

Pervaporation Separation of Binary Organic-Aqueous Liquid Mixtures Using Crosslinked PVA Membranes.

I. Characterization of the Reaction between PVA and PAA

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SYNOPSIS

For the purposes of the water-selective membrane material development for pervaporation separation, poly(vinyl alcohol) (PVA) was crosslinked with a low molecular weight of poly(acrylic acid) (PAA). The crosslinking reactions between PVA and PAA were characterized through IR spectroscopy, differential scanning calorimetry (DSC), and tensile tests when varying the reaction conditions, that is, time, temperature, amounts of crosslinking agents, PAA. It was found that the crosslinking reaction was fast: in other words, that the reaction mainly occurred at the initial step of each reaction condition. The best reaction conditions for preparing the crosslinked PVA membranes were found to be: reaction time not over 1 h, reaction temperature in the range of 150–180°C. PAA contents of 15–20 wt % were found satisfactory with respect to the application areas. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The pervaporation separation technique is very interesting because of its separation capability of azeotropic, close boiling, or aqueous-organic mixtures with energy savings. Many studies have been successfully carried out on the separation of water-ethanol mixtures. Recently pervaporation membrane materials are being developed worldwide. Poly(vinyl alcohol) (PVA) is still the object of pervaporation researchers because of its chemical and physical natures, and its excellent permselective characteristics even though the PVA composite membrane material known as GFT membrane has been commercialized.¹

According to Huang et al.,²⁻⁵ materials, including water-soluble polymer, 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 such as crosslinking a polymer,^{3,5} grafting a selective species onto an inert film,^{5,6} copolymerization,⁷⁻⁹ and blending a hydrophilic polymer with a relatively hydrophobic polymer¹⁰ have been tried. In reality, the introduction of a dicarboxylic acid such as maleic acid as the crosslinking agent into 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.¹ Therefore, the modifications of PVA chemical structure through esterification using other chemicals having carboxylic groups are still worth consideration. Another motivation of the chemical modification of PVA is to prepare polymeric membranes more resistant that are to the toxic organic chemicals such as phenol drained from the chemical or electronic industries. Table I summarizes the crosslinking methods of water-soluble PVA polymer published in the literature for membrane applications.

In this study, PVA was crosslinked by the heat treatment using a low molecular weight (2,000) of PAA through the reaction between the hydroxyl group in PVA and the carboxylic group in PAA. The

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Table I Crosslinking Methods of PVA Polymer for Membrane Applications

Crosslinking Agent	Crosslinking Condition or Method	Applications	Reference
Formaldehyde	H ₂ SO ₄ /Na ₂ SO ₄ /H ₂ O	RO ^a	11-13
Glutaraldehyde	HCl/H ₂ O	RO	14, 15
Oxalic acid/boric acid	KCr(SO ₄) ₂ /H ₂ O	RO	16
Heat treatment	120-175°C	RO	17
Gamma irradiation	0.5-20 mrad	RO	18
Electron-beam irradiation	—	GAS ^b	19
Dicarboxylic acid/Cr(III) solutions/ketones	—	RO	20
Maleic acid	Heat treatment at 150°C	PV ^c	1
	Triethanolamine/water	PV	21
Amic acid	Heat treatment	PV	22

^a RO: reverse osmosis.^b GAS: gas separation.^c PV: pervaporation.

reason for the selection of M_w 2,000 of PAA is the chain mobility of PAA in PVA. If the molecular weight of PAA were high enough, the crosslinking reaction between the hydroxyl group in PVA and the carboxyl group in PAA may not occur because of the inflexibility of the PAA chain in the PVA network. The effect of the crosslinked PVA membrane on the permselectivity using a lower molecular weight of PAA than 2,000 will be presented in the next paper. The objectives of this paper are to characterize the crosslinking reactions between PVA and PAA through the measurements of thermal and physical properties and infrared spectroscopies under the various conditions of reaction temperature, reaction time, and the amount of PAA contents. Figure 1 shows the postulated crosslinking mechanism between PVA and PAA.

