Modification of Poly(vinyl alcohol) Membranes Using Sulfur-succinic Acid and Its Application to Pervaporation Separation of Water–Alcohol Mixtures

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ABSTRACT: For the purposes of the water-selective membrane material development for pervaporation separation, we crosslinked poly(vinyl alcohol) (PVA) with sulfur-succinic acid (SSA), which contains —SO_3OH, by heat treatment and investigated the effect of the crosslinking density on the separation of water–alcohol mixtures by pervaporation technique. The crosslinking reaction between PVA and SSA was characterized through Fourier transform infrared spectroscopy and differential scanning calorimetry tests by varying the amount of the crosslinking agent, the reaction temperature, and the swelling measurements of each pure component. The separation performance of the water–methanol mixture is not good due to the existence of sulfonic acid, hydrophilic group, in the crosslinking agent. However, for the water–ethanol mixture, the flux of 0.291 kg/m^{2}h and the separation factor of 171 were obtained at 70°C when PVA-crosslinked membrane containing 7 wt % SSA was used. The same membrane also showed flux of 0.206 kg/m^{2}h and a separation factor of 1969 at the same operating temperature. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 1717–1723, 1998

Key words: poly(vinyl alcohol); sulfur-succinic acid; crosslinking; pervaporation

INTRODUCTION

In membrane material science, it is difficult to select a polymer which is suitable for separating polar–polar mixture systems, such as water–alcohol mixtures, because of complex interactions between the membrane material and the feed mixture to be separated. According to Huang and colleagues,[1–4] materials, including water-soluble polymers, for dense membranes, should be related on the basis of maintaining a proper hydrophilic/hydrophobic balance criterion for a given separation system. In order to adjust and control the hydrophilic/hydrophobic balance properties of a membrane, several techniques have been tried, such as crosslinking a polymer,[2,4] grafting a selective species onto an inert film,[4,5] copolymerization,[6–8] and blending a hydrophilic polymer with a relatively hydrophobic polymer.[9] In reality, the introduction of a dicarboxylic acid (such as maleic acid) as the crosslinking agent into poly(vinyl alcohol) (PVA) enhances the selectivity of the membrane to water because the carboxylic group has a relatively high polarity and a strong interaction with water through hydrogen bonding.[10] Therefore, the modifications of PVA chemical structure

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Table I Crosslinking Methods of PVA Polymer Published in the Literature for Membrane Applications

Crosslinking Agent or Method	Crosslinking or Condition	Applications[a]	Ref.
Formaldehyde	$H_2SO_4/Na_2SO_4/H_2O$	RO	13–15
Glutaraldehyde	HCl/H_2O	RO	16, 17
Oxalic acid/boric acid	$KCr(SO_4)\cdot 2H_2O$	RO	18
Heat treatment	120–175°C	RO	19
γ-irradiation	0.5–2.0 Mrad	RO	20
Electron-beam irradiation	—	GAS	21
Dicarboxylic acid/Cr(II) solution/ketones	—	RO	22
Maleic acid	Heat treatment at 150°C	PV	10
	Triethanoamine/H_2O	PV	23
Amic acid	Heat treatment	PV	24
Poly(acrylic acid) (*MW* 2,000)	150°C for 1 h	PV	25–28

[a] RO: reverse osmosis; GAS: gas separation; PV: pervaporation.

through esterification using other chemicals having carboxylic groups are still worth consideration. Furthermore, the introduction of another hydrophilic group, such as sulfuric acid, would be expected to leave the resulting polymer more hydrophilic. It is reported that the nylon 6/poly(acrylic acid) blended membrane showed an increase of the separation efficiency and then a decrease.[2] This supported the existence of the hydrophilic/hydrophobic balance criterion.

PVA has been studied intensively as a membrane because of its good film-forming, highly hydrophilic, and good chemical-resistant properties. Membrane selectivity can generally be increased through the modification of the chemical structure of polymers by crosslinking, grafting, etc.

