaction solution. Usually, as the crosslinking reaction progresses, the chain mobility of a polymer can be more reduced by crosslinks; thereby, the resulting polymer tends to have a more rigid and compact structure. In this figure, when the GA content is increased, the crosslinked SA membrane is observed to have a more compact structure that could be confirmed by an increase in the value of 2θ in X-ray diffractometry. Therefore, this result can also be more evidence for the crosslinking reaction between SA and GA.

Swelling Measurement

When the GA content was higher than 5 vol % in the reaction solution, stable membranes against water could be prepared. Below 5 vol % of GA content, crosslinking occurred insufficiently due to lack of crosslinking agent in the solution, so that the resulting membrane could not be stable enough in water. Swelling measurements of the crosslinked membranes were conducted in 90 wt

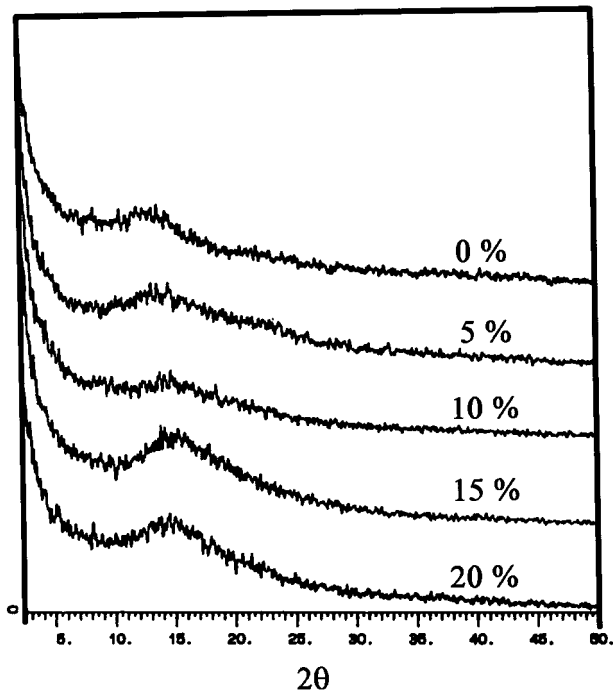


Figure 4 Wide-angle X-ray diffraction patterns of the SA membrane crosslinked at a different GA content in the reaction solution.

% ethanol content of aqueous solution. Figure 5 exhibits the plot of the content of liquid absorbed in the crosslinked membrane versus the GA con-

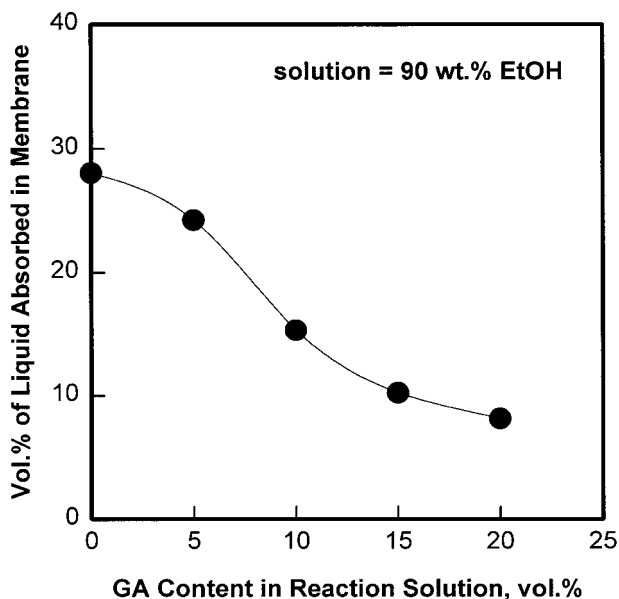


Figure 5 Solubilities of liquid absorbed in the SA membranes crosslinked at different a GA content in the reaction solution measured in a 90 wt % ethanol (EtOH) content of an aqueous solution at 40°C.

