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Separation of Acetic Acid/Water Mixtures by Pervaporation through Poly(Vinyl Alcohol)-Sodium Alginate Blend Membranes

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Separation of Acetic Acid/Water Mixtures by Pervaporation through Poly(Vinyl Alcohol)–Sodium Alginate Blend Membranes

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Abstract: Dense pervaporation (PV) membranes were prepared by blending hydrophilic polymers, poly(vinyl alcohol) (PVA), and sodium alginate (SA), which were then crosslinked with glutaraldehyde (GA) for the separation of acetic acid/water mixtures. These membranes (PVA-SA) were characterized for morphology, intermolecular interactions, thermal stability, and physico-mechanical properties using XRD, FTIR, TGA and tensile testing respectively. The effect of experimental parameters such as feed composition and permeate pressure on separation performance of the crosslinked membranes was determined. Sorption studies and porosity measurement were carried out to evaluate the extent of interaction and degree of swelling of the polyion membranes, in acetic acid and water as well as in mixtures of acetic acid and water. Further the results were compared with the commercial membrane (Sulzer pervap 2205). The membrane appears to have a good potential for dehydrating 90 wt% acetic acid with a reasonably high selectivity of 21.5 and a substantial water flux of 0.24 kg/m^2/h/10 μm. Separation factor was found to improve with decreasing

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feed water concentration whereas the corresponding flux decreased. Higher permeate pressures caused a reduction in both flux and selectivity.

Keywords: PVA-SA blend, pervaporation, acetic acid/water, membrane characterization

INTRODUCTION

Pervaporation (PV) technique, which is economical, safe, and ecofriendly is considered to be a promising alternative to conventional energy intensive technologies such as extractive or azeotropic distillation in liquid mixture separation. This method has been useful particularly for the separation of azeotropes, close boiling mixtures, isomers, heat sensitive and hazardous compounds (1).

Hydrophilic membranes have been extensively used in PV based dehydration of organic solvents (2–4). It is well accepted that the permeable components are transported in dense membranes according to solution–diffusion process (5) in which the component sorption in the membrane plays a major role. Most of the research efforts of PV have concentrated on the separation of alcohol–water systems (6–10), whereas the separation of acetic acid–water mixtures has received relatively lesser attention (11–16). Acetic acid is one of the top twenty organic intermediates used in the chemical industry and its mixture in water is encountered in the synthesis of several important intermediates like acetic acid itself, vinyl acetate, acetic anhydride, pthalic anhydride, etc. Separation of acetic acid from water by normal binary distillation is quite difficult due to low relative volatility, especially at acetic acid concentrations in excess of 90 wt.% and thus more energy intensive and expensive distillation or sometimes solvent extraction (17) is used. Most commercially available PV membranes are prepared as composites. The first commercial PV membranes was prepared by GFT (now SULZER CHEMTECH, Germany) for the dehydration of ethanol by using crosslinked poly(vinyl alcohol) (PVA) on micro porous polyacrylonitrile substrate (18–21).

Poly(vinyl alcohol), a 1,3-diglycol polymer, with a molecular weight of 44 per repeat unit is a very effective material for pervaporation based dehydration because of its film forming ability, highly hydrophilic nature and good chemical resistance to organic solvents. However, to overcome its poor stability in aqueous solution, PVA must be insolubilized by crosslinking or grafting. Crosslinking is a commonly used method to stabilize PVA membranes. Yeom and Lee (22) prepared PVA membranes crosslinked with glutaraldehyde for the pervaporation of acetic acid–water mixtures. Poly(acrylic acid) was used by Lee et al. to crosslink PVA membranes for the separation of ethanol-water mixtures (23). Sulphosuccinic acid, formaldehyde, and citric acid were also proved to be potential crosslinking agents for PVA polymer membrane (24–26). Sodium alginate (SA), a polysaccharide extracted from seaweeds, has shown excellent performance as a membrane material for the dehydration of ethanol (27, 28). The drawbacks of SA membranes in their possible use for such applications are water solubility and mechanical weakness. Recently, Yeom and Lee (29) crosslinked SA with glutaraldehyde in acetone solution with HCl as catalyst, to address the problem of dissolution in aqueous solvents.

In the present study, SA was blended with PVA to overcome the drawbacks of the former as well as to combine the good pervaporation characteristics of both the homopolymers for dehydrating acetic acid/water mixtures. Blending of the two polymers resulted in the spontaneous formation of polymer complex, which was further crosslinked with glutaraldehyde to reduce swelling and increase structural strength besides thermal and mechanical stabilities. The separation performance of the membrane was compared with the results observed for commercial sulzer membrane. The work also explores the effect of varying water concentration in the binary feed mixture on membrane flux and selectivity. Characterization by FTIR analysis, wide angle X-ray diffraction (WAXD), TGA, DSC, tensile strength measurements and sorption studies have been used to explain interaction mechanisms between the polymers and PV results. Effect of porosity % and permeate pressure on separation performance were evaluated.

EXPERIMENTAL

Materials

PVA, of weight average molecular weight (M_w) 1,25,000, degree of hydrolysis 98–99% was purchased from Loba Chemie, Mumbai, India. The degree of polymerization of PVA was 1570 ± 50 and the saponification degree was 99%. SA, used for blending with PVA, was obtained from Loba Chemie, acetic acid of purity 99.9%, Isopropanol, HCl, and Glutaraldehyde were purchased from S.D. Fine Chemicals, Mumbai. Commercial membrane (pervap 2205) was purchased form SULZER CHEM TECH, Germany. Deionized water of conductivity 0.02 mS/cm was generated in the laboratory itself for the preparation of feed solutions.

Preparation of Membranes

A homogeneous non-porous membrane of PVA - SA was prepared by solution casting and solvent evaporation technique. 7 g of PVA was dissolved in 93 ml of deionized water to form a 7 wt.% solution at 90°C. 7 wt.% of SA solution was prepared at room temperature and mixed with 7% PVA solution in the ratio of 1 : 3 respectively. The mixture was then stirred for a period of half an hour to form a homogeneous solution. The bubble free blend solution was cast to the desired thickness on a clean glass plate and the solvent was allowed to evaporate slowly at room temperature for a period of 24 h. The resultant membrane was removed from the glass plate and dried in a vacuum oven at 50°C for 6 hrs followed by crosslinking with 5 vol.% of glutaraldehyde in a Isopropanol–water (90/10 vol.%) bath containing 1 vol.% of hydrochloric acid as catalyst. After crosslinking for 120 min, the membranes were stored in distilled water for 24 hrs to remove traces of unreacted glutaraldehyde in the membrane, if any, to prevent further crosslinking (30).

