

Effects of the Degree of Crosslinking on Properties of Poly(vinyl alcohol) Membranes

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ABSTRACT: Asymmetric poly(vinyl alcohol) (PVA) membranes were prepared by the phase inversion technique, and crosslinked with glutaraldehyde. The degree of crosslinking of the membrane was controlled by varying the crosslinking conditions. The effects of the degree of crosslinking on the swelling characteristics, contact angles, critical surface tensions, and pervaporation characteristics were examined. A method for the evaluation of the degree of crosslinking, which needs only the glutaraldehyde concentration of the crosslinking solution to be measured after the crosslinking reaction, is proposed, and was found useful. The degree of swelling of PVA membrane for water decreases abruptly as the degree of crosslinking increases. However, the degree of swelling for ethanol is nearly independent of the degree of crosslinking. The critical surface tension of the membrane increases more or less within the range of 37.0—40.0 dyn cm⁻¹ with increasing degree of crosslinking below 30%. But, it is nearly constant at 40.5 dyn cm⁻¹ above 30%. The wetting behavior of the membrane may not be greatly affected by the degree of crosslinking. The selectivity factor and permeate flux of the membrane in the pervaporation of the ethanol–water mixture of 95 wt% ethanol concentration decrease similarly with increasing degree of crosslinking. The pervaporation characteristics seem to be closely related to the swelling behavior. The degree of crosslinking is an important variable for swelling behavior and pervaporation characteristics.

KEY WORDS Poly(vinyl alcohol) Membranes / Degree of Crosslinking / Contact Angle, Critical Surface Tension / Swelling Characteristics / Pervaporation Characteristics /

Poly(vinyl alcohol) (PVA) membranes have been investigated extensively for desalination, pervaporation, biomedical separation and many other applications.^{1–3} The pervaporation process through PVA membranes is used industrially for separations of organic solvents from aqueous solution.⁴ PVA is a hydrophilic polymer and PVA membrane is highly selective to water.

The majority of commercially available membranes are prepared by the so-called phase inversion technique. The phase inversion technique of forming an asymmetric PVA membrane consists of casting, precipitation

and crosslinking. PVA is dissolved in water, and this solution is cast on a support, *i.e.*, a glass or metal plate or a nonwoven textile fabric. The cast PVA solution is then precipitated by immersing it in an aqueous solution of inorganic salts. The precipitated PVA film is still soluble to water, and can not be used as a membrane for separations of aqueous mixtures. To increase the stability of PVA membrane, it should be crosslinked with a crosslinking agent.

Crosslinking may affect the hydrophilicity and mechanical strength of PVA membranes. Swelling characteristics and surface properties

plate. PVA film means the film formed before crosslinking. Therefore, H_0 can be calculated from the following equation:

$$H_0 = (\rho V_p W_p / M_u) / (V_p / 1000) \quad (5)$$

$$= 1000 \rho W_p / M_u$$

where M_u is the molecular weight of a repeat unit $-(\text{CH}_2\text{CH}-)$ of PVA and equal to 44, and

ρ and W_p are the density and weight fraction of PVA, respectively, of aqueous PVA casting solution. We assume that ρ is equal to 1.0 g cm^{-3} .

The degree of crosslinking, D_c , of crosslinked PVA membranes can be defined in terms of the hydroxyl group concentration:

$$D_c = \frac{H_0 - H}{H_0} \times 100 (\%) \quad (6)$$

However, it is difficult to measure H in crosslinked PVA membranes. To replace H in eq 6 with measurable variables, the following equation derived from eq 4 can be used:

$$H = H_0 - 4(G_0 - G)V_c / V_p \quad (7)$$

EXPERIMENTAL

Preparation of PVA Membranes

Asymmetric PVA membranes were prepared by the phase inversion technique. PVA (obtained from Aldrich Chem. Co.) with an average degree of polymerization of 1700 and degree of saponification of 98% was used. A PVA solution of 15 wt% was prepared by dissolving PVA in water at temperatures of 70–90°C. PVA solution was cast on a stainless steel plate. The effective area and depth of the casting plate were 300 cm^2 (120 mm W \times 250 mm L) and 0.5 mm, respectively. Therefore, the casting volume (V_p) was 15 cm^3 . For calculation of hydroxyl group concentration (H) of PVA membrane, the volume of PVA membrane is assumed to be equal to the casting volume. The PVA solution was poured onto the plate and