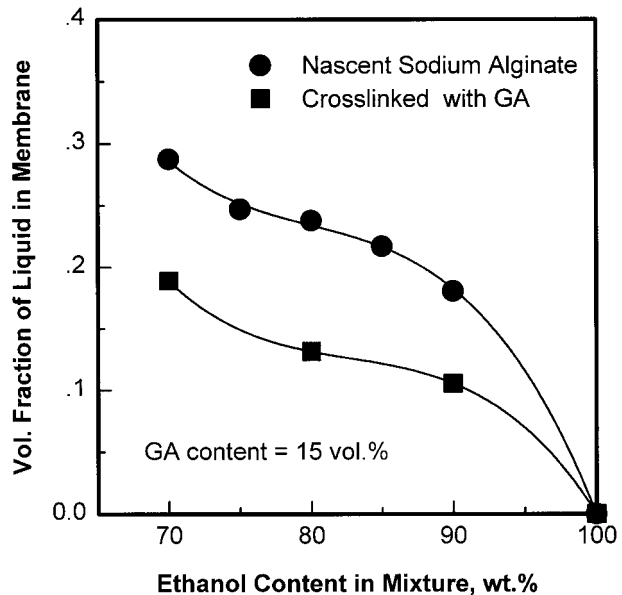


Figure 6 Volume fractions of liquid absorbed in the nascent SA membrane and the membrane crosslinked at 15 vol % of GA content against ethanol content in an ethanol–water mixture at 40°C, respectively.

tent in the reaction solution. With increasing the GA content, the liquid content in the membrane decreased rapidly until 10 vol % and then decreased slightly. In principle, as crosslinking density in a polymeric material increases, the material has a more compact network structure by which less amount of solvent can be absorbed in it. Thus, this result shows a good agreement with those of IR and X-ray diffractometry in light of the fact that the resulting membrane has higher crosslinking density with increasing GA content. Preferential sorption properties of the nascent and crosslinked SA membranes were investigated in different composition of ethanol–water mixtures, respectively. The crosslinked membrane was one fabricated at 15 vol % of GA content. Results of the measurement are shown in Figures 6 and 7 and are summarized as follows:

- As the water content in the mixture increases, the amount of liquid absorbed in the swollen membrane increases, and the ethanol content of the absorbed liquid increases as much.
- When the membrane is crosslinked, the solubility of liquid in the swollen membrane is reduced, whereas the ethanol content in the liquid increases.

As the water content in mixture increased, the

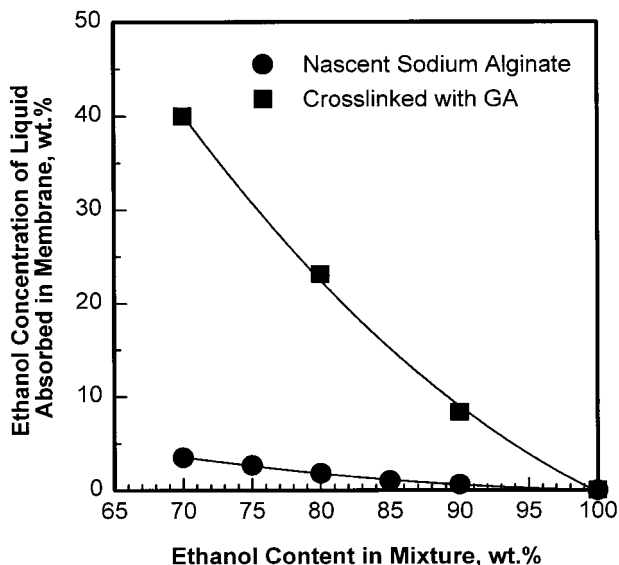


Figure 7 Ethanol contents of liquid absorbed in the nascent SA membrane and the membrane crosslinked at 15 vol % of GA content against ethanol content in a mixture at 40°C, respectively.

hydrophilic membranes would attract more water molecules from the mixture. The more absorbed water could come with more ethanol molecules into the membrane by strong interaction between water and ethanol molecules, although the ethanol has very poor affinity toward the membrane. This phenomenon is called “coupling sorption.”⁵ Thus, with increasing water content in the mixture, the coupling sorption could occur more pronounced, and it made the solubility of the liquid and the ethanol content of the absorbed liquid increased. As shown in these figures, the nascent SA membrane presents an excellent preferential sorption of water. The reduced liquid solubility observed in the crosslinked membrane obviously results from the crosslinking structure in the membrane as described previously. It is reported^{5,7} that GA is miscible in both water and ethanol, indicating that aldehyde group has affinity to both of them. The acetal group has a good affinity toward alcohol rather than water. From these facts, it could be postulated that the crosslinked SA membrane would have less affinity to water (i.e., less preferential sorption of water). Possibly another cause for less affinity of the crosslinked membrane toward water might be to acidify some of the salt groups by the catalyst HCl and reduce the number of the salt groups in SA. The completely acidified SA (i.e., alginic acid) is insoluble in water. However, the extent of the acidification is not much likely to be significant

in the reaction system of this study, because SA membrane treated with the reaction solution containing no GA was soluble in water.