Pervaporation Procedure

Experiments were carried out on a 100 ml batch level with an indigenously constructed pervaporation manifold (Fig. 1) operated at a vacuum as low as 0.25 mmHg in the permeate line. The membrane area in the pervaporation cell assembly was approximately 20 sq. cm. The experimental procedure is described in detail elsewhere (31). The acetic acid aqueous feed was stirred vigorously during experiments to minimize concentration polarization.

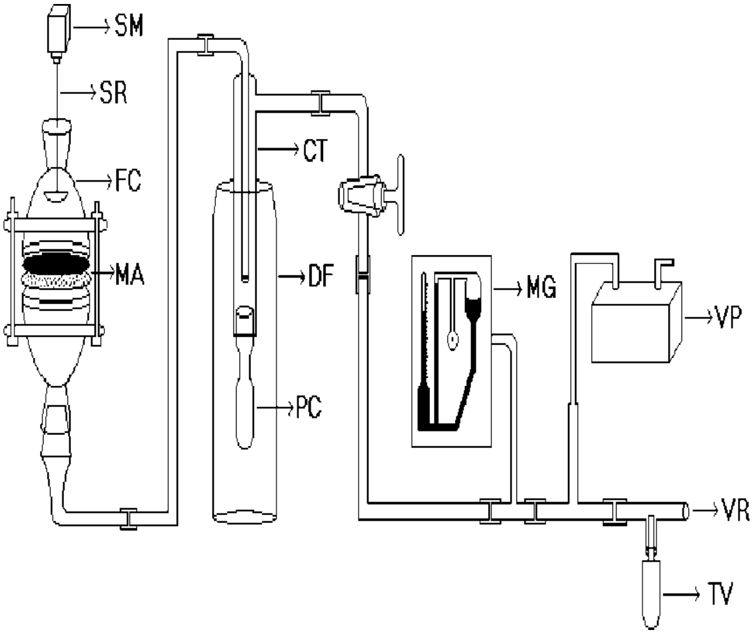


Figure 1. Schematic of vaccum pervaporation set-up. SM: stirring motor, SR: stirring rod, FC: feed chamber, MA: membrane assembly, CT: condenser trap, DF: Diwar flask, PC: permeate collector, MG: McLeod gauge, VP: vacuum pump, VR: vacuum release, TV: Teflon valve.

Permeate was condensed and collected in a liquid nitrogen cold trap for a duration of 6–8 hours. Each experiment was commenced only after PV equilibrium was reached (12 hrs). Tests were carried out at room temperature (30 ± 2°C) and repeated twice using fresh feed solution to check for reproducibility. The collected permeate was weighed after allowing it to attain room temperature in a Sartorius electronic balance (accuracy: 10^{-4} gms) to determine the flux and then analyzed by gas chromatography to evaluate the membrane selectivity.

Representation of the Results

The permeation and separation characteristics of PVA-SA membranes towards acetic acid/water mixtures were expressed as permeation rate (flux) (Q), selectivity or separation factor (α) and pervaporation separation index (PSI).

The permeation rate, Q was determined by using the equation

$$Q = \frac{m}{At} \tag{1}$$

where m represents the mass of the water in permeate (kg), A is the membrane area (m^2) and t represents the time of operation (h). PV flux on a commercial level is generally reported for a membrane of 10 μm thickness. The observed flux for a membrane of any given thickness is converted to flux for 10 μm by multiplication of the corresponding factor assuming linear relationship between thickness and flux.

The membrane selectivity is the ratio of permeability coefficients of water and acetic acid and is calculated from feed and permeate compositions as follows,

$$\alpha = \frac{\mathrm{Y_{water}/Y_{acetic\ acid}}}{\mathrm{X_{water}/X_{acetic\ acid}}} \tag{2}$$

where x and y represent the weight fractions in feed and permeate respectively.

Membrane Characterization

FTIR Studies

The FTIR spectra of PVA, crosslinked PVA (XPVA) and GA crosslinked PVA-SA (XPVA-SA) blends were scanned using Perkin-Elmer-283B FTIR Spectrometer over the range 4000–400 cm^{-1} and 1200–400 cm^{-1}. The samples were prepared as KBr pellets. These spectra are shown in Figs. 2 and 3.

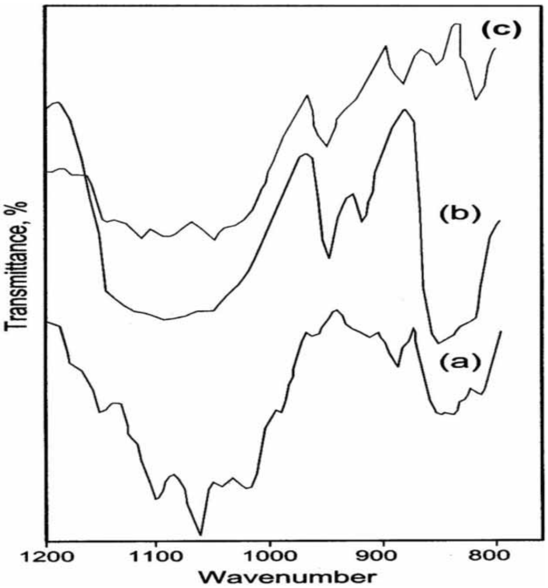


Figure 2. FTIR spectra of (a) PVA; (b) XPVA; (c) PVA-SA blend.

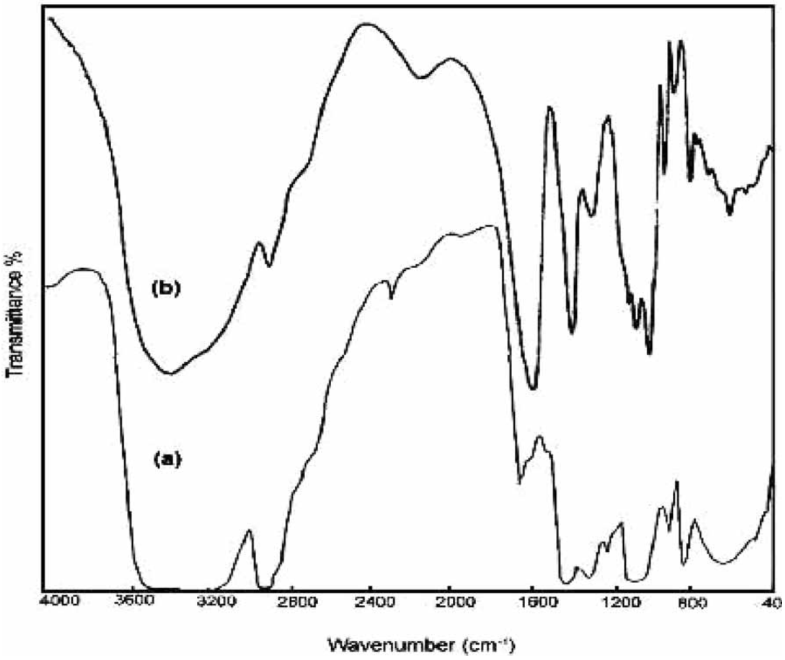


Figure 3. FTIR spectra of (a) PVA; (b) SA.