Table I. Composition on aqueous precipitation solution

Component	Concentration/ mol l^{-1}
Sodium sulfate	1.41
Sodium hydroxide	0.625

Table II. Composition on aqueous crosslinking solution

Component	Concentration/ mol l^{-1}
Glutaraldehyde	0.03 (0.06 ^a)
Sulfuric acid	0.15
Sodium sulfate	0.96

^a This concentration was used only for the preparation of PVA membrane whose degree of crosslinking was 75%.

spread out with a knife. The plate was kept in air for 10 min at ambient temperature of 20–22°C. The resulting system was then placed in the precipitation bath (250 mm W \times 400 mm L \times 150 mm H) at room temperature. The precipitation solution given in Table I was poured carefully over the PVA solution on the casting plate. The PVA solution remained in contact with the precipitation solution for 60 min. As a result, the PVA solution precipitated to form a film. The PVA film formed in the precipitation step is still soluble in aqueous solution. To increase the stability of the film toward aqueous solutions, it must be crosslinked with a crosslinking agent.

The crosslinking solution used in our experiments consisted of glutaraldehyde, sulfuric acid, and sodium sulfate as given in Table II. Sodium sulfate is used to prevent PVA film from being dissolved in crosslinking solution during crosslinking reaction. The PVA film obtained in the precipitation step was crosslinked by immersing it in the crosslinking solution. The crosslinking apparatus containing PVA film was immersed in a constant temperature bath. After the apparatus was preheated to the reaction temperature, the

crosslinking solution preheated separately to the reaction temperature was introduced into the crosslinking chamber to prevent PVA film from being crosslinked below the reaction temperature. The volume of crosslinking solution (V_c) was 400 cm³. The crosslinking temperature was 40°C. The degree of crosslinking of PVA membrane was controlled by varying the crosslinking time in the range of 0–60 min.

Determination of Degree of Crosslinking

The crosslinking solution was sampled and analyzed after formation of the PVA membrane with the desired degree of crosslinking to measure the decrease of glutaraldehyde concentration. The glutaraldehyde concentration was analyzed by titration. This is the sodium bisulfite method based on addition reactions of bisulfite salt to aldehydes.⁶ Using eq 6 and 7, the degree of crosslinking of the prepared membrane was calculated.

FT-IR spectra were also measured by using a spectrometer of Bio-Rad Digilab Division Model FT-S80 to verify the results of degree of crosslinking calculated from eq 6 and 7.

Determination of Degree of Swelling

The degree of swelling, D_s , is defined as follows:

$$D_s = \frac{W_m - D_m}{D_m} \times 100 (\%) \quad (8)$$

where D_m is the weight of dry membrane, and W_m is the weight of swollen membrane. Swelling characteristics were determined for both water and ethanol. The weight of the swollen membrane was measured after immersing the dry membrane in water or ethanol for 1 h at room temperature. The immersion time of 1 h was sufficient for equilibrium swelling and determined by measuring the variance of weight of swollen membrane as a function of time.

Surface Property Studies

The surface properties of PVA membrane were studied by measuring contact angles with a Dynamic Contact Angle Analyzer of Model DCA 322, which is the dynamic Wilhelmy plate technique.⁷ The wetting liquids used for measuring contact angles are tricresyl phosphate, aniline, 1-bromonaphthalene, ethylene glycol, and methylene iodide. These chemicals were obtained from Aldrich Chem. Co.

The critical surface tension of PVA membranes was estimated by Zisman's method,¹⁰ using the measured contact angles.

Pervaporation Studies

The pervaporation apparatus is shown in Figure 1. The pervaporation module (M) was equipped with a membrane of effective area of 152 cm² (8 cm W × 19 cm L). An aqueous ethanol solution of 95 wt% ethanol concentration was preheated in the feed reservoir (V), and fed to the pervaporation module with the feed pump (P). The feed flow rate of ethanol solution was 300 ml min⁻¹. The temperature of ethanol solution at the inlet and outlet of the pervaporation module was maintained at 56 and 50°C, respectively. The pressure in the permeate side was maintained at 5 mmHg with

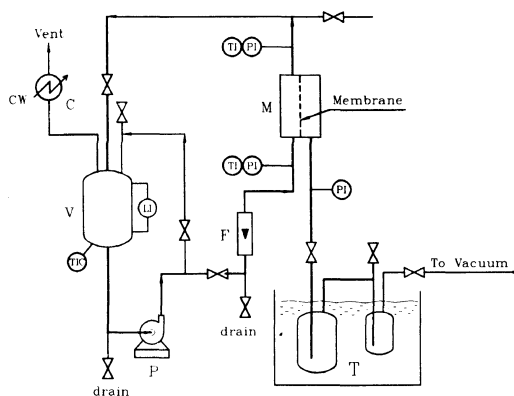


Figure 1. Schematic diagram of the pervaporation apparatus. C, condenser; CW, cooling water; F, feed flowmeter; LI, level indicator; M, pervaporation module; PI, pressure indicator; P, feed pump; TI, temperature indicator; T, permeate trap; TIC, temperature indicating & controller; V, feed reservoir.

a vacuum pump. Vapor permeated through the membrane was condensed and collected in the dry ice-methanol trap (T). The retentate was recycled to the feed reservoir. The ethanol concentration in the feed solution was maintained nearly constant, because the mass of permeate collected during an experiment was very small compared with that of the feed solution.

