Blend Membranes of Chitosan and Poly(vinyl alcohol) in Pervaporation Dehydration of Isopropanol and Tetrahydrofuran

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ABSTRACT: Blend membranes of a natural polymer, chitosan, with a synthetic polymer, poly(vinyl alcohol) (PVA), were prepared by solution casting and crosslinked with a urea formaldehyde/sulfuric acid (UFS) mixture. Chitosan was used as the base component in the blend system, whereas PVA concentration was varied from 20 to 60 wt %. Blend compatibility was studied by differential scanning calorimetry, and Fourier transform infrared spectroscopy was used to study membrane crosslinking. Membranes were tested for pervaporation dehydration of isopropanol and tetrahydrofuran (THF) at 30°C in close proximity to their azeotropic compositions. Membrane performance was assessed by calculating flux and selectivity. Swelling experiments performed in water + organic mixtures at 30°C were used to explain the pervaporation results. The blend membrane containing 20 wt % PVA when tested for 5 and 10 wt % water–containing THF and isopropanol feeds exhibited selectivity of 4203 and 17,991, respectively. Flux increased with increasing concentration of water in the feed. Selectivity was highest for the 20 wt % PVA-containing blend membrane. The results of this study are unique in the sense that the crosslinking agent used—the UFS mixture—was novel. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 1918–1926, 2007

Key words: pervaporation; poly(vinyl alcohol); chitosan; blend membranes

INTRODUCTION

In membrane-based pervaporation (PV) separation, different types of polymers have been used for a variety of aqueous–organic mixtures. The PV technique has many inherent advantages as an alternative to traditional distillation for separating azeotropes.[1] However, the key to the success of PV is the development of novel membranes resistant to liquids or their mixtures under test conditions, giving high selectivity and flux to water. Even though research in this area has been actively pursued over many decades, yet achievement of a simultaneous increase in flux and selectivity has been a major challenge. Only a handful of polymeric membranes have been successful in commercial applications, yet research to develop newer membranes has been actively pursued using a variety of crosslinking agents to enhance membrane performance. In particular, the development of blend membranes has been an attractive area of PV study because one component of the blend provides the desired permeability characteristics and the other improves the mechanical strength properties.[2–6] Poly(vinyl alcohol) (PVA) has been the most widely used membrane for water–alcohol separation in pervaporation, but because PVA is hydrophilic, it swells and thus hinders separation.

Because of recent environmental concern and awareness in public sectors, new trends are moving in the direction of using environment-friendly polymers that can easily be degraded after their intended applications. Blends of PVA with chitosan, polyvinylpyrrolidone, or pectin have been investigated in this pursuit.[7] Chitosan (CS), a naturally occurring carbohydrate polymer [(1-4)-2-amino-2-deoxy-β-D-glucan] is found in all arthropods, in some invertebrates (e.g., squid and cuttlefish), and in some microorganisms. It can be readily prepared from chitin by N-deacetylation with alkali treatment. CS has been widely used in PV separation of aqueous–organic mixtures.[8,9] A search of the literature indicated that CS has been used not only as a membrane for separation,[10–12] but also in drug delivery applications.[13–16]

However, in the present study, advantage was taken of the hydrophilic nature of both PVA and CS polymers in order to prepare blend membranes that were not only hydrophilic but also exhibited a good combination of flux and selectivity and at the same time were environmentally friendly.

In previous studies, CS/PVA blend polymers have shown good mechanical strength in addition to good membrane performance characteristics.[17,18] However, their thermal stability is enhanced by treatment with formaldehyde.[13] Both CS and PVA have water-soluble and film-forming properties that offer good tensile strength, flexibility, and barrier properties.[19,20] Nevertheless, there could be low selectivity and low flux for the separation of water–organic mixtures if PVA or chitosan alone is used as membranes.[10,21] Attempts to prepare the blends of either PVA or CS with other polymers have resulted in poor permselectivity, but crosslinking of PVA or CS membranes has produced membranes that are more water selective, thereby reducing the risk of membrane deterioration upon the accidental overshoot in high water content during PV dehydration.