Pervaporation

Effect of Crosslinking Agent Content in the Reaction Solution

It is well known that a membrane with higher crosslinking density has less solubility of a liquid and less polymeric chain mobility, leading to less free volume in the membrane. Therefore, both the solubility and diffusivity of a permeating liquid through the membrane can be reduced in the pervaporation process to decrease the flux of the permeant. An increase in the swelling degree of a membrane in a liquid makes the membrane more flexible, thereby decreasing an energy required for diffusive transport through the membrane and increasing the diffusivity of the permeant, which is called a “plasticizing effect of a permeant.”

Figure 8 shows the effect of the crosslinking density of the membrane on the membrane perfor-

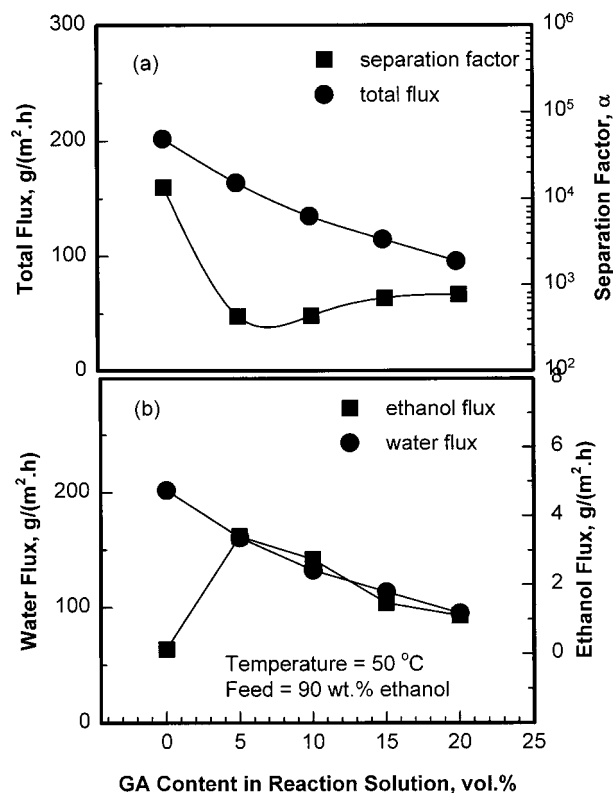


Figure 8 Pervaporation performance through the SA membranes crosslinked at a different GA content in reaction solution: feed composition = 90 wt % ethanol and an operating temperature = 50°C.

mance in the pervaporation separation of an ethanol–water mixture. Compared with the nascent membrane, the crosslinked membranes were found to have lower flux and separation factor in Figure 8(a). The decline of flux can be expected from the formation of more crosslinks in the membrane, but the change in separation factor is unexpected, in view of the fact that decreasing flux is commonly accompanied by increasing selectivity and vice versa. It was already mentioned in the swelling experiment that the crosslinked SA membrane has less affinity toward water because of the presence of the aldehydes pendent to SA chains and the acetal groups that have good affinity toward ethanol. This could explain the reason for the reduced separation factor in the crosslinked membrane. With increasing the GA content, the flux decreases slightly, whereas the separation factor increases, which is a typical tendency of membrane performance with crosslinking density. More detail on the observation will be discussed with individual flux data. Looking at the permeation rates of each individual component in Figure 8(b), water flux was much larger than that of ethanol; therefore, the shape of the water flux curve was almost similar to that of total flux. Because the crosslinked membranes had the hydrophobic groups (acetal or ether groups), as can be seen from the IR spectra the membrane would be more in favor of ethanol permeation than the nascent, thus manifesting a pronounced drop of the separation factor. With increasing GA content, the fluxes of both the individual components show a decrease as a result of the formation of a more crosslinking structure in the membrane.