XRD Analysis

A Siemens D 5000 powder X-ray diffractometer was used to study the solid state morphology of the membranes in powdered form. X-rays of 1.5406 Å wavelength was generated by a Cu-K source. The X-ray diffractograms of PVA and blend membranes are shown in Fig. 4. The angle of diffraction was varied from 0° to 65° to identify the changes in the crystal structure and intermolecular distances between the intersegmental chains after crosslinking.

Thermal Analysis

DSC. The DSC spectra of crosslinked PVA and SA-PVA blend membranes were obtained on Perkin-Elmer DSC Model 7. Measurements were

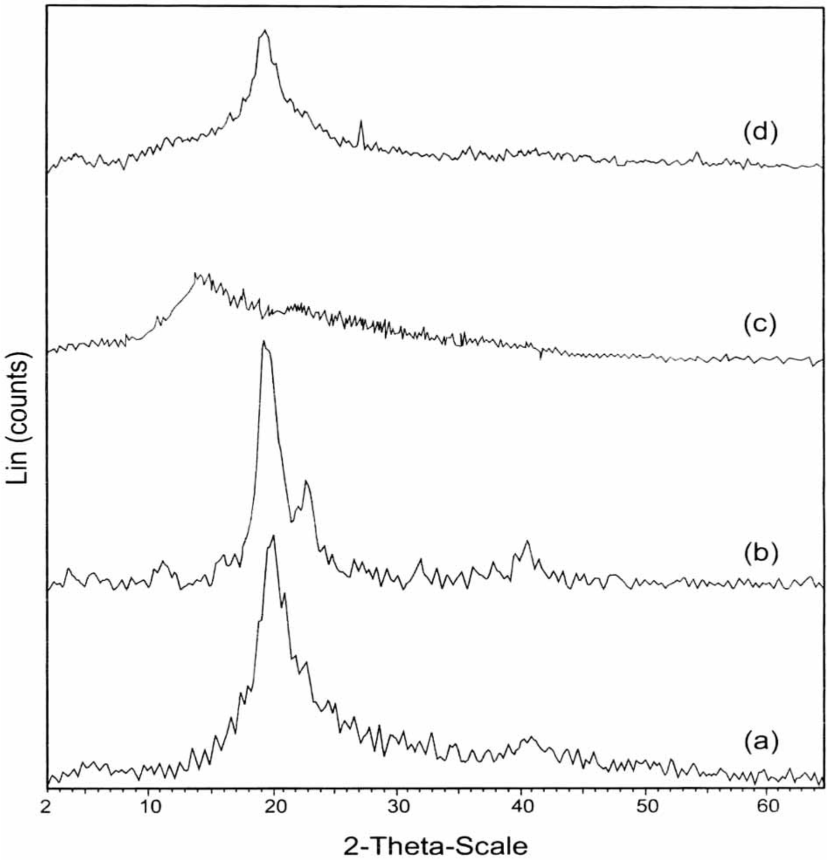


Figure 4. X-ray diffraction of (a) PVA; (b) XPVA; (c) SA; (d) PVA-SA blend.

performed over the temperature range of 30°C to 200°C at a heating rate of 5°C/min in hermetically sealed aluminium pans. Membrane samples were allowed to attain steady state with the solvents and the sample pan conditioned in the instrument before running the experiment. Results are shown in Fig. 5.

TGA. Thermal stability of the polymer films was examined, using Seiko 220TG/DTA analyzer from 25°C to 700°C at a heating rate of 10°C/min with continuous flushing using pure nitrogen gas at 200 ml/min. The samples were subjected to TGA both before and after crosslinking to determine the thermal stability and decomposition characteristics. Results are shown in Fig. 6.

Sorption Characteristics

In order to evaluate membrane-liquid affinities, weighed samples of circular pieces of the polymer films (3 cm dia.) were soaked in acetic acid/water

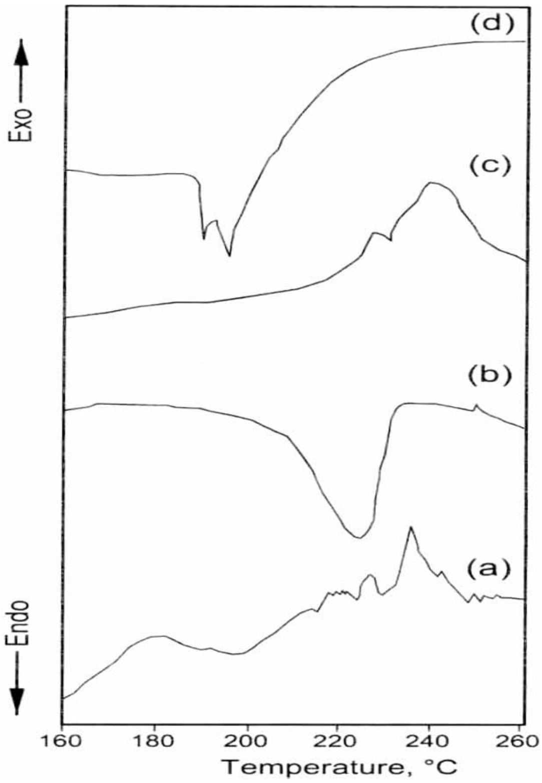


Figure 5. DSC spectra of (a) PVA; (b) XPVA; (c) SA; (d) PVA-SA blend.