Our previous studies[2–4] on blend membranes of sodium alginate (NaAlg) with PVA at different ratios showed the limited flux and selectivity data for various aqueous–organic mixtures. In a recent study, a CS membrane was developed using toluene-diisocyanate as a crosslinking agent, but the performance of this membrane was not extremely satisfactory for the dehydration of 1,4-dioxane.[10] Among the various crosslinking agents used to crosslink hydrophilic polymers, a mixture of urea–formaldehyde prepared in sulfuric acid (UFS) was found to be excellent for crosslinking NaAlg/hydroxyethyl cellulose blend membranes, even though glutaraldehyde often has been used.[5] To the best of our knowledge, no reports are available on blend membranes of CS and PVA crosslinked with UFS for applications in PV dehydration of either isopropanol or tetrahydrofuran (THF). The present article reports the results of PV dehydration of blend membranes of CS and PVA for isopropanol and THF. The performance of the blend membranes was much superior to that previously reported. Our idea was to use CS as the base polymer and to prepare its blends by adding 20, 40, or 60 wt % PVA and then crosslinking the membrane with the UFS mixture in order to provide good strength. Chitosan was chosen because of its ease of availability and biodegradability in addition to its compatibility with PVA.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) (MW: 125,000) was purchased from S.D. Fine Chemicals (Mumbai, India). Chitosan with a number-average molecular weight of 500,000 and a degree of deacetylation of 84% was purchased from Aldrich Chemical Co. (Milwaukee, WI). Isopropanol (AR-grade sample), THF (AR), urea-formaldehyde-sulfuric acid (UFS), glacial acetic acid, and ethanol were all purchased from S.D. Fine Chemicals (Mumbai, India) and were used as received. Deionized water with a conductivity of 20 μS/cm was produced in the laboratory using Permeonics pilot plant (Vadodara, India) through a nanofiltration membrane module.

Membrane preparation

Blend membranes of CS and PVA were prepared by solution casting. The required amount of CS was dissolved in 2% aqueous acetic acid solution by stirring with a magnetic stirrer (Jenway, model 1103, Essex, UK) for 24 h. To this, different amounts of PVA (20, 40, or 60 wt %) were added, the solution was mixed uniformly, filtered to remove any suspended particles, poured onto a clean glass plate, and dried at room temperature. After complete drying, the blend membranes were peeled off carefully from the glass plate and crosslinked with a mixture of 2.5 wt % urea, 2.2 wt % formaldehyde, and 2.5 wt % sulfuric acid containing 50 wt % aqueous ethanol at room temperature for 2 h. The crosslinked membranes containing 20, 40, and 60 wt % PVA were designated as CS/PVA-20, CS/PVA-40, and CS/PVA-60, respectively. The pristine chitosan was designated as CS. Crosslinked membranes were washed and rinsed repeatedly with deionized water and dried at room temperature for about 24 h. Membrane thickness as measured by a micrometer screw gauge ranged between 35 and 40 μm.

Fourier transform infrared spectra

Fourier transform infrared (FTIR) spectra were recorded in the wavelength region of 4000–400 cm^{-1} using a Nicolet (Madison, WI) FTIR spectrometer (model Impact 410). About 2 mg of the sample was ground thoroughly with KBr, and pellets were made under a hydraulic pressure of 600 kg/cm^2.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) thermograms of uncrosslinked CS/PVA blend membranes were obtained on a Rheometric Scientific (Model DSC-SP, UK). Thermograms were recorded from 30°C to 400°C at a heating rate of 10°C/min in a nitrogen atmosphere.