Prichard[11] and Finch[12] described the chemical/physical properties and applications of PVA in some detail, and Prichard[11] has tried to introduce several modification methods. Table I summarizes the crosslinking methods published in the literature for membrane applications.

In this study, we tried to crosslink PVA by heat treatment using a sulfursuccinic acid (SSA) through the reaction between the hydroxyl group in PVA and the carboxylic acid group in SSA. The membrane that results from varying the SSA content is also characterized through the measurements of infrared spectroscopies, thermal properties, and swelling degrees of pure component. The crosslinked membranes are then applied to pervaporate the water–methanol, ethanol, and isopropyl alcohol mixtures to investigate the effects of introducing hydrophilic groups, carboxylic acid, and sulfuric acid to the water-soluble polymer PVA. The pervaporation is carried out for 10 wt % of water in each feed mixture with varied crosslinking agent content in base polymer, PVA, at 60 and 70°C. Figure 1 shows the postulated reaction mechanism between PVA and SSA.

EXPERIMENTAL

Materials

Fully hydrolyzed PVA with a molecular weight of 50,000 was purchased from Showa Chemical Co. (Tokyo, Japan) Sulfur-succinic acid as a crosslinking agent was from Aldrich Co. (Milwaukee, USA) Methanol, ethanol and isopropyl alcohol (IPA) were analytical grade from Merck (Darmstadt,

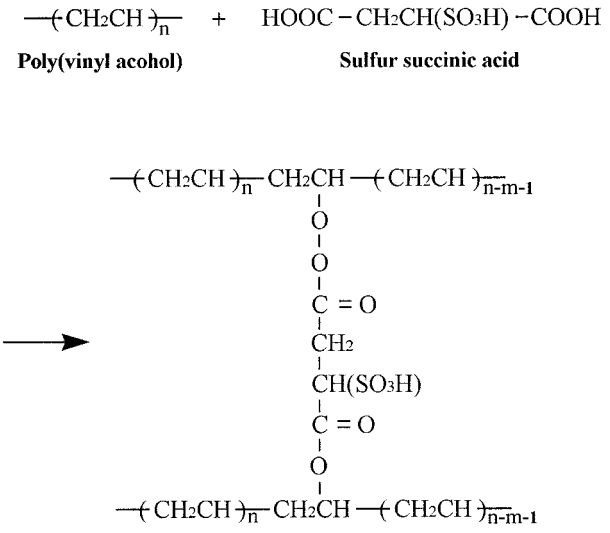


Figure 1 Postulated reaction mechanism of PVA and sulfur succinic acid.

Germany). The water used was the ultrapure water produced from the MPI system.

Membrane Preparation

Aqueous 10 wt % PVA solutions were prepared by dissolving preweighed quantities of dry PVA in ultrapure water and heating at 90°C for at least 6 h. Then the PVA solutions were mixed together with the SSA by varying each component composition to form a homogeneous solution for at least 1 day at room temperature. Homogeneous membranes were cast onto a Plexiglas plate using a Gardner knife with predetermined drawdown thickness. The membranes were allowed to dry in air at room temperature, and completely dried membranes were then peeled off. The dried membranes were heated in a thermosetted oven at the desired reaction time, 1 h, and temperature, 150°C. The resulting membranes were then stored in solution to be separated for further use. The membrane thickness was about 0.2–0.25 mm.