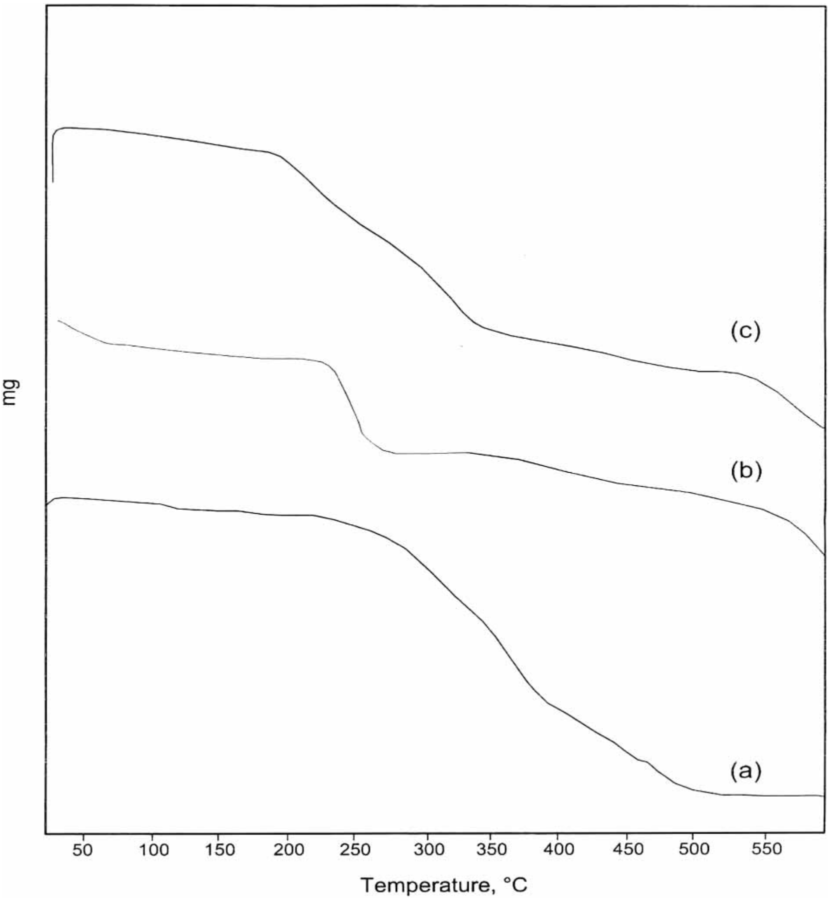


Figure 6. TGA curves of (a) XPVA; (b) SA; (c) PVA-SA blend.

mixtures of various concentrations. The films were taken out after different soaking periods and quickly weighed after carefully wiping out excess liquid to estimate the amount absorbed at the particular time "t". The film was then quickly placed back in the solvent. The process was repeated until the films attained steady state as indicated by constant weight after a certain period of soaking time. The percentage sorption was calculated from the equation:

$$\text{Sorption } [\%] = \frac{Ms - Md}{Md} * 100 \qquad (3)$$

where Ms = mass of the swollen polymer in gms; Md = mass of the dry polymer in gms.

$$\text{Degree of swelling} = \frac{Ms}{Md} \tag{4}$$

Porosity Calculation

After the membrane was equilibrated in water, the volume occupied by water and the volume of the membrane in wet state is determined (32). The membrane porosity was obtained by

$$porosity\ (\%) = \left[\frac{w_s - w_d}{d_{water}}\right] \times \frac{100}{V} \tag{5}$$

where W_s and W_d stand for the weights of the membranes in the swollen and dry states respectively, d_{water} is the density of pure water at room temperature and V the volume of the membrane in the swollen state.

Mechanical Properties

Universal Testing Machine (UTM), Model AGS-10kNG of Shimadzu, Japan make with an operating head load of 5 kN was used to determine the tensile strength of the membranes. Cross-sectional area of the sample of known width and thickness was calculated. The films were then placed between the grips of the testing machine. The grip length was 5 cm and the speed of testing was set at the rate of 12.5 mm/min. Tensile strength was calculated using the equation:

$$Tensile\ strength = \frac{Max.\ Load}{Crosssectional\ area}\,\text{N/mm}^2 \tag{6}$$

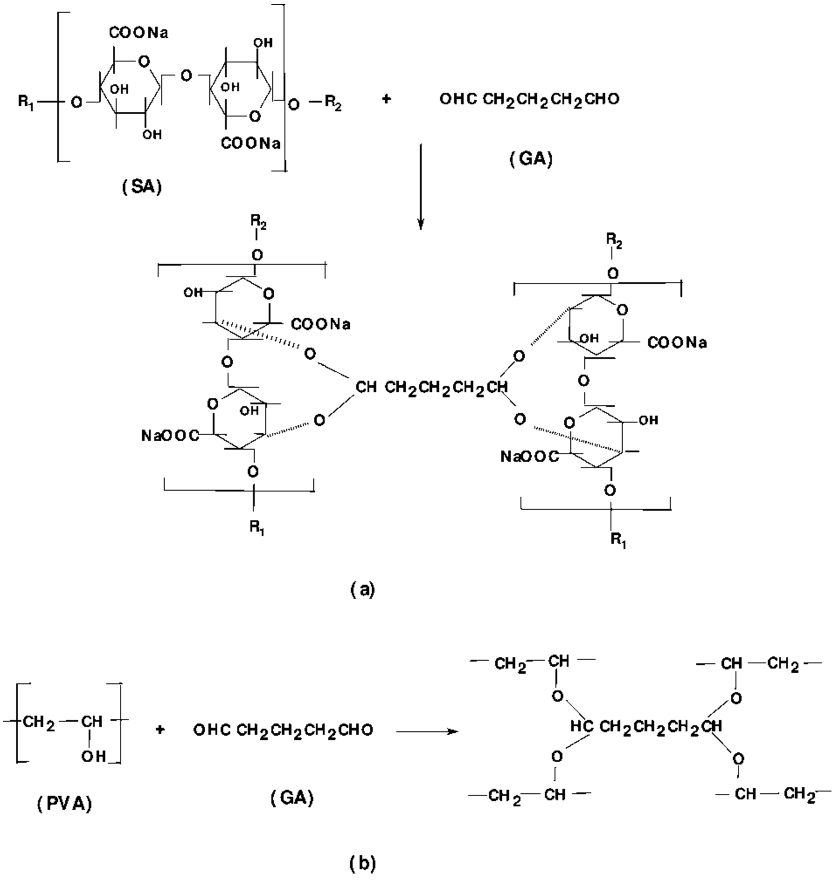
Analytical Procedure

The feed and permeate samples were analyzed using a Nucon Gas Chromatograph (Model 5765) installed with Thermal Conductivity Detector (TCD) and Tenax packed column of 2 meters length. The oven temperature, which was programmed, was maintained initially at 70°C for 3 minutes followed by an increase in temperature at 25°C/min up to 220°C. The injector and detector temperatures were maintained at 230°C each. The sample injection size was 1 μl and pure hydrogen was used as the carrier gas at a pressure of 1 Kg/cm^2. The GC response was calibrated for this particular column and conditions with known compositions of acetic acid-water mixtures and the calibration factors were fed into the software to obtain correct analysis for unknown samples.