All of the membranes used in this study were kept under the same thermal condition to make sure that identical thermal histories are imposed on them before measuring membrane performance. Pervaporation of 90 wt % ethanol content of feed was performed with the crosslinked SA membranes at different operating temperatures. Each operation was repeated several times. Separation factor was little changed, but flux was observed to be changed tremendously with repeating the operation in Figure 9. Figure 9 shows the Arrhenius plots of the fluxes with operating temperature. In all of the membranes, a significant decrease in flux could be observed in repeating the run. Flux at a temperature was reduced significantly in the second run, then decreased less and less, and leveled off to a value while repeating the run further. After the third run, the flux at a temperature was not changed

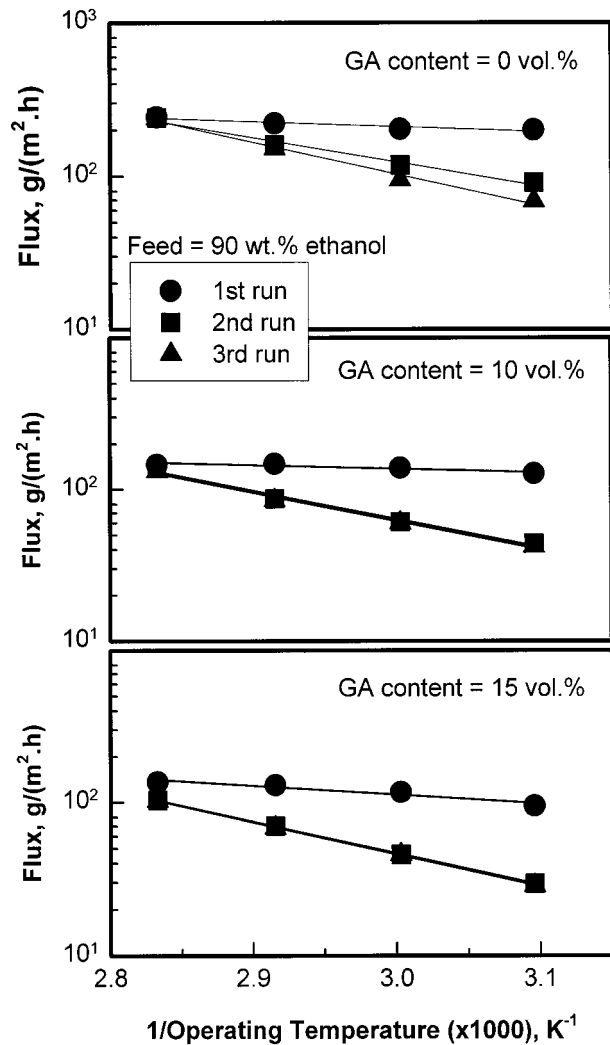


Figure 9 Fluxes with inverse operating temperature through the SA membranes crosslinked at a different GA content in the repeating operation: feed composition = 90 wt % ethanol content.

so much. The flux change is more pronounced at lower operating temperature. It is reported² that a decrease in flux can happen with repeating the run due to the relaxation of polymeric chains taking place in a glassy membrane. The relaxation process takes place only in glassy material. In the pervaporation process using a glassy membrane, a phase gradient can be developed in the membrane from rubbery state at feed side to a glassy state at permeate side through the transition state. The relaxation process is faster in a phase with higher mobility. The change of flux shown in Figure 9 can be, thus, explained in terms of the relaxation process during the run: as the run is repeated, relaxation progresses, slows down more and more owing to the densification of membrane

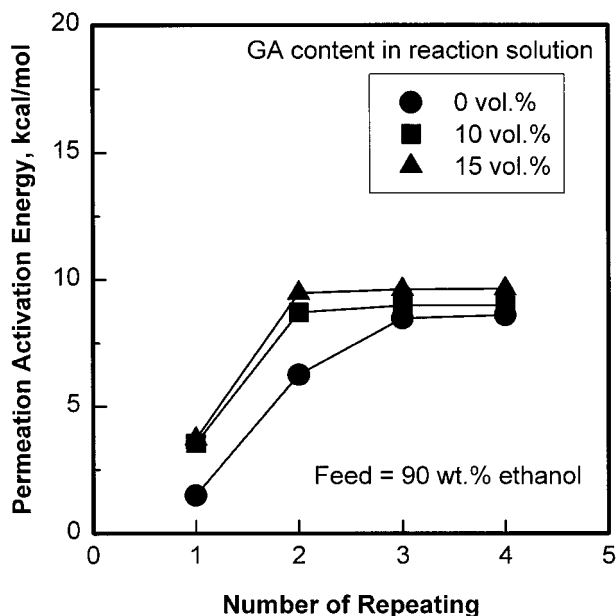


Figure 10 Plots of permeation activation energy of the SA membranes crosslinked at a different GA content in the reaction solution, with repeating operation: feed composition = 90 wt % ethanol content.