To evaluate pervaporation characteristics, the permeate flux and selectivity factor were used. The permeate flux is expressed in $\text{lm}^{-2} \text{h}^{-1}$, and the selectivity factor is defined as follows:

$$\alpha_{w/e} = \frac{y_w/y_e}{x_w/x_e} \quad (9)$$

where x_w , x_e , y_w , and y_e denote the weight fractions of water and ethanol in the feed solution and permeate, respectively.

The ethanol concentrations in the feed solution and in the permeate were analyzed with a gas chromatograph of Model HP5890. The column was a PEG-600(1/8 in. & 5 ft), and the detector, TCD.

RESULTS AND DISCUSSION

Degree of Crosslinking

The FT-IR spectra of PVA membranes prepared by varying the degree of crosslinking are presented in Figure 2. The degree of crosslinking was calculated from the glutaraldehyde concentrations measured after formation of membranes by eq 6 and 7. The spectra show some interesting changes notably at the wave numbers of 3330 and 2920 cm^{-1} . The O-H stretching vibration band at 3330 cm^{-1} weakens and the C-H stretching band at 2920 cm^{-1} strengthens as the degree of crosslinking increases. This indicates that FT-IR spectra may be used as a measure of the degree of crosslinking of PVA membranes.

The absorbance ratios of C-H stretching band to O-H stretching band, A_{2920}/A_{3330} , are

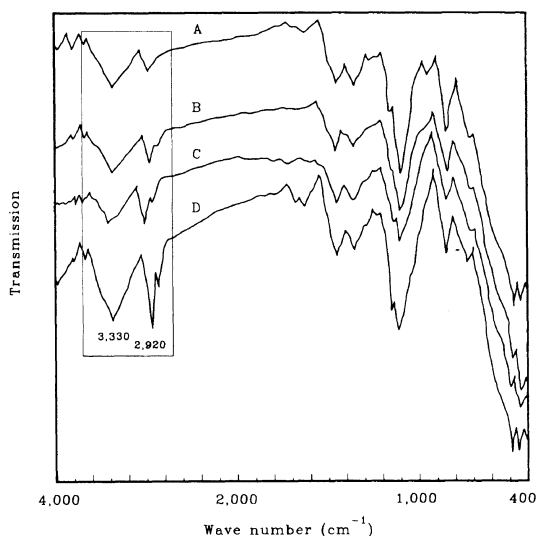


Figure 2. FT-IR spectral changes of PVA membranes with different degrees of crosslinking. D_c (%): A, 0; B, 8; C, 38; D, 75.

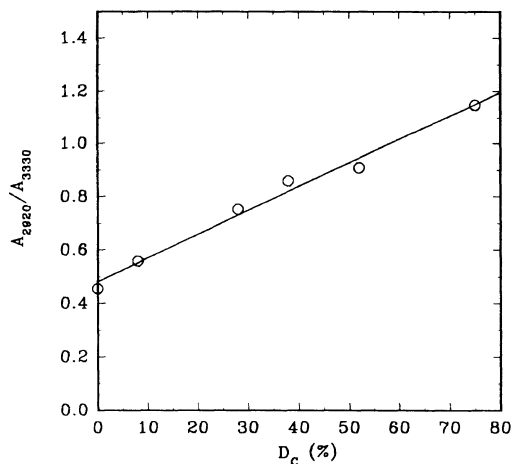


Figure 3. Relationship between absorbance ratio measured by FT-IR and degree of crosslinking calculated from glutaraldehyde concentration.

compared with the degrees of crosslinking determined from the glutaraldehyde concentrations. A linear relationship can be confirmed as shown in Figure 3. From this agreement the calculation method of the degree of crosslinking, using the glutaraldehyde concentration and eq 6 and 7, is proven useful for the

determination of the degree of crosslinking of PVA membrane crosslinked with glutaraldehyde. In the following discussion, the values of degree of crosslinking calculated from the glutaraldehyde concentrations are used.