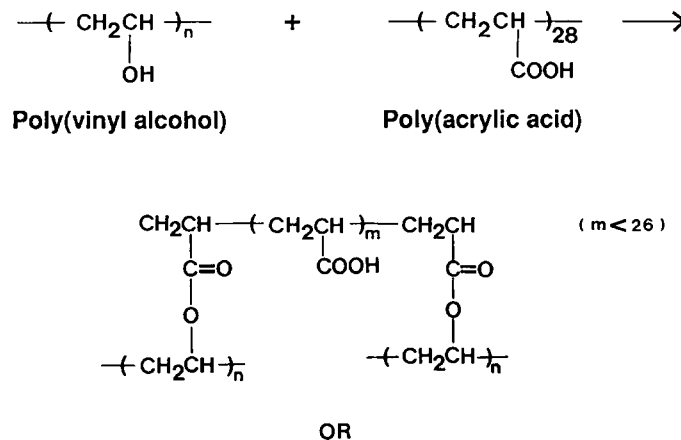
EXPERIMENTAL

Materials

Fully hydrolyzed PVA with molecular weight of 50,000 and PAA with molecular weight of 2,000 (25 wt % in water) were purchased from Showa Chemical Co. and Aldrich Co., respectively. Used water was the ultra-pure water produced from an MPI system.

Membrane Preparation

Aqueous 10 wt % PVA solutions were prepared by dissolving preweighed quantities of dry PVA in ultra-pure water and heating them at 90°C for at least 6 h. Aqueous 25 wt % PAA solutions were diluted

**Figure 1** Postulated reaction mechanism of PVA and PAA.

to 10 wt % solutions. Then two polymer solutions were mixed together 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 blended membranes were heated in a thermosetted oven for desired reaction times and temperatures. The resulting membranes were then stored in solutions to be separated for further use.

Infrared Analysis

Infrared spectra were measured with FT-IR Spectroscopy of Bio-Rad Co., Model Digilab Division FTS-80. The thickness of specimens ranged from 0.02 to 0.03 mm.

Differential Scanning Calorimetry

The thermal analysis were measured by a DuPont 2000. Sample weight ranged from 5 to 7.5 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 thermal diagram as melting temperature, T_m .

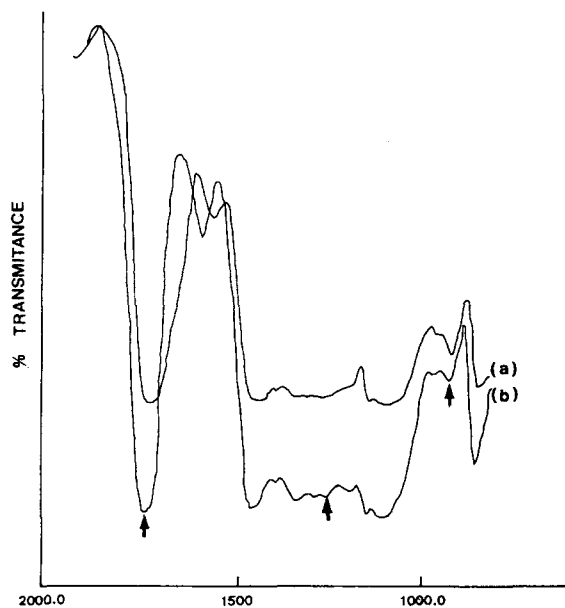


Figure 2 IR spectra of (a) untreated PVA:PAA = 75 : 25 film and (b) treated PVA:PAA = 75 : 25 film at 180°C for 45 min.

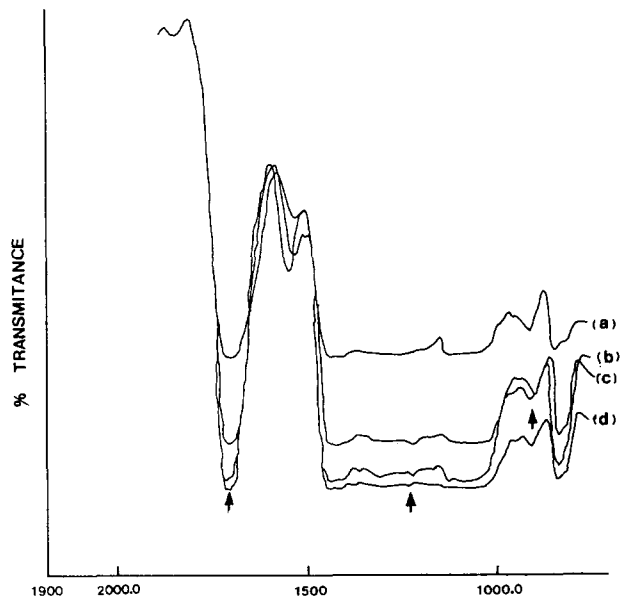


Figure 3 IR spectra of blended films with varying reaction times: crosslinking agent, PAA, content 20 wt %, reaction temperature 180°C.