Infrared Analysis

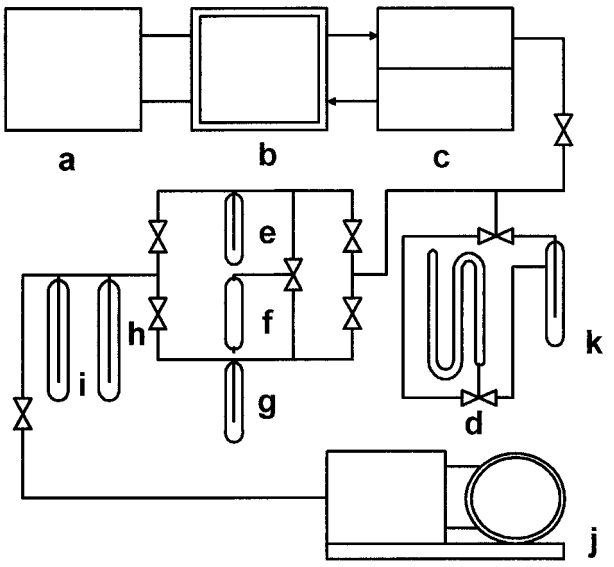
Infrared (IR) spectra were measured with a Perkin–Elmer 1725X Fourier transform infrared (FTIR) spectroscope. The thickness of specimens ranged from 0.02 to 0.03 mm.

Differential Scanning Calorimetry (DSC)

The thermal analyses were performed with a DuPont 2000. Sample weights ranged from 5 to 8 mg. The samples were heated from 30 to 300°C at a heating rate of 10°C/min. The intercept point of the slopes was taken as the glass transition temperature (T_g) and the peak point of the thermal diagram as melting temperature (T_m).

Swelling Measurement

The sorption capacity of the membrane was measured by immersing the membrane samples in the pure component at 60°C. After being wiped with the cleansing tissue, the membranes were weighed as quickly as possible. This procedure was repeated about 20 times until satisfactory reproducibilities were obtained. Then the samples were dried in a vacuum oven at room temperature to a constant weight. The swelling degrees, Q, were calculated as follows:



a - Temperature Controller
b - Feed tank
c - Permeation cell
d - Vacuum manometer
e,g - Cold traps for collecting samples
f - Drying tube
h,i -Cold traps
j - Vacuum pump
k - Trap

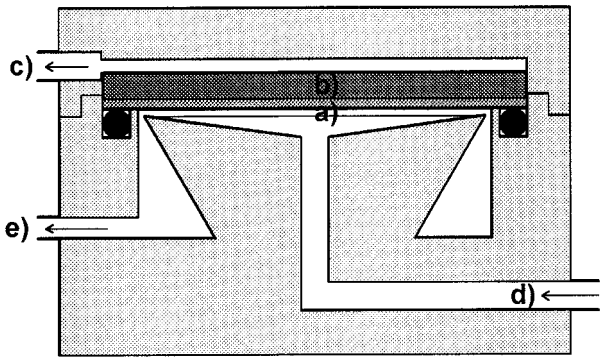
Figure 2 Schematic diagram of pervaporation apparatus used in this study.

$$Q = \frac{m - m_o}{m_o} \times 100$$

where m is the mass of the swollen sample and m_o is the original mass.

Pervaporation

The apparatus used in this study is illustrated in Figure 2. The pervaporation separation experiments were performed employing a stainless-steel pervaporation cell (Fig. 3).[26–28] The feed mixture enters the cell through the center opening, flows rapidly through the thin channel, and leaves the cell through the side opening, which allows relatively higher fluid velocity parallel to the membrane surface. The effective membrane area was 14.2 cm^2. The four-necked feed tank has a solution capacity of approximately 1,000 mL. From the feed tank, which was kept at a constant temperature by the water bath, the feed mixture was cir-



a) membrane
b) porous support
c) permeate
d) feed mixture in
e) feed mixture out

Figure 3 Configuration of the pervaporation cell used in this study.

culated through the cell. The pressure at the downstream side was kept below 2 mmHg by a vacuum pump. The pervaporation experiments of alcohol–water mixtures containing 10 wt % water were conducted at 60 and 70°C. Upon reaching steady-state flow conditions, product samples were collected at timed intervals, isolated from the vacuum system, and weighed. The composition analysis of the permeate was done by gas chromatography. The following relationship was used to calculate the separation factor:

$$\alpha_{i/j} = \frac{(y_i/y_j)}{(x_i/x_j)}$$

where x is the feed composition, y is the permeate composition, and component i is the preferentially permeating component.