material, and finally reach the point that the relaxation time is too long on the experimental time scale; therefore, relaxation cannot be important any more beyond the point, or the resulting flux constant with repeating the run. Relaxation rate presumably tends to be fast in the first run; then, with repeating the run, the rate decreases to 0, wherein relaxation time is too long. With increasing temperature, membrane mobility is higher, and relaxation occurs faster so that the membrane can undergo fast relaxation at the beginning before reaching steady-state permeation and then, in slow relaxation regime, resulting in a smaller extent of relaxation progressing in steady-state permeation. Thus, the next run can give out a pronounced decline in flux at low temperature, and the decline of flux is less and less with increasing temperature further.

Figure 10 presents the plots of permeation activation energies in the crosslinked SA membrane with repeating the run. Activation energies were determined from the slope of each line in Figure 9. In all of the cases, with repeating the run, the activation energy increases rapidly at the beginning and then increases less and less, and finally levels off to a value. Because the more relaxed membrane has a more dense structure and lower membrane mobility, the higher activation energy should be required for the permeation of permeant molecules through the membrane. The perme-

ation activation energy reaches earlier at the level-off value for a membrane fabricated at a higher crosslinking agent content. It is because crosslinking makes membrane mobility so reduced that relaxation in the membrane with a higher crosslinking density can be slower and reach earlier to the limit point, at which the relaxation can be negligible. Permeation activation energy comes earlier to the level-off value for a membrane fabricated at a higher crosslinking agent content. The level-off value is observed higher for a membrane fabricated at a higher GA content (as shown in Fig. 11). According to the so-called "solution-diffusion mechanism," permeation activation energy (E_p) can be expressed a function of the heat of sorption (ΔH_s) and the diffusion activation energy (E_d) as follows:

$$E_p = \Delta H_s + E_d \quad (4)$$

A membrane with a higher crosslinking density must have a higher heat of sorption and higher diffusion activation energy due to less solubility of the liquid and more compact structure, respectively. Therefore, it is understandable that the membrane crosslinked at a higher GA content has a higher permeation activation energy.

Effect of Feed Composition

Pervaporation separation of the ethanol–water mixture with the SA membrane crosslinked at 10

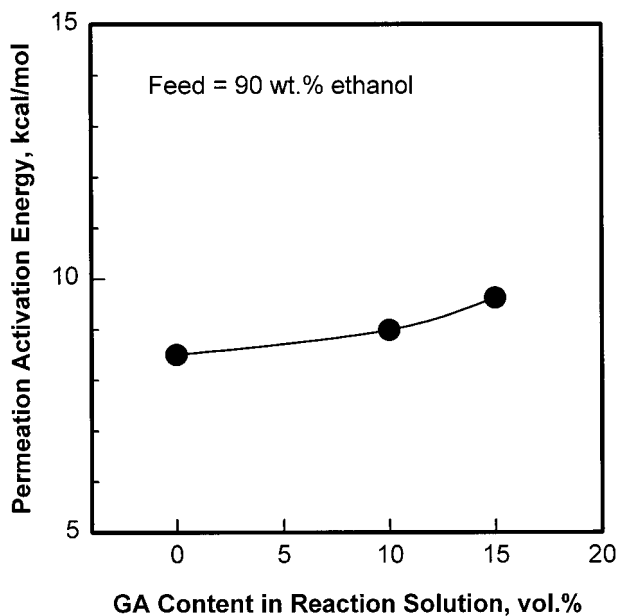


Figure 11 Level-off permeation activation energy of the crosslinked SA membrane with GA content in the reaction solution.