Tensile Testing

The universal testing instrument (Instron model 1125) was used for tensile studies of the resulting membranes. The dumbbell-shaped membrane specimens were about 6-mm wide, 110-mm long end-to-end, and 0.02–0.03-mm thick. All samples were tested at room temperature, at a crosshead speed of 10 mm/min. At least 15 specimens for each resulting membranes were tested. The ultimate tensile strength, ultimate elongation, and tensile modulus were then measured and averaged.

RESULTS AND DISCUSSION

Figure 2 shows the IR spectra of the untreated (just blended) and the treated (reacted) PVA/PAA film with composition of 75 : 25 wt %. It has been reported that the carbonyl band ($C=O$) in the ester group can be found at 1730 cm^{-1} .^{21,22} This carbonyl band increases quantitatively for the treated PVA/PAA film. The 1240 cm^{-1} peak arises from the $C-O$ stretch mode in PAA and 920 cm^{-1} is the $O-H$ out-of-plane motion of the carboxylic group in PAA.²² While the $C-O$ stretch mode of the treated PVA/PAA film increases, the peak intensity of $O-H$ out-of-plane motion decreases due to the crosslinking 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 PAA. Figure 3 shows the effect of various crosslinking times for the sample of PVA: PAA = 80 : 20 treated at 180°C for 45 min. While the reaction time increases, the peak intensities of the carbonyl band and the C=O stretch mode increase gradually and the peak intensity of O—H out-of-plane motion decreases. When we compare the difference of the peak intensities of the carbonyl band in the ester group, the differences are smaller and smaller as the reaction time increases. In other words, most of the crosslinking reaction occurs at the initial reaction time and, therefore, the optimum crosslinking time can be considered as below 45 min. Figure 4 illustrates the effect of PAA content in the membrane. This figure also shows the same trend as the previous figures.

Figure 5 shows the effect of PAA contents in the PVA/PAA membrane on the T_g and the T_m . As expected, the T_g and the T_m increase gradually with increasing PAA contents. The T_g of PVA homopolymer is known as 71–99°C. Because the T_g of PVA: PAA = 95 : 5 sample is over 120°C, there must be some reaction in the blended membrane. The increase of T_m for all the samples could be the evidence of the crosslinking reaction. However, when the PAA content is more than 15 wt %, the T_g values are not seriously changed. Therefore, the optimum PAA contents of the membrane can be considered as 15

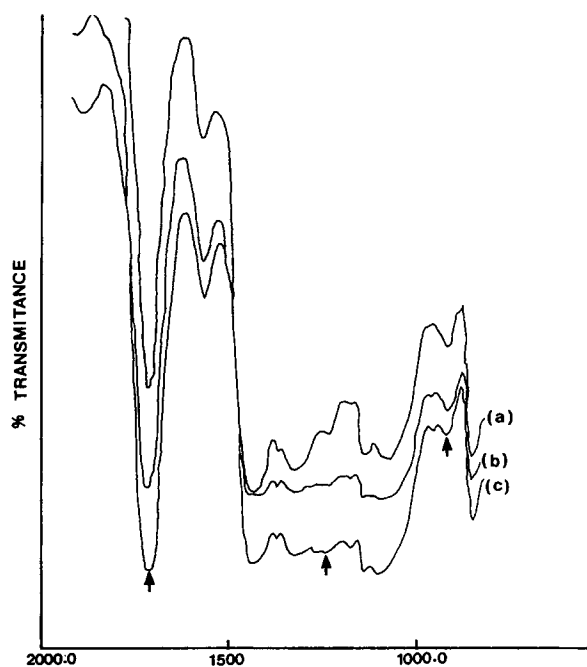


Figure 4 IR spectra of blended films with varying crosslinking agent, PAA, contents treated at 180°C. PVA: PAA = (a) 95 : 5, (b) 85 : 15, and (c) 75 : 25.

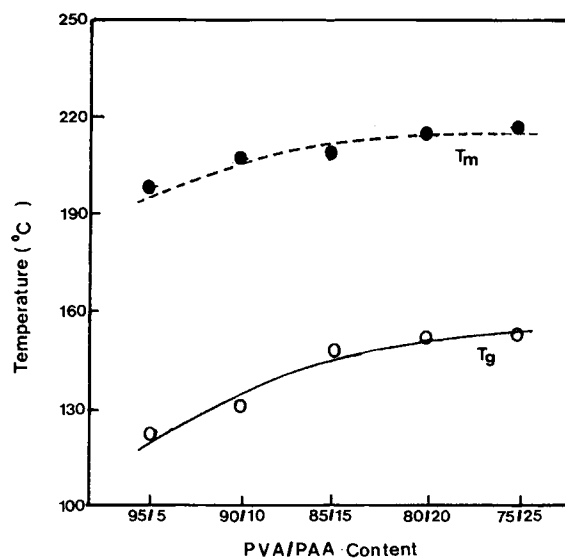


Figure 5 Effect of PAA contents on T_g and T_m . Reaction conditions: 180°C for 45 min.