Swelling Characteristics

To investigate the swelling characteristics of crosslinked PVA membranes, the degrees of swelling of the dry PVA membranes for both water and ethanol were determined as a function of the degree of crosslinking according to eq 8. The results are shown in Figure 4. The amounts of water and ethanol absorbed by the uncrosslinked PVA membrane are approximately 3.3 and 0.7 times their own masses, respectively. This is expected since PVA is soluble in water, but not in ethanol. The degree of swelling for water decreases abruptly as the degree of crosslinking increases. However, the degree of swelling for ethanol is nearly independent of the degree of crosslinking. If the amount of ethanol absorbed by PVA membrane be mainly dependent on the void volume or porous portion of the membrane, the degree of crosslinking may not greatly affect the porous structure of the membrane. But, the solubility or swelling of the membrane for water is greatly affected by the degree of crosslinking. From these results it can be expected that water permeability in pervaporation process decreases sharply with the increasing degree of crosslinking.

Contact Angles and Critical Surface Tensions

The advancing contact angles (θ) of five wetting liquids for the active (upper) surfaces of the asymmetric PVA membranes of different degrees of crosslinking were measured by the Wilhelmy plate technique,⁷ and are reported in Table III. The surface tensions of the wetting liquids used in analyzing the contact angles are available in the literatures.^{8,9} It can be seen that the contact angle does not vary largely with the degree of crosslinking.

From the contact angle data, the critical

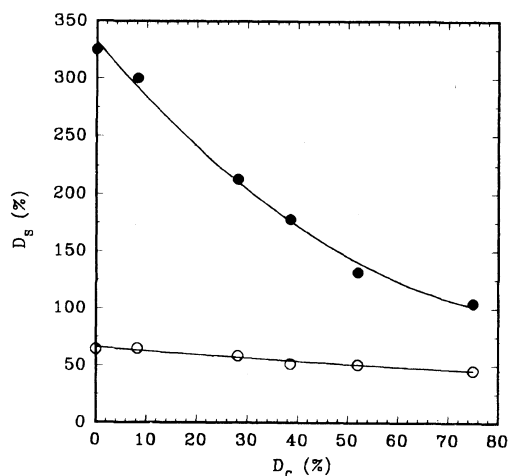


Figure 4. Swelling characteristics of PVA membranes as a function of the degree of crosslinking. ●, for water; ○, for ethanol.

surface tensions for the PVA membranes were obtained by Zisman's method.¹⁰ The critical surface tension concept provides a useful means of summarizing wetting behavior and predicting the hydrophilicity-hydrophobicity balance.

The critical surface tension obtained mentioned above for the PVA membranes is shown in Figure 5 as a function of degree of crosslinking. The critical surface tension of the uncrosslinked PVA membrane was 37.0 dyn-cm⁻¹, which is in good agreement with that of PVA reported in the literature.¹¹ The critical surface tension of the crosslinked PVA membrane increases more or less within the range of 37.0–40.0 dyn cm⁻¹ with increasing degree of crosslinking below 30%.

However, it is nearly constant at 40.5 dyn-cm⁻¹ above 30%. It seems that the degree of crosslinking does not greatly affect the critical surface tension of PVA membrane. The wetting behavior of PVA membranes may not be largely modified by controlling the degree of crosslinking, when PVA membranes are crosslinked with glutaraldehyde.

Pervaporation Characteristics

The asymmetric PVA membranes prepared

Degree of Crosslinking of PVA Membranes

Table III. Advancing contact angles for PVA membranes

Degree of crosslinking of PVA membranes (%)	Wetting liquid ^a	Contact angle (degree)
0	TP	39
	AN	44
	BN	50
	EG	51
	MI	70
8	TP	34
	AN	39
	BN	47
	EG	57
	MI	68
28	TP	16
	AN	30
	BN	35
	EG	46
	MI	60
38	TP	18
	AN	29
	BN	38
	EG	50
	MI	63
52	TP	17
	AN	38
	BN	41
	EG	56
	MI	68
75	TP	15
	AN	26
	BN	41
	EG	45
	MI	63

^a TP, tricresyl phosphate; AN, aniline; BN, 1-bromonaphthalene; EG, ethylene glycol; MI, methylene iodide.

by varying the degree of crosslinking were used in pervaporation studies with the ethanol-water mixture of 95 wt% ethanol concentration. The selectivity factor defined by eq 9 and permeate flux were measured, and shown in Figure 6 as a function of degree of crosslinking. The pervaporation conditions are described in the experimental part. The selectivity factor and permeate flux decrease similarly with increasing degree of crosslinking. The decreasing of the selectivity factor and permeate flux with