vol % of GA content was performed at various feed compositions. When the operation was repeated, a serious decline in flux could be also observed through the whole range of feed composition but the separation factor did not change as much, not much different from Figure 14. Figure 12 exhibits the plots of the permeation activation energies with feed composition in repeating the operation. Permeation activation energy was determined from the slope of each line in the Arrhenius plots of fluxes and plotted with feed composition. Permeation activation energy at feed composition also increased with repeating the run, resulting from the relaxation occurring in the membrane. When the ethanol content in feed was higher, the permeation activation energy was observed to be more increased with repeating the run. The observation may result from a different relaxation process, depending on feed composition. At a lower ethanol content in feed, because more liquid could be absorbed in the membrane and the larger plasticization action of the absorbed liquid is executed on the membrane, the membrane mobility becomes bigger so that the relaxation can occur faster at the beginning, and more relaxation progresses before reaching a steady-state permeation. The resulting membrane could have more dense structure and be more stable from the thermodynamical point of view. That is why the permeation activation energy is more increased with decrease-

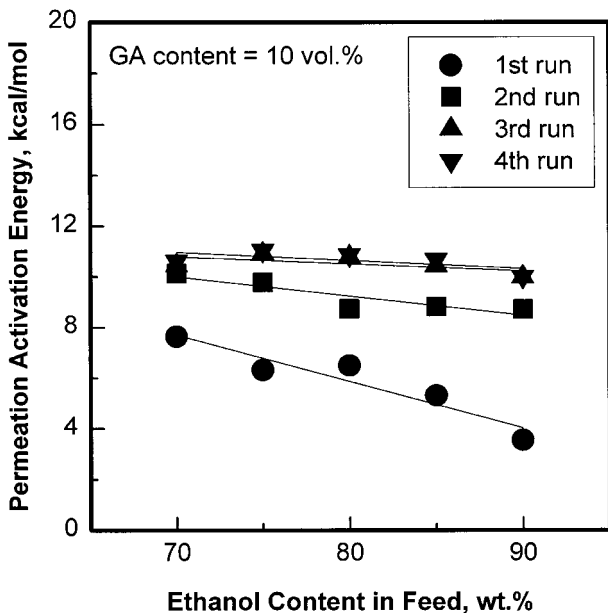


Figure 12 Permeation activation energy of the SA membrane crosslinked at 10 vol % GA content in the reaction solution against feed composition in the repeating operation.

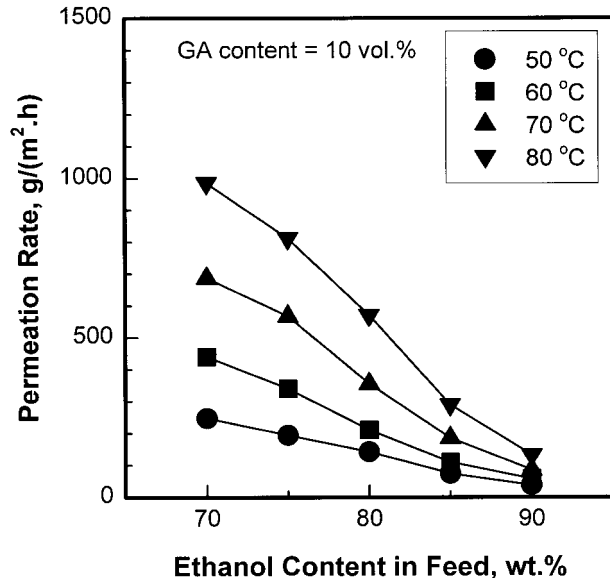


Figure 13 Permeation rate in steady state through the SA membrane crosslinked at 10 vol % GA content with feed composition.

ing ethanol content. Permeation activation energy in the second run was observed to increase more rather than that in the first run at higher ethanol content in feed as a result of continuous and slow relaxation process. Permeation activation energy at a feed composition increases less and less with repeating the run. The increase of the activation energy was more significant at a higher ethanol content in feed.

Figure 13 presents the plots of fluxes with feed composition. Fluxes are the level-off value obtained in repeating the run. The crosslinked SA membrane shows relatively an excellent pervaporation performance: fluxes of 60–1000 g/(m²h) and separation factors of 450–2600 for the given feed composition and temperature ranges, compared with PVA membranes. Flux data with feed composition show a normal trend as in the permeation of aqueous ethanol through hydrophilic membranes: smaller flux at a higher ethanol content in feed and high flux at a higher temperature. However, it is interesting to note the change in separation factor with feed composition (Fig. 14): the separation factor, on the whole, decreased with increasing ethanol content in feed; but, with increasing temperature, the separation factor had a decrease at low ethanol content and an increase at a high ethanol content in feed. Selectivity should normally show a decrease with temperature, but the membrane used in this study gave out the opposite tendency of separation factor with temperature in the range of high ethanol