RESULTS AND DISCUSSION

Membrane Characterization

Scheme 1 represents the structures of the polymers used in the study and also represents the structure of crosslinked PVA. In the scheme, a and b reveal the formation of acetal linkages when SA and PVA are crosslinked with glutaraldehyde. Glutaraldehyde acts as a crosslinking agent for both of the two polymers, and the aldehyde groups present in it react with the hydroxyl groups of PVA and SA. This can also be confirmed by FTIR. On blending, the −OH groups of SA form a hydrogen bond with the hydroxyl groups of PVA. It was noticed that both the homopolymer solution and the blend



Scheme 1. (a) Structural representation of Sodium Alginate (SA) crosslinked with glutaraldehyde (GA); (b) Structural representation of PVA crosslinked with glutaraldehyde (GA).

solutions of PVA-SA were optically clear to the naked eye. No separation into two layers or any precipitation was noticed in the blend solution which was allowed to stand for one month at room temperature.

Fourier Transform Infrared Spectroscopy

All the membranes were scanned in the spectral range of 4000–400 cm^{-1} but in order to figure out the occurrence of crosslinking, spectral range of 1200-400 cm^{-1} also provided. Figure 2 represents the FTIR spectra of PVA, XPVA, XPVA-SA in the range 1200–400 cm^{-1} and the spectras of PVA, SA in the range 4000–400 cm^{-1} are given in Fig. 3. The spectrum of PVA (Fig 3(a)) shows a prominent peak at 3600 cm^{-1} corresponding to hydroxyl group of PVA. The formation of acetal linkage due to crosslinking reaction is evidenced by C–O–C stretching peak at 1030 cm^{-1} in Fig. 2 (b) of the FTIR spectrum. It is evident that the crosslinking reaction between PVA and glutaraldehyde occurred only after the diffusion of the HCl catalyst into the membrane in the presence of water from the crosslinking solution since the reaction of the hydroxyl groups of the PVA with the aldehyde groups of the glutaraldehyde can take place only with the aid of protons (H^+). The bands at 1620 and 1416 cm^{-1} present in the spectrum of sodium alginate (Fig. 3(b)) are assigned to asymmetric and symmetric stretching peaks of carboxylate salt groups. In addition, the bands around 1320 cm^{-1} (C–O stretching), 1130 cm^{-1} (C–C stretching), 1090 cm^{-1} (C–O stretching), 1020 cm^{-1} (C–O–C stretching), and 950 cm^{-1} (C–O stretching) are attributed to its saccharide structure (33).

X-ray Diffraction

The microstructures of PVA, SA, and XPVA-SA membranes were studied using XRD. In this study, dried samples of 20 μm thickness were used. Figure 4 (a–d) presents the XRD patterns of dried PVA, XPVA, SA, and XPVA-SA membranes. From the spectra, moderately sharp peaks of PVA membrane can be noticed, indicating its semi-crystalline nature. It can be noted that all dried PVA membranes including the blends showed very similar XRD patterns and appeared to be semi crystalline. All the XRDs showed broad peaks at around 10° of 2θ, indicating the average intermolecular distance of the amorphous part and relatively sharp semicrystalline peaks centered at around 20° of 2θ. From this result, it can be inferred that in spite of the crosslinking, the average intermolecular distances in PVA and its blends are almost the same.

From the figure it can be seen that there are two distinct bands having their maxima at $2\theta = 10^\circ$ and 2θ about 20°.these two peaks are related to two types of crystals: crystal 1 and crystal 2. Crystal 1, which corresponds to the peak at 9.95°, is responsible for separation, as it comprises functional group −OH and has undergone significant change after crosslinking (33). A reduction in

d_{eff} value from 9.95 °A for uncrosslinked to 9.73 °A for crosslinked polymer is an indication of shrinkage in cell size or intersegmental spacing which would improve the selective permeation property of the membrane. The crosslinked blend showed a reduction in d_{eff} value from 9.95 Å to 9.68 Å, which results the occurrence of crosslinking of the blend.

Thermal Properties

DSC. Thermal properties of the blends were examined by DSC. It was of particular interest to estimate how the thermal transition of PVA blends varied with blending, since sodium alginate homopolymer used in this work did not show any significant transition in the temperature range of the DSC scan.

The results of the measurements are shown in Fig. 5. The homogeneous PVA, represented by curve (a), gives a relatively small melting endotherm with a peak (T_m) at around 201–208°C. On blending, a decrease in the endothermic peak can be observed. The tendency that the T_m of the blend is somewhat lower than that of PVA implies that a comparable but enhanced relative crystallinity occurs upon blending. This is also confirmed by FTIR analysis.

TGA. The thermal degradation behavior of crosslinked PVA and its blend was examined with weight loss at specific temperature by TGA, as shown in Fig. 6. It can be noted that crosslinked PVA exhibits two weight loss stages at 250°C–360°C and 430°C–460°C followed by a final decomposition of the polymer that begins around 460°C. The weight loss in the first and second stages can be attributed to decomposition of the acetal linkage formed during crosslinking and splitting of the main chain before final decomposition of the polymer.

Sodium alginate shows one weight loss stage ranging from 200–250°C indicating the main chain decomposition of the polymer followed by a final decomposition at 530°C. The crosslinked blend of PVA and sodium alginate also exhibits three weight loss stages ranging from 200°C–270°C, 290°C–340°C, and 540°C–570°C followed by a final decomposition at 540°C. The blend appears to be stable upto 340°C, beyond which splitting of the chain is likely. The final decomposition of the blend is likely to occur only at around 570°C. Thus from the TGA studies it can be said that crosslinking does not exhibit a major impact on the thermal stability of the polymer and the resulting crosslinked blend is as stable as the individual homopolymers.

Sorption Characteristics

The effect of equilibrium sorption percentage of PVA-SA blend membrane in acetic acid/water mixtures at different compositions is shown in Table 1. From the data, it was evidenced that the sorption percentage increased

Table 1. Effect of feed concentration on degree of swelling, percentage sorption

Feed water concentration (wt%)	Degree of swelling	Sorption %
8.68	1.32	32.98
15.78	1.41	41.36
28.54	1.54	54.35
53.45	1.65	65.17
60.65	1.70	70.40

steadily from 32.98 to 70.4 with increasing water concentration 8–60 wt%. In 100 wt% water compositions, the sorption was very high (225%) and in pure acetic acid it was 5.7%. This shows the hydrophilic nature of the membrane, which has affinity for water and is capable of being selective towards the same during separation. However, absorption of large amounts of water at higher feed concentrations could cause enhanced swelling and a subsequent fall in membrane selectivity due to plasticization of the polymer chains.