RESULTS AND DISCUSSION

Figure 4 shows the IR spectra of the treated (reacted) PVA/SSA films at 150°C for 1 h with 3, 5, and 7% of the SSA content to PVA. It has been reported that the ester (—CO—O—) band can be found at 1735 cm^{-1}.[23,25] The peak intensity of this carbonyl band increased quantitatively as the SSA content increased. The 1240 cm^{-1} peak arose from the C—O stretch mode in the ester group and 920 cm^{-1} was the O—H out-of-plane motion of the carboxylic group in SSA. While the C—O stretch mode increased as the SSA content increased, the peak intensity of O—H out-of-plane motion decreased due to the reaction. Therefore, it is clear that the spectral changes are evidences of crosslinking reaction between the hydroxyl groups of PVA and the carboxylic groups of SSA. Figure 5 illustrates the IR spectra of the reacted PVA with 5 wt % SSA for 10 min at various reaction temperatures. As the reaction temperature increased, the several spectra changed. First, the intensity of the carbonyl band, C=O, in the ester group that appeared at 1720 cm^{-1} increased as the temperature increased. Also, the peak intensity of O—H in SSA decreased due to the reaction as the temperature increased, while the C—O peak in the ester that appeared at 1240 cm^{-1} increased slightly. The increases in the characterization peak of the ester group means that there must be some reaction between the carboxylic acid and the hydroxyl group. Furthermore, the resulting membranes resisted in boiling water and there was no weight change before and after immersing the sample in boiling water.

The thermal results are illustrated in Table II. As can be seen, the T_g and T_m increase with increased SSA contents in the samples. The increases in T_g and T_m could be evidence of some reaction of SSA and PVA membrane. In general, if the crosslinking agent in the polymeric film in-

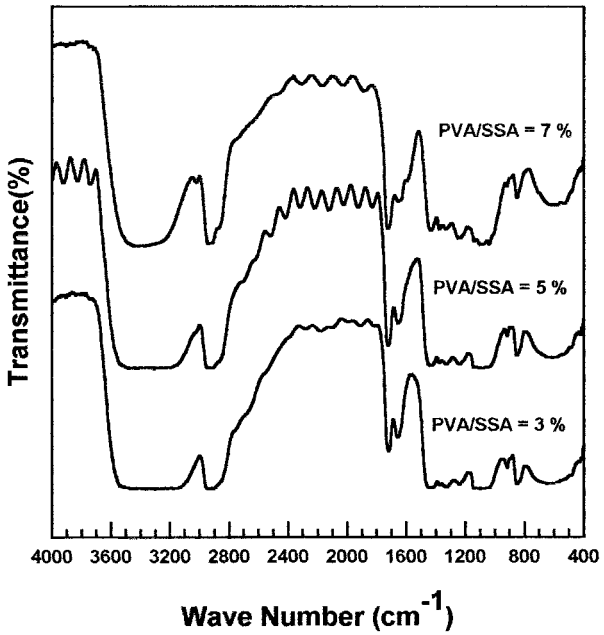


Figure 4 IR spectra of the reacted PVA/SSA membranes containing 3, 5, and 7 wt % of the SSA content to PVA at 150°C for 1 h.

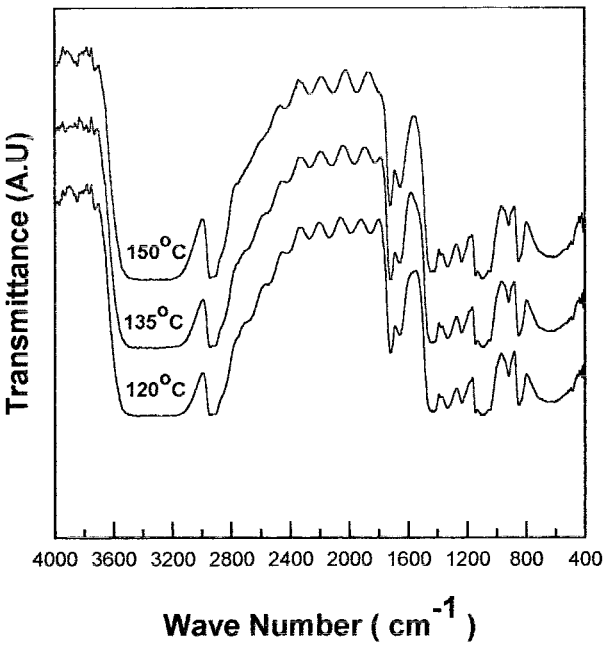


Figure 5 IR spectra of reacted PVA with 5 wt % SSA for 10 min at 120, 135, and 150°C.