Swelling experiments

Equilibrium swelling experiments on all membranes were performed in feed mixtures of water with isopropanol or THF with compositions ranging from 10 to 80 wt % water at 30°C ± 0.5°C in an electronically controlled incubator (WTB Binder, model BD-53, Tuttilgen, Germany) as per procedures reported previously.[22,23] The circularly cut (diameter = 2.5 cm) disk-shaped membranes were stored in a desiccator over anhydrous calcium chloride maintained at 30°C for about 48 h before the swelling experiments were performed. Weight was measured on a Mettler digital microbalance (model AE 240, Greifensee, Switzerland) sensitive to ±0.01 mg. The experiments were continued until complete equilibrium was attained. Triplicate measurements were reproducible within a 3% standard error. These data are presented in Table I.

Pervaporation experiments

Pervaporation experiments were performed in an apparatus designed in-house.[24,25] This apparatus consisted of a stirred stainless-steel cell around which water was circulated to maintain the desired temperature. The effective surface area of the membrane in the PV cell was 32.43 cm², with a diameter of 6.4 cm and a volume capacity of about 250 cm³. The temperature of the feed mixture was kept constant using a thermostatically controlled water jacket. The PV cell was provided with an efficient three-blade stirrer powered by a DC motor in the feed compartment. The downstream side of the PV apparatus was continuously evacuated using a vacuum pump (Toshniwal, Mumbai, India) at a low pressure of 10 torr.

The test membrane was equilibrated for about 2 h with the feed mixture before starting the PV experiment. For each feed mixture, PV runs lasted up to 5–6 h. After establishment of a steady state, permeate vapors were collected in glass tube traps immersed in liquid nitrogen. The feed mixtures composed of water and isopropanol used in the PV experiments were 10–20 wt % water, whereas the feed mixtures composed of water and THF were 5–15 wt % water. Each time a required amount of fresh solution was added to continuously enrich the depleted solvent mixture in the feed compartment. The permeate collected in the trap was weighed, and its composition was determined by measuring its refractive index and comparing it with a standard graph of refractive index versus mixture composition. The composition of the permeate was determined at 30°C by measuring the refractive index of the liquid mixture using a refractometer (Atago, model 3T, Tokyo, Japan). From the PV data, selectivity (α) was calculated:

$$\alpha = \left(\frac{y_A}{1 - y_A}\right)\left(\frac{1 - x_A}{x_A}\right) \tag{1}$$

where x_A is the mole fraction of water in the feed and y_A is the mole fraction of water in the permeate. Flux, J (kg/m²h), was calculated using the weight of the permeate, w (kg), effective membrane area, A (m²), and time, t (h) as

$$J = w/At \tag{2}$$

The results of flux and selectivity obtained at 30°C are presented in Tables II and III for the water + isopropanol and water + THF feed mixtures, respectively. In all cases, results were obtained in triplicate, but averages (< 3% standard error) are reported.

The enrichment factor, β, was calculated using the equation

$$\beta = \frac{C_w^P}{C_w^F} \tag{3}$$

where P and F are the weight fractions of the permeate and the feed, respectively; the subscript w stands for water, J_w is the water flux, and C is the concentration.

TABLE I
Results for Degree of Swelling of Membranes in Water + Isopropanol and Water + THF mixtures at 30°C

Water in mixture (wt %)	CS	CS/PVA-20	CS/PVA-40	CS/PVA-60
Water + IPA				
10	0.263	0.589	0.721	1.037
20	0.372	0.716	0.966	1.549
30	0.432	0.779	1.290	2.120
40	0.437	0.834	1.563	2.472
50	0.462	0.940	1.710	2.637
Water + THF				
10	0.549	0.652	0.797	1.663
20	0.686	0.856	1.162	2.170
30	0.851	1.024	1.421	2.563
40	0.985	1.220	1.569	2.691
50	1.023	1.320	1.698	2.896