Mechanical Properties

XPVA, SA, and XPVA-SA membranes exhibited tensile strengths of 51.31, 21.88 and 42.78 N/mm^2 respectively. From Table 2, the decrease in the mechanical strength can be observed in PVA-SA blend membrane when compared to that of the XPVA membrane. PVA crosslinked membrane exhibited highest mechanical strength of 51.31 N/mm^2, followed by PVA-SA blend membrane (42.78), followed by SA (21.88). This effect can be explained from the fact that the blending of SA with PVA leads to an intermolecular interaction between them i.e., the $-$OH and COO-groups in SA form hydrogen bonds with the hydroxyl groups of PVA but this interaction does not significantly destroy the crystalline component of PVA. The lower mechanical strength of PVA-SA blend can be attributed to the polymer slippage, which seems to downplay the intermolecular interactions between the PVA and SA. It was

Table 2. Tensile Strength and % elongation of XPVA, SA and XPVA-SA

Polymer	Tensile strength (N/mm^2)	Elongation at break (%)
XPVA	51.31	7.5
SA	21.18	6.9
PVA-SA	42.78	6.8

also observed that the tensile strength and % Elongation of XPVA - SA decreased after blending.

Effect of Porosity

Table 3 gives the % porosity values of PVA and XPVA-SA membranes. PVA membrane exhibits the highest porosity values compared by XPVA-SA blend. On crosslinking the % porosity of PVA-SA blend decreased due to formation of acetal linkages. Therefore GA crosslinked PVA-SA blend membranes gave greater selectivities than the individual polymers as they preferentially absorb one component due to low porosity. High porosity of the membranes, allows both the feed components to absorb and permeate freely, which results in higher flux and lower selectivities (34).

Table 4 gives the comparison of PV performance of PVA-SA membrane with the literature available for acetic acid-water separation. From the comparison table it was found that PVA-SA membrane performed better flux and selectivity than many others (35–42).

Effect of Feed Concentration on Flux and Selectivity

Figures 7 and 8 describe the effect of feed water concentration on separation performance of commercial (Pervap 2205) and GA crosslinked PVA-SA blend membranes in terms of permeate parameters such as flux and selectivity. These investigations were made over a wide range of feed concentrations (8–60 wt.% water) at a temperature of 30°C, constant pressure of 0.25 mm Hg and a membrane thickness of 50 μm. It can be noticed that the PV flux increased with increasing concentration of water component in the feed mixture. Water flux increased from 0.32 to $0.47\,\mathrm{Kg/m^2 h \cdot 10\,\mu m}$ for commercial membrane and 0.24 to $0.74\,\mathrm{Kg/m^2 \cdot h \cdot 10\,\mu m}$ for PVA-SA blend membrane. At lower water concentration smaller differences in flux between commercial and synthesized membrane was observed and this difference increased in favor of synthesized blend membrane at higher feed water concentrations possibly due to increased swelling of the blend membrane. Selectivity, on the other hand, decreased from 60.4 to 8.06 for commercial

Table 3. % porosity of PVA and GA crosslinked PVA-SA blend membranes

Polymer	Porosity %
PVA	66.69
PVA-SA	25.71

Table 4. Comparison of flux and selectivity of PVA-SA blend membrane with values reported in literature

Membrane	Temperature (°C)	Feed water concentration (wt %)	Flux $(\mathrm{Kg/m^2 \cdot h})$	Selectivity	Reference
PVA with 100% hydroxyl content	25	10	0.05	7.00	(35)
PVA/PEI	25	10	1.40	1.80	(35)
PVA/PAA	25	10	0.30	6.60	(35)
PVA/PHC	25	10	0.25	5.00	(35)
PVA/PVP	25	10	0.80	2.40	(35)
PVA crosslinked with maleic acid	5	13	0.35	6.22	(36)
PVA crosslinked with GA (5 vol%)	35	10	0.10	263	(37)
SA/PAN cross- linked with PVA	50	10	0.094	18.0	(38)
PVA-g-PAAm (48% of PAAm)	25	10	0.008	8.53	(39)
PVA-g-PAAm (93% of PAAm)	25	10	0.042	5.36	(39)
PVA	35	20	0.056	6.71	(39)
PVA-g-PAAm	35	20	0.056	3.90	(40)
PVA/PAA	25	10	0.300	6.60	(41)
PVA/PHC	25	10	0.140	7.90	(41)
PVA/PVP	25	10	0.800	2.40	(41)
PVA-g-AN (52%) (PVA-2)	30	10	0.090	14.6	(42)
PVA/SA	33	10	0.049	21.5	Present work

GA: glutaraldehyde; PEI: polyethyleneimine; PAA: poly(acrylic acid); SA: sodium alginate; PHC: poly(hydroxycarboxylic acid); PVP: poly(*N*-vinyl-2-pyrrolidone); PAAm: poly(acryl amide); PAN: poly(acrylonitrile).

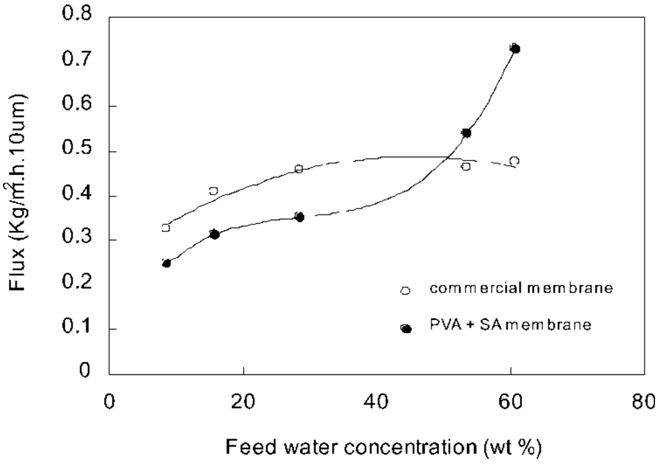


Figure 7. Effect of feed composition on flux.

membrane and 21.5 to 4.05 for PVA - SA blend membrane respectively. Greater swelling plasticizes the membranes which enables unrestricted permeation of both components.