content in feed: a higher separation factor at higher temperature, indicating that high temperature favors pervaporation performance in the separation of ethanol-concentrated mixtures. The reason for that is not clear. It might be related to the relaxation of the membrane during the process. Usually, when temperature is higher, the motion of polymeric chains is so active that the resulting membrane structure can be loose enough to decrease separation factor with temperature. However, it was discussed that the relaxation occurs faster at a higher temperature, and the relaxation progresses more slowly and continuously with operating time at a high ethanol content in feed. In this case, when the operating temperature increases, two opposite results might occur: the loose polymer structure by active polymeric chain motion and densification of the polymer structure by relaxation. When the ethanol content is high in feed, the latter would be pronounced to such an extent that the separation factor could increase with temperature.

CONCLUSIONS

For the pervaporation separation of ethanol-water mixtures, crosslinked SA membranes with GA were prepared by a solution method, wherein a nonsolvent of PVA (acetone) was used in a reaction solution instead of aqueous salt solutions. Stable membranes in aqueous solution could be obtained by this method at the GA content above 5 vol %. From IR spectroscopy, wide angle X-ray diffractometry, and swelling measurements, the reaction between SA and GA could be characterized and the aldehyde groups—as well as the acetal groups, as a result of crosslinking reaction—were observed increased with increasing the GA content in the reaction solution. From the measurement of preferential sorption, it was observed that the crosslinking could reduce both the solubility of water in the membrane and the permselectivity of the membrane toward water with the expense of membrane stability against water.

In the pervaporation separations of ethanol-water mixtures with ethanol content of 70–90 wt % at temperatures ranging from 40 to 80°C, the crosslinked membrane yields an excellent mem-

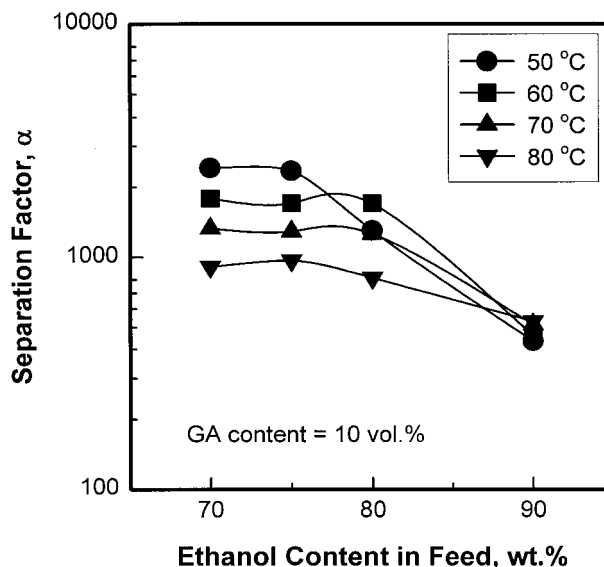


Figure 14 Separation factor in steady state through the SA membrane crosslinked at 10 vol % GA content with feed composition.

brane performance: fluxes of 60–1000 g m⁻² h⁻¹ and separation factors of 450–2600. Relaxation phenomena in the membrane during pervaporation were elucidated through an analysis on experimental data of membrane performance measured by repeating the operation in the given temperature. A significant decline in flux could be observed due to the relaxation of polymeric chains, and the extent of the flux decline was dependent on the operation temperature, the crosslinking density, and feed composition.

REFERENCES

1. A. Mochizuki, S. Amiya, Y. Sato, H. Ogawara, and S. Yamashita, *J. Appl. Polym. Sci.*, **40**, 385 (1990).
2. C. K. Yeom, J. G. Jegal, and K. H. Lee, *J. Appl. Polym. Sci.*, **62**, 1561 (1996).
3. C.-K. Yeom and K.-H. Lee, *J. Membr. Sci.*, **109**, 257 (1996).
4. J. W. F. Spitzen, Ph.D. thesis, Twente University, The Netherlands, 1988.
5. C. K. Yeom and R. Y. M. Haung, *J. Membr. Sci.*, **67**, 39 (1992).
6. C. K. Yeom and K.-H. Lee, *J. Appl. Polym. Sci.*, **59**, 1271 (1996).
7. E. Ruckenstein and F. Sun, *J. Membr. Sci.*, **95**, 207 (1994).