TABLE II
Pervaporation Results of Water + Isopropanol Mixtures at 30°C

Water in feed (wt %)	J (kg m^{-2} h^{-1})	α	Water in permeate (wt %)	β
PVA				
10	0.095	77	89.57	12.79
15	0.133	50	89.01	8.47
20	0.450	30	88.20	6.3
CS				
10	0.087	5134	99.83	14.26
15	0.090	866	99.35	9.46
20	0.099	81	95.32	6.8
CS/PVA-20				
10	0.113	17991	99.95	14.28
15	0.130	1625	99.66	9.49
20	0.164	25	86.46	6.17
CS/PVA-40				
10	0.149	8562	99.90	14.27
15	0.161	524	98.93	9.42
20	0.193	23	85.32	6.09
CS/PVA-60				
10	0.214	6419	99.86	14.26
15	0.228	491	98.86	9.41
20	0.282	68	94.50	6.75

RESULTS AND DISCUSSION

Fourier transform infrared spectral studies

Figure 1 displays the Fourier transform infrared (FTIR) spectra of uncrosslinked and crosslinked membranes prepared from the CS-PVA-20 blend. The UFS system could successfully crosslink —NH$_2$ groups of chitosan and —OH groups of PVA. For the uncrosslinked membrane, a peak around 1580 cm^{-1} was assigned to the stretching vibration of —C=O in —NH$_3^+$—OOCCH$_3$ of the CS acetate salt, but this band disappeared in the FTIR spectra of the crosslinked membrane. The increase in intensity and shift of the band to a higher region, that is, 1200–1500 cm^{-1}, indicates an increased number of —CH$_2$ groups[26] in the crosslinked membranes. A large increase in this band resulted from a large increase in C—O bonds as well as crosslinking of the membranes. The peaks observed around 1120–1135 cm^{-1} in the UFS-crosslinked membranes corresponded to C—O—C linkage vibrations. A strong peak appearing around 1120–1150 cm^{-1} was assigned to the formation of an ionic bond between the two chitosan chains. Because of this, a broad peak at around 2090

TABLE III
Pervaporation Results of Water + THF Mixtures at 30°C

| Water in feed (wt %)	J (kg m^{-2} h^{-1})	α	Water in permeate (wt %)	β
PVA				
5	0.210	210	91.72	26.20
10	0.217	86	90.57	12.93
15	0.222	50	89.76	8.55
CS				
5	0.083	1940	99.03	28.29
10	0.086	697	98.73	14.10
15	0.086	60	91.32	8.69
CS/PVA-20				
5	0.098	4203	99.55	28.44
10	0.104	946	99.06	14.15
15	0.134	120	95.46	9.09
CS/PVA-40				
5	0.129	2116	99.11	28.31
10	0.147	1026	99.13	14.16
15	0.154	150	96.35	9.17
CS/PVA-60				
5	0.174	2548	99.26	28.36
10	0.201	1170	99.24	14.17
15	0.223	163	99.65	9.49
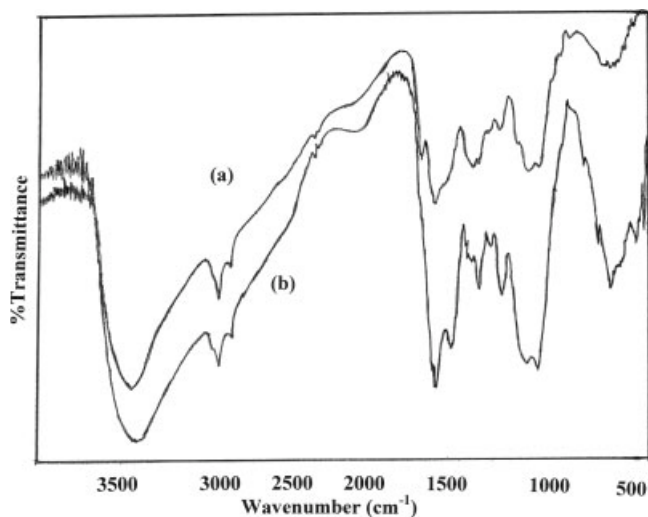
Figure 1 FTIR spectra of (a) uncrosslinked CS/PVA blend and (b) crosslinked CS/PVA blend.

cm^{-1} was attributed to the $-NH_3^+$ group[27] because of the formation of an ether linkage resulting from the reaction between a hydroxyl group and methylolurea. The band appearing at about 702 cm^{-1} was a result of the S—O—C linkage of the crosslinked chains, indicating the reaction between $HOSO_3^-$ and methylolurea. FTIR spectra confirmed the successful crosslinking of the membranes in the presence of the UFS mixture.