creases and then this film is reacted at the specified reaction conditions, the arrangement of the polymer network is hindered by the crosslinking reaction. In result, the crystallinity may decrease. However, since the reacted film has the crosslinking and crystallinity portions at the same time, it is not quite clear in which portion the transport of small molecules is more dominant.[29]

Table III shows the results of the swelling measurements for each pure component at 60°C. As the SSA contents increased, the swelling degrees decreased due to the decrease of the free volume, even though the membrane contains more of the hydrophilic functional group. Also, the sorption capability decreased with increasing the carbon number in alcohol. From these results, it could be predicted that the separation efficiency is best for water–IPA mixtures since the sorption difference between water and IPA is the largest and the diffusivity is the smallest due to the size of IPA and the compact network.

Table II Typical Thermal Results of T_g and T_m for the Reacted PVA/SSA Membranes

Membranes	T_g (°C)	T_m (°C)
Pure PVA	[b]71.2	—
3%[a]	122.5	205.3
5%[a]	144.9	217.5
7%[a]	175.1	233.8

[a] SSA contents in PVA by weight.
[b] Fully hydrolyzed; taken from Huang and Rhim.[23]

Table III Swelling Degree Measurements for Each Pure Component at 60°C (wt %)

	Solutions			
[a]Membranes	Water	MeOH	EtOH	IPA
3%	43.35	18.18	15.26	6.52
5%	42.06	17.26	14.12	4.90
7%	41.33	15.20	13.70	2.80

[a] SSA contents in PVA by weight.

Next, we will discuss the pervaporation separation characteristics of water–alcohol mixtures using the PVA/SSA membranes at 60 and 70°C. The membranes were prepared at a reaction temperature of 150°C for 1 h. Figure 6 shows the pervaporation results for the water–methanol mixture in terms of the separation factor and the permeability. As expected, the permeabilities decreased and the separation factors increased as the SSA content increased in PVA. In fact, as the crosslinking density in a polymer increases, the resulting material has a more compact network structure, leading to less chain mobility. Therefore, both the free volume in the polymer and the amount of solvent swelling decrease.[24] In other words, as the crosslinking density increases, the solubility of the liquid mixture declines and the diffusivity, which is governed by the free volume, decreases due to the rigidity of the polymer chains. This might cause the permeation rate through the

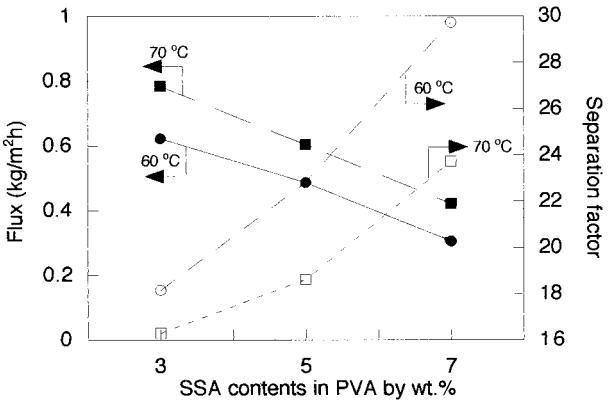


Figure 6 Permeabilities and separation factors for water : methanol = 10 : 90 mixtures by wt.