Effect of Permeate Pressure

The separation characteristics of PVA-SA blend membrane were studied for varying permeate pressures from 0.25 to 9 mm Hg, at constant membrane

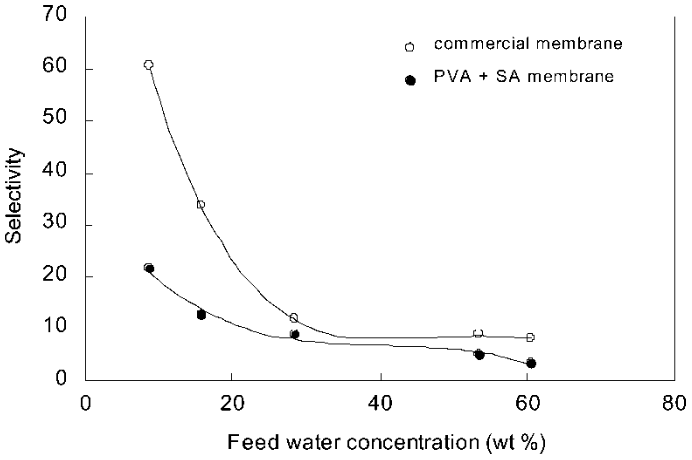


Figure 8. Effect of feed composition on selectivity.

thickness (50 μm) and 90% acetic acid feed. Figure 9 shows that the membrane exhibits considerable lowering of flux from 0.24 to 0.18 kg/m^2 hr · 10 μm with increasing permeate pressures (decreasing vacuum) for the same degree of swelling (1.32) in azeotropic composition. Diffusion through the membrane is the rate determining step in the pervaporation process and the diffusing water molecules experience larger driving force under high vacuum, which enhances the desorption rate at the downstream side. Lower vacuum reduces the driving force, thus slowing desorption of molecules. In such cases, the relative volatilities of the two components of the mixture govern separation factor of the membranes. Acetic acid having higher vapor pressure than water, permeates competitively with the latter, thus lowering the concentration of water in permeate. Therefore selectivity decreased from 21.51 to 12.88 as the pressure increased from 0.25 to 9 mm Hg.

CONCLUSIONS

GA crosslinked PVA-SA blends appear to have promising potential for dehydration of aqueous solutions of acetic acid at containing <10 wt.% water. The performance of blend membrane compared well with that of commercial Sulzer membrane. Characterization of the membranes by FTIR, WAXD, porosity, and sorption studies not only proved crosslinking but also greater affinity of the blend membrane towards water, besides providing deeper insight into separation mechanisms involved. DSC and TGA confirmed thermal stability of the blend membranes which were found to have good ability for dehydrating acetic acid to >99 wt.% purity.

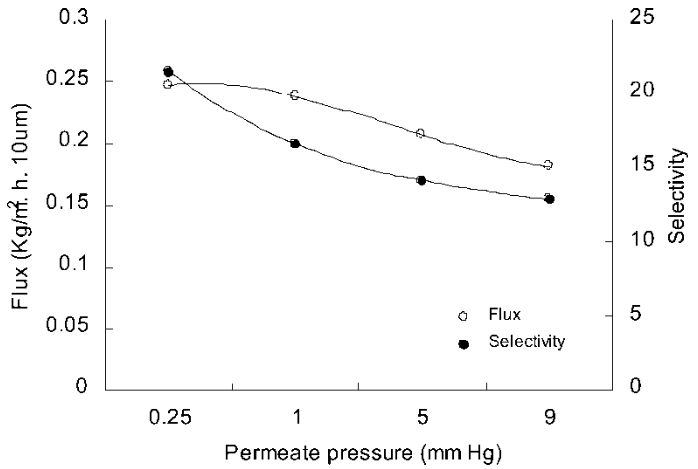


Figure 9. Effect of permeate pressure on flux and selectivity.

With increasing feed water concentration, the blend membrane's performance was found to be affected substantially by increase in the extent of swelling of the polymer which resulted in a rise in flux but reduction in selectivity. Permeate pressure caused a reduction in both flux and selectivity for both the membrane types.

REFERENCES

1. Feming, H.L. and Slater, C.S. (1992) Pervaporation. In *Membrane Handbook*. Ho, W.S.W. and Sirkar, K.K. (eds.), Van Nostrand Reinhold: New York, 105.
2. Lee, Y.M. and Oh, B.K. (1997) In situ complex membrane: dehydration of pyridine aqueous solution by pervaporation. *Macromol Symp.*, 118: 425–435.
3. Dogupathy, S.P. (2001) Pervaporation of aqueous alcohol mixtures through a photopolymerised composite membrane. *J. Membr. Sci.*, 185: 201–205.
4. Kim, K.J., Park, S.H., So, W.W., and Moon, S.J. (2001) Pervaporation separation of aqueous organic mixtures through sulfated Zirconia—poly(vinyl alcohol) membrane. *J. Appl. Polm. Sci.*, 79: 1450–1455.
5. Soltanieh, M. and Zaare, T. (1996) Asl, A modified solution—diffusion model for separation of ethanol—water azeotropic mixtures in pervaporation. *Chem. Eng. Commum.*, 153: 405–412.
6. Yoshikawa, M., Yukoshi, T., Sanui, K., and Ogata, N. (1986) Selective separation of water–ethanol mixture through synthetic polymer membranes having carboxylic acid as a functional group. *J. Polym. Sci. Part A Polym. Chem.*, 24: 1585–1597.
7. Xu, Y.F. and Huang, R.Y.M. (1988) Pervaporation separation of ethanol-water mixtures using ionically crosslinked blended poly(acrylic acid) (PAA)-nylon 6 membranes. *J. Appl. Polym. Sci.*, 36: 1121–1128.
8. Will, B. and Lichtenthaler, R.N. (1992) Comparison of the separation of mixtures by vapor permeation and pervaporation using PVA composite membranes Part I. Binary alcohol–water systems. *J. Membr. Sci.*, 68: 119–125.
9. Chiang, W.Y. and Huang, C.C. (1993) Separation of liquid mixtures by using polymer membranes Part IV. Water–alcohol separation by pervaporation through modified acrylonitrile poly(vinyl alcohol) copolymer. *J. Appl. Polym. Sci.*, 48: 199–203.
10. Ohya, H., Matsumoto, K., Negishi, Y., Hino, T., and Choi, H.S. (1992) The separation of water and ethanol by pervaporation with PVA-PAN composite membranes. *J. Membr. Sci.*, 68: 141–148.
11. Rhim, J.W., Yoom, S.W., Kim, S.W., and Lee, K.H. (1997) Pervaporation separation and swelling measurement of acetic acid–water mixtures using crosslinked PVA membranes. *J. Appl. Polym. Sci.*, 63: 521–527.
12. Nguyen, T.Q., Essamri, A., Clement, R., and Nell, J. (1987) Synthesis of membranes for the dehydration of water–acetic acid mixture by pervaporation Part 1. Polymer material selection. *Makromol. Chem.*, 188: 1973–1984.
13. Huang, R.Y.M. and Yeom, C.K. (1991) Development of crosslinked poly(vinyl alcohol) (type II) and permeation of acetic acid–water mixtures. *J. Membr. Sci.*, 62: 59–73.
14. Yoshikawa, M., Shimidzu, T., Maeda, Y., Magara, K., and Tsugaya, H. (1993) Pervaporation of aqueous acetic acid mixture through poly(acrylicacid-co-acrylonitrile) membranes. *J. Membr. Sci.*, 82: 157–162.