Differential scanning calorimetry analysis

One of the most commonly used methods to estimate the compatibility of polymer blends is determining the glass-transition temperature (T_g) compared to those of the component polymers. In blends in which one component is crystalline, observation of the melting point (T_m) depression of such a polymer can be used as evidence of blend compatibility.[28–30] In the present study, the compatibility of uncrosslinked blend membranes was determined from a depression in the melting point of the blends (see Fig. 2). Uncrosslinked blend membranes whose melting transitions were 188°C, 187°C, and 185°C for CS/PVA-20, CS/PVA-40, and CS/PVA-60 membranes, respectively. A systematic decrease in the melting transition temperature from 188°C to 185°C with increasing PVA content of the blend suggests blend compatibility at these compositions.

Membrane swelling

Sorption properties of the membrane depend on the morphological setup of the polymer, but sorption data cannot be directly correlated to permeability data because diffusion through membranes could

influence the permeability of the liquids. Membrane swelling controls PV performance[31]; hence, the degree of membrane swelling (DS) is important. This was calculated from the sorption data using

$$DS = \frac{W_\infty - W_0}{W_0} \qquad (4)$$

where W_0 is the initial dry weight of the membrane and W_∞ is the swollen weight of the membrane at equilibrium. These results are presented in Table I. The degree of swelling of the blend membranes in feed mixture compositions containing from 10 to 80 wt % water varied in this order: CS/PVA-60 > CS/PVA-40 > CS/PVA-20 > CS. Notice that the higher the content of PVA in the blend membrane, the higher was the swelling. In addition, by increasing the amount of water in the feed mixture, the DS also increased over the whole composition scale of the mixture for pure CS as well as of the blend membranes of CS and PVA. The blend membranes exhibited a higher DS than did the plain CS membrane as a result of the hydrophilic —OH groups of PVA, probably because of higher preferential sorption of water. In addition, it is possible that the presence of hydrophilic PVA helped to create extra free volume space within the blend matrix, thereby enhancing liquid permeation rate. The DS results, displayed in Figure 3, suggest varying interactions of the membranes with the feed mixtures because of differences in their physical properties, which varied with composition. This resulted in varying interactions of liquid feed mixture molecules with the polymer membrane because of chain relaxation processes.[17,32] However, at thermodynamic equilibrium, the DS of a polymer depends on its crosslink density, tempera-
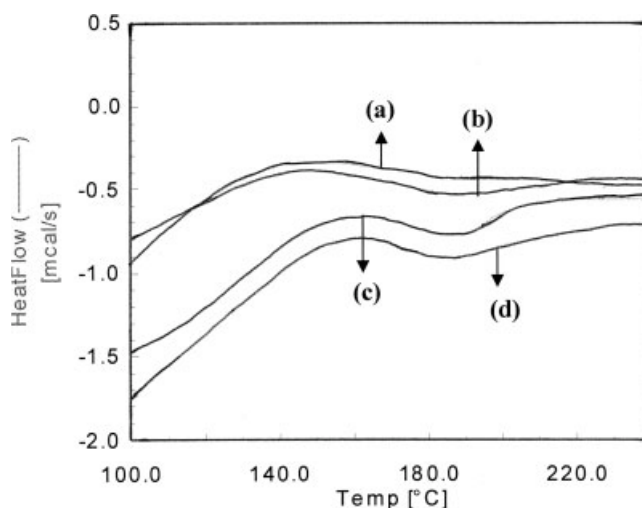