wt % of PAA. The effect of the reaction time on the thermal properties for the PVA:PAA = 80 : 20 sample is shown in the Figure 6. The reaction time varies from 25 to 90 min. While in the case of T_g the increasing ratio at the initial reaction time range of 25–45 min is steep, there are small changes after 45 min. In other words, most of the crosslinking reaction occurs at the initial step of the crosslinking reaction and the reaction proceeds slowly after the initial reaction because of the difficulty of the chain

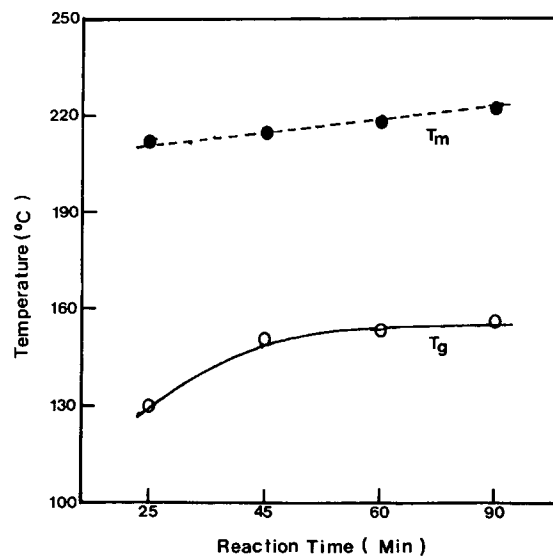


Figure 6 Effect of crosslinking times on T_g and T_m for PVA:PAA = 80 : 20 sample reacted at 180°C.

mobilities due to the initial crosslinking reaction. However, the T_m shows a monotonous increase with increasing reaction time. From the above discussion, the optimum reaction conditions are as follows:

1. Reaction time: because the reaction can occur actively at the initial step, it is not necessary that the reaction time is as long as or over 1 h. Therefore, the optimum reaction time could be 45 min.

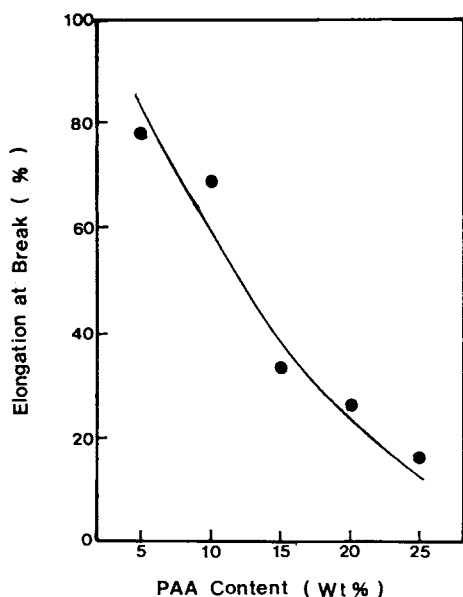
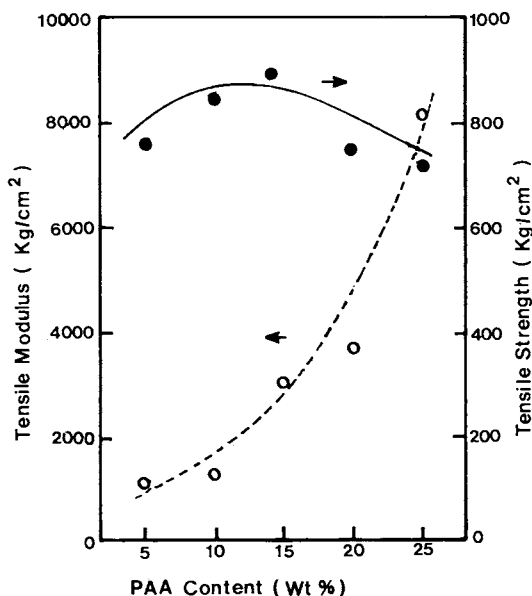


Figure 7 Effect of PAA contents on (a) tensile strength and (b) tensile modulus elongation at break.