15. Sano, T., Ejiri, S., Yamada, K., Kawakami, Y., and Yanagishita, H. (1997) Separation of acetic acid–water by pervaporation through silicate membrane. *J. Membr. Sci.*, 123: 225–233.
16. Wang, X.P. (2000) Modified alginate composite membranes for the dehydration of acetic acid. *J. Membr. Sci.*, 170: 71–79.
17. Helsel, R.W. (1977) Removing carboxylic acids from aqueous wastes. *Chem. Eng. Prog.*, 73: 55.
18. Uragami, T. and Shinomiya, H. (1990) Concentration of aqueous alcoholic solutions through a modified silicone rubber membranes by pervaporation and evaporation. *J. Membr. Sci.*, 51: 273–292.
19. Feng, X. and Huang, R.Y.M. (1996) Pervaporation with chitosan membranes I. Separation of water from ethylene glycol by a chitosan/polysulfone composite membrane. *J. Membr. Sci.*, 116: 67–76.
20. Nawawi, M., Ghazali, M., and Huang, R.Y.M. (1997) Pervaporation dehydration of isopropanol with chitosan membranes. *J. Membr. Sci.*, 124: 53–62.
21. Ren, J. and Jiang, C. (1998) *Sep. Sci. Technol.*, 33: 517.
22. Yeom, C.K. and Lee, K.H. (1996) Pervaporation separation of water–acetic acid mixtures through poly (vinyl alcohols) membranes crosslinked with glutaraldehyde. *J. Memb. Sci.*, 109: 257–265.
23. Lee, K.H., Kim, H.K., and Rhim, J.W. (1995) Pervaporation separation of binary organic—aqueous liquid mixtures using crosslinked PVA membranes.III Ethanol–water mixtures. *J. Appl. Polym. Sci.*, 58: 1707–1712.
24. Rhim, J.W., Yeom, C.K., and Kim, S.W. (1998) Modification of ploy (vinyl alcohol) membranes using sulfur–succinic acid and its applications to pervaporation separation of water–alcohol mixtures. *J. Appl. Polym. Sci.*, 68: 1717–1723.
25. Hilmioglu, N.D., Yildirim, A.E., Sakaoglu, A.S., and Tulbentci, S. (2001) Acetic acid dehydration by pervaporation. *Chem. Eng. Process.*, 40: 263–267.
26. Burshe, M.C., Sawant, S.B., Joshi, J.B., and Pangarkar, V.G. (1997) Sorption and permeation of binary water–alcohol systems through PVA membranes crosslinked with multifunctional crosslinking agents. *Sep. Purf. Technol.*, 12: 145–156.
27. Shi, Y., Wang, X., and Chen, G. (1996) Pervaporation characteristics and solution–diffusion behaviors through sodium alginate dense membrane. *J. Appl. Polym. Sci.*, 61: 1387–1394.
28. Jegal, J.G. and Lee, K.-H. (1996) development of polyion complex membranes for the separation of water–alcohol mixtures. III. Preparation of polyion complex membrane based on the K-Carrageenan for the pervaporation separation of water–ethanol. *J. Appl. Polym. Sci.*, 60: 1177.
29. Yeom, C.K., Jegal, J.G., and Lee, K.H. (1998) Characterization of sodium alginate membrane crosslinked with glutaraldehyde in pervaporation separation. *J. Appl. Polym. Sci.*, 62: 209–219.
30. Kim, J.H., Kim, J.Y., Lee, Y.M., and Kim, K.Y. (1992) Properties and swelling characteristics of cross-linked poly(vinyl alcohol)/chitosan blend membranes. *J. Appl. Polym. Sci.*, 45: 1711–1717.
31. Sridhar, S., Ravindra, R., and Khan, A.A. (2000) Recovery of monomethylhydrazine liquid propellent by pervaporation technique. *Ind. Eng. Chem. Res.*, 39: 2485–2490.
32. Chen, Z., Deng, M., Chen, Y., He, G., Wu, M., and Wang, J. (2004) Preparation and performance of cellulose acetate/Polyethyleneimine blend microfiltration membranes and their applications. *J. Memb. Sci.*, 235: 73–86.
33. Smitha, Biduru, Sundergopal, Sridhar, Suryanarayana Murthy, G., and Satyajai, Mayor (2005) Pervaporation of tertiary Butanol/water mixtures

through chitosan membranes cross-linked with toluylene diisocyanate. *J. Chem. Technol. Biotechnol.*, 80: 1416–1424.

34. Kang, Y.S., Lee, S., Kim, U.Y., and Shim, J.S. (1990) pervaporation of water–ethanol through crosslinked and surface modified ply(vinyl alcohol) membrane. *J. Membr. Sci.*, 51: 215–226.
35. Nguyen, Q.T., Essamri, A., Clement, R., and Neel, J. (1987) Synthesis of membranes for the dehydration of water–acetic acid mixtures by pervaporation, I Polymer material selection. *Makromol. Chem.*, 188: 1973.
36. Yeom, C.K. and Lee, K.H. (1996) Pervaporation separation of water–acetic acid mixtures through poly(vinyl alcohol) membranes crosslinked with glutaraldehyde. *J. Membr. Sci.*, 109: 257.
37. Huang, R.Y.M. and Rhim, J.W. (1993) Modification of poly(vinyl alcohol) using maleic acid and its application to the separation of acetic acid–water mixtures by the pervaporation technique. *Polym. Int.*, 30: 129.
38. Wang, X.N. (2000) Modified alginate composite membranes for the dehydration of acetic acid. *J. Membr. Sci.*, 170: 71.
39. Aminabhavi, T.M. and Naik, H.G. (2002) Synthesis of graft copolymeric membranes of poly(vinyl alcohol) and polyacrylamide for the pervaporation separation of water/acetic acid mixtures. *J. Appl. Polym. Sci.*, 83: 244–258.
40. Koops, G.H., Nolten, J.A.M., Mulder, M.H.V., and Smolders, G.A. (1993) Poly(vinyl chloride) poly(acrylonitrile) composite membranes for the dehydration of acetic acid. *J. Membr. Sci.*, 81: 57–70.
41. Rudin, A. (1982) *The Elements of Polymer Science and Engineering*; Academic Press: New York, Chapter 3, pp. 102.
42. Alghezawi, N., Sanlý, O., Aras, L., and Asman, G. (2005) Separation of acetic acid–water mixtures through acrylonitrile grafted poly(vinyl alcohol) membranes by pervaporation. *Chemical Engi. Processing.*, 44: 51–58.