Figure 2 DSC thermograms of (a) uncrosslinked CS membrane, (b) CS/PVA-20 membrane, (c) CS/PVA-40 membrane, and (d) CS/PVA-60 blend membrane.
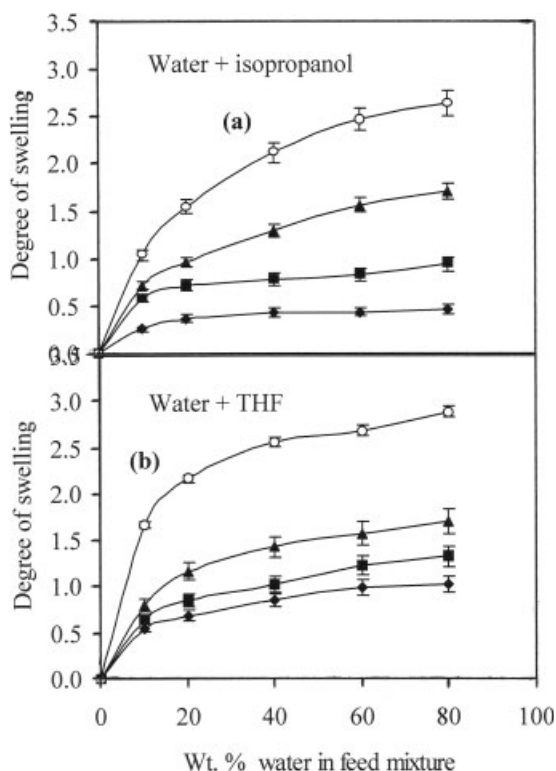
Figure 3 Degree of swelling curves at 30°C of: (a) water + isopropanol mixture and (b) water + THF mixture [(◆) pristine CS membrane, (■) CS/PVA-20 membrane, (▲) CS/PVA-40 membrane, (○) CS/PVA-60 membrane].

ture, and the size of the migrating molecule, in addition to polymer–solvent interactions. In the present study, the DS decreased nonlinearly with an increasing amount of PVA in the membrane, suggesting no systematic trend.[30]

Overall, it was observed that membranes with different ratios exhibited varying extents of swelling. Membrane swelling would then result in an increase of flux because of permeation of more water molecules from the feed mixture. Also, low crystalline regions of the blend matrix helped to increase the liquid permeation.[33] In a study by Srinivasa et al.,[34] the moisture sorption of CS/PVA (80 : 20) blends was investigated. As PVA is a water-soluble polymer, it is readily miscible with CS. Also, hydrophilic PVA blends with CS to produce a matrix that increases water uptake capacity. However, the advantage is that the blend remains essentially insoluble in nonacidic aqueous media because of hydrogen-bonding interactions between the hydroxyl groups of PVA and the amine groups of CS. The DS results for the blend membranes, presented in Table I, show the degree of swelling affected the water flux because the blends could preferentially absorb greater amounts of water from the feed through the swollen regions. Blair et al.[7] studied similar blends and found that the presence of PVA in CS disrupted the

crystalline regions of CS, thus increasing the amorphous content of the overall matrix.

Pervaporation results

In a previous study, Ming et al.[35] developed blend membranes of CS and PVA crosslinked with formaldehyde in order to study the effect of the CS composition as well as the water concentration of the feed mixture on their PV characteristics. They found that with an increasing CS content in the blend, the water concentration also increased. In another study, Bahrami et al.[36] developed CS/PVA blend membranes by solution-casting, followed by crosslinking with glutaraldehyde; these membranes showed improved strength and flexibility in both wet and dry conditions as compared those in membranes of the individual component. The water uptake capacity of the membranes increased with an increasing amount of PVA in the blend. However, crosslinking of the membranes with glutaraldehyde reduced the hydrophilicity of the blend membranes.