membrane to decrease.[27] However, the permeation rate is much higher than that of the other membranes, such as PVA/poly(acrylic acid) membranes,[28] because of the introduction of hydrophilic group, sulfonic acid. This leads to a lower separation factor even though the membrane is crosslinked. Figure 7 illustrates the separation characteristics of water–ethanol mixtures. As expected, the permeabilities are lower than those of the water–methanol mixture, while the separation factors are higher. In general, as the carbon number in alcohol increases, the hydrophilicity decreases. This means that the membrane absorbs more methanol than ethanol, since the membrane is very hydrophilic due to the existence of the sulfonic acid. Also, the diffusivity of ethanol in the membrane could be lower than that of methanol since the molecular size of ethanol is larger than that of methanol. The flux of 0.291 kg/m^{2}h and the separation factor of 171 were obtained at 70°C. The separation efficiencies of the water–isopropyl alcohol mixture are illustrated in Figure 8. These permeabilities are lower than those of water–methanol and water–ethanol mixtures, while the separation factors are much higher. This might be due both to the solubility of the mixture to be separated in the membrane and to the diffusivity. In this case, the flux and the separation factor show 0.206 kg/m^{2}h and 1969 at 70°C, respectively.

CONCLUSIONS

We have tried to crosslink PVA membranes using SSA for the separation of water–alcohol mixtures by the pervaporation technique. The esterification between the hydroxyl group in PVA and the carboxyl group in SSA has been characterized by FTIR spectroscopy, DSC tests, and swelling measurements. From these studies, it could be considered that there must be more crosslinking reaction as the contents of the crosslinking agent increase. The ratio of SSA to PVA varied from 3 to 7 in weight. These membranes were then applied to separate the water–methanol, –ethanol, and –isopropyl alcohol mixtures at 60 and 70°C. The separation performance of the water–methanol mixture was not good due to the existence of sulfonic acid in the crosslinking agent. However, for the water–ethanol mixture, the flux of 0.291 kg/m^{2}h and the separation factor of 171 were obtained at 70°C when PVA membrane crosslinked with 7 wt % SSA was used. The same membrane showed the flux of 0.206 kg/m^{2}h and the separation factor of 1969 at the same operating temperature. Therefore, it could be said that the developed PVA membrane is more suitable for the separation of the water–isopropyl alcohol mixture.

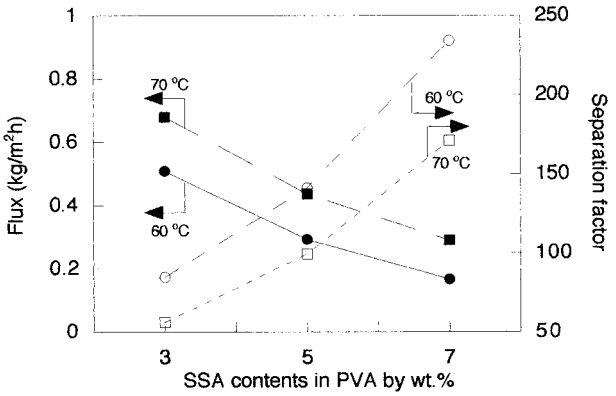


Figure 7 Permeabilities and separation factors for water : ethanol = 10 : 90 mixtures by wt.

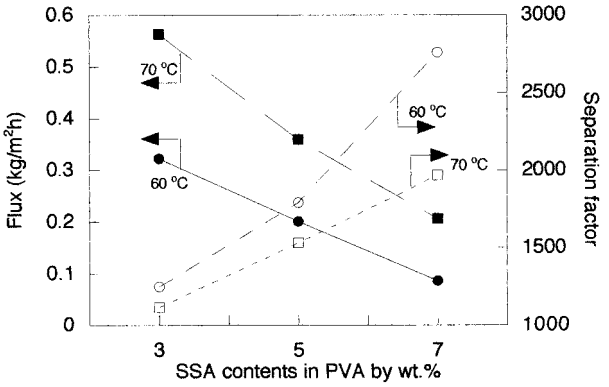


Figure 8 Permeabilities and separation factors for water : isopropyl alcohol = 10 : 90 mixtures by wt.

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