2. Reaction temperature: if the reaction temperature is too high, it could be difficult to control the crosslinking reaction rate. If the reaction temperature is low, the crosslinking reaction could not be satisfied. Therefore, the crosslinking temperature could be in the range of 150–180°C.

Figure 7 indicates the measurements of the physical properties with varying PAA contents in the PVA/PAA membranes. Generally speaking, the modulus has a higher value when the crosslinking agent content increases, but, in case of the tensile strength, this rule is not necessarily followed.²² While the tensile strength increases with increasing PAA content of 15 wt % and decreases after 15 wt %, the tensile modulus increases gradually with increasing PAA contents. As expected, the elongation at break decreases gradually. The reason for the decrease of the tensile strength after 15 wt % is the brittleness of the samples (the tensile modulus and the elongation are shown in the figures). Therefore, the optimum PAA content in the membrane can be considered as 15 wt % of PAA, the same as Figure 5. Figure 8 illustrates the effect of the crosslinking reaction time on the physical properties. As the crosslinking time increases, the tensile strength and the tensile modulus increase and the elongation decreases. From the viewpoint of the physical properties, it can be considered that the optimum reaction conditions are reaction time below 60 min and reaction temperature similar to the case of thermal tests.

CONCLUSIONS

The characterization of the crosslinking reactions between PVA and PAA has been investigated in detail through the IR, DSC, and tensile studies. From this work, several conclusions can be drawn as follows:

1. The crosslinking reaction between PVA and PAA was identified through the studies of thermal, mechanical, and IR spectroscopy.
2. It was found that the crosslinking reaction was fast: in other words, the reaction was determined at the initial step of each reaction condition.
3. The best reaction conditions for preparing the crosslinked PVA membranes were found to be: reaction time not over 1 h; reaction temperature in the range of 150–180°C; and

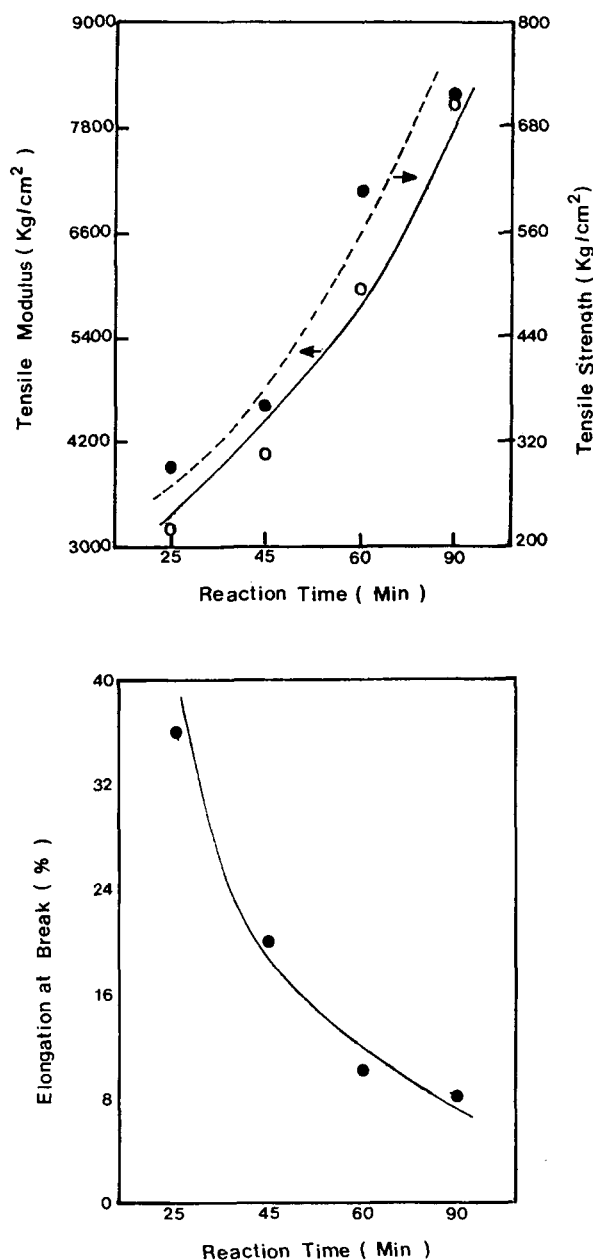


Figure 8 Effect of crosslinking times on (a) tensile strength and (b) tensile modulus elongation at break.

15–20 wt % of PAA in PVA, good for the PAA contents depending on its application areas.

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