The flux and selectivity results of the present study are presented in Tables II and III for the water + isopropanol and water + THF feed mixtures,
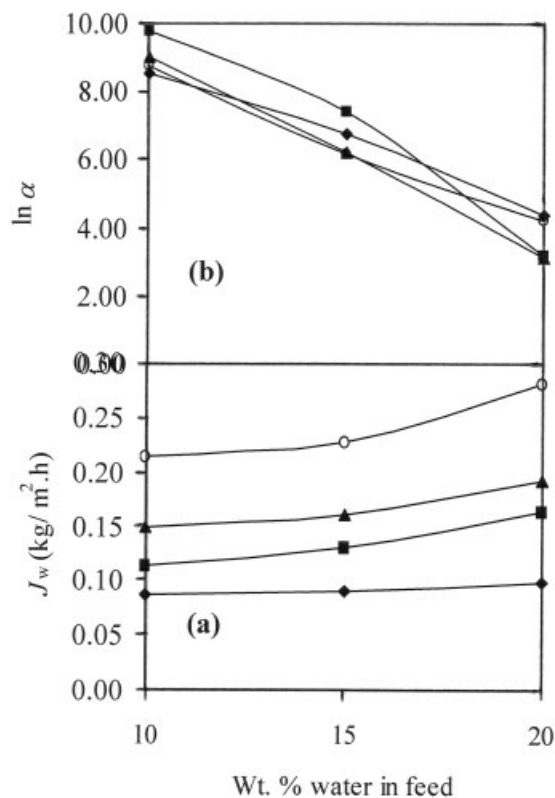

Figure 4 (a) Water flux versus weight percent water and (b) ln(α) versus weight percent water in water + isopropanol feed mixture for CS + PVA blend membranes at 30°C [(◆) pristine CS membrane, (■) CS/PVA-20 membrane, (▲) CS/PVA-40 membrane, (○) CS/PVA-60 membrane].

Figure 5 (a) Water flux versus weight percent water and (b) ln(α) versus weight percent water in water + THF feed mixture for CS + PVA blend membranes at 30°C [(◆) pristine CS membrane, (■) CS/PVA-20 membrane, (▲) CS/PVA-40 membrane, (○) CS/PVA-60 membrane].
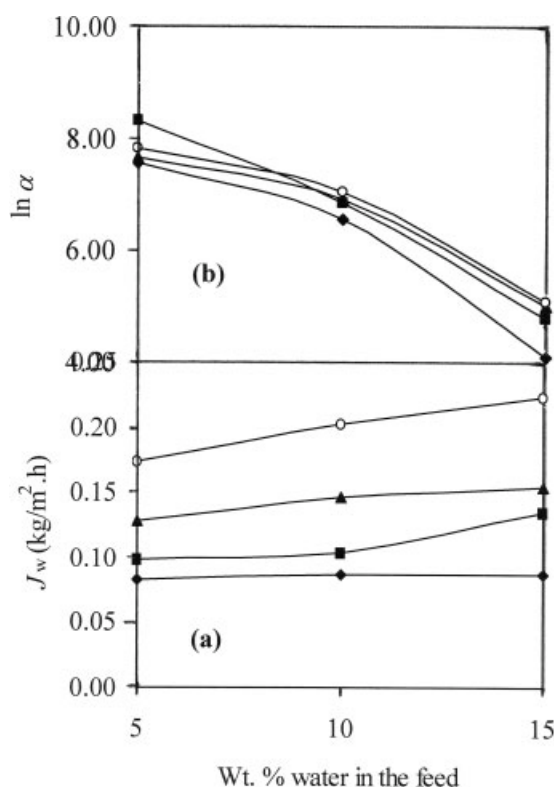
respectively. With an increasing concentration of water in the feed mixture, selectivity decreased drastically with a slight increase in flux. For instance, in the neat CS membrane, for water + isopropanol system, the highest observed selectivity, 5134, with a flux of 0.087 kg m^{-2} h^{-1} for 10 wt % water in the feed decreased to 81 and 0.099 kg m^{-2} h^{-1}, respectively, for 20 wt % water in the feed. At higher concentrations of water in the feed mixture, the membranes swelled to a greater extent, so that polymeric chains would be mobile to favor transport of a large number of water molecules. On the other hand, water could also exert stronger intermolecular interactions with the CS membrane than could isopropa-