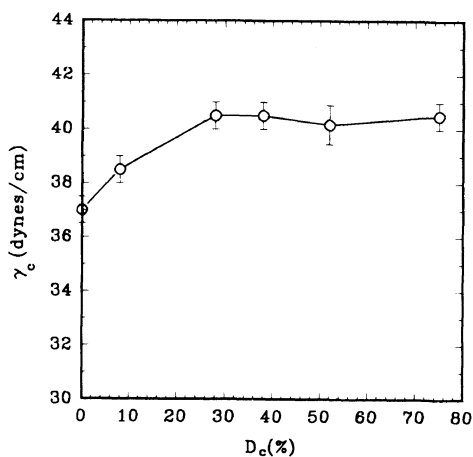


Figure 5. Variation of critical surface tension of PVA membrane with the degree of crosslinking.

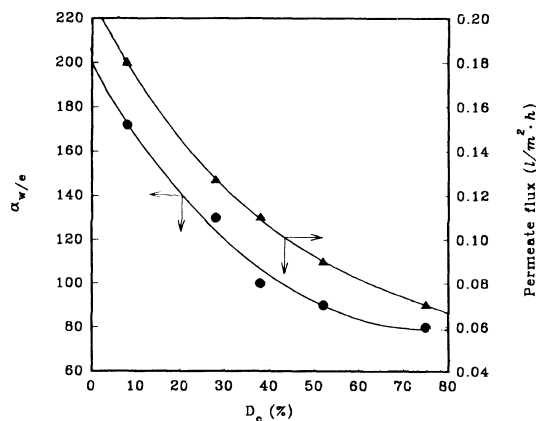


Figure 6. Selectivity factor and permeate flux of PVA membranes as a function of the degree of crosslinking. ●, selectivity factor, $\alpha_{w/e}$; ▲, permeate flux.

increasing degree of crosslinking is the same as that of the degree of swelling for water shown in Figure 4. This indicates that pervaporation characteristics are closely related to swelling behavior. The selectivity factor and permeate flux of PVA membrane can be modified by controlling the degree of crosslinking. The degree of crosslinking is an important variable for swelling behavior and pervaporation characteristics of PVA membranes. Comparing Figure 6 with Figure 5, it can be found that the critical surface tension or wetting behavior

does not have important effect on the pervaporation characteristics.

While crosslinkages enhance the stability of PVA membrane toward water, the selectivity factor and permeate flux decrease with increasing degree of crosslinking. Therefore, the degree of crosslinking should be optimized to prepare a pervaporation PVA membrane with good stability and pervaporation characteristics.

Asymmetric PVA membranes prepared using glutaraldehyde as a crosslinking agent show a selectivity factor of 80–200 and permeate flux of 0.06–0.20 $\text{lm}^{-2} \text{h}^{-1}$, which are much higher than those of PVA membranes crosslinked with other crosslinking agents.^{12,13} The crosslinking method of PVA membrane using glutaraldehyde may become an important means of preparing a pervaporation PVA membrane for industrial applications.

CONCLUSIONS

Asymmetric PVA membranes were prepared by the phase inversion technique. The crosslinking of PVA membrane with glutaraldehyde was effectuated and the degree of crosslinking of the membrane was controlled by varying the crosslinking conditions. PVA membranes of different degrees of crosslinking were examined by determining their swelling characteristics, contact angles, critical surface tension, and pervaporation characteristics.

The proposed method for the evaluation of degree of crosslinking of PVA membrane crosslinked with glutaraldehyde was verified to be useful. The degree of crosslinking of the membrane could be modified easily by varying the crosslinking conditions. The degree of swelling of PVA membrane for water is greatly affected by the degree of crosslinking. It decreases abruptly as crosslinking increases. However, the degree of swelling for ethanol is

nearly independent of the degree of crosslinking. The critical surface tension increases more or less within the range of 37.0–40.0 dyn cm^{-1} with increasing degree of crosslinking below 30%. But, it is nearly constant at 40.5 dyn cm^{-1} above 30%. The wetting behavior of PVA membrane may not be greatly affected by the degree of crosslinking. The decreasing of the selectivity factor and permeate flux of PVA membranes with increasing degree of crosslinking is the same as that of the degree of swelling for water. It shows that the pervaporation characteristics are closely related to the swelling behavior. The degree of crosslinking is an important variable for the swelling behavior and pervaporation characteristics of PVA membranes. However, the critical surface tension or wetting behavior may not have an important effect on pervaporation characteristics.

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