nol because the water had greater hydrogen-bonding ability as well as plasticization effect than the isopropanol. By adding 20 wt % PVA to the CS (i.e., CS/PVA-20), we observed a threefold increase in selectivity (i.e., 17,991) with only a slight increase in flux (0.113 kg m^{-2} h^{-1}) for 10 wt % water in the feed. However, when 20 wt % water–containing feed mixture was tested, selectivity dropped drastically, to 25, indicating these membranes may not be good for feed mixtures containing higher water concentrations. Any slight improvement in flux (ca. 0.164 kg m^{-2} h^{-1}) would be greatly sacrificed with the lowest selectivity (ca. 25). To further investigate the effect of the increase in the amount of PVA in the blend, we prepared two blend membranes by adding 40 and 60 wt % PVA to CS, designated as CS/PVA-40 and CS/PVA-60, respectively. With increasing PVA content, membrane selectivity decreased greatly, but flux increased because of the increased hydrophilicity of the blend membranes. In any case, the CS/PVA-20 membrane exhibited a favorable PV performance in terms of selectivity compared to other blend membranes in separating water + isopropanol mixtures.

The pervaporation results of the feed mixtures of water + THF ranging from 5 to 15 wt % water are presented in Table III. It was observed that the selectivity of the CS membrane was 1940 when tested for 5 wt % water in the feed, which decreased to a selectivity of 60 when tested for 15 wt % water in the feed, but flux did not vary much with a change in concentration of water in the feed. For blend membranes of CS containing 20 wt % PVA (CS/PVA-20), selectivity was 4203 for the 5 wt % water–containing feed mixture, which decreased to 120 when tested for the 15 wt % water–containing feed. The flux for the CS/PVA-20 membrane increased from 0.098 to 0.134 kg m^{-2} h^{-1} over the range of water concentrations from 5 to 15 wt %. For membranes containing 40 and 60 wt % PVA (CS-PVA-40 and CS-PVA-60, respectively), selectivity values were low, 2328 and 2049, respectively, when tested for 5 wt % water in the feed, but flux values increased with an increasing amount of PVA in the blend as well as an increase of water in the feed mixture.

TABLE IV
Comparison of PV Performance of Membranes in Present Study with That of Membranes Reported in the Literature for Water + Isopropanol Mixtures at 30°C

Membrane	Water in feed (wt %)	J (kg m^{-2} h^{-1})	α	Reference
CS/PVA(80 : 20)	10	0.1133	17,991	Present work
CS/poly(acrylic acid)	50	0.027	—	41
NaAlg + 5 wt % PVA + 10 wt % PEG (40–50 μm)	10	0.072	3,591	31
NaAlg/GG-g-pAAm (40–50 μm)	10	0.043	891	3
NaAlg/PVA (75 : 25) (40–50 μm)	10	0.025	195	2

NaAlg, sodium alginate; pAAm, polyacrylamide; PVA, poly(vinyl alcohol); PEG, poly(ethylene glycol).

TABLE V
Comparison of PV Performance of Membranes in Present Study with That of Membranes Reported
in the Literature for Water + Tetrahydrofuran Mixtures at 30°C

Membrane	Water in feed (wt %)	J (kg m^{-2} h^{-1})	α	Reference
CS/PVA(80/20)	5	0.0978	4203	Present work
NaAlg–HEC-10—GA + UFS crosslinked (40–50 μm)	10	0.184	1516	5
NaAlg—GA crosslinked (40–50 μm)	10	0.209	291	4
NaAlg + 10 wt % PEG + 15 wt % PVA (40–50 μm)	10	0.091	591	42
PVA/PVP(40 : 60) with 5 wt % DAS	5	0.154	—	43

HEC, hydroxyethyl cellulose; PVP, polyvinylpyrrolidone; DAS, 4,4′- diazostilbene-2,2′-disulfonic acid disodium salt.

Figures 4 and 5 show comparisons of the results of water flux [Figs. 4(a) and 5(a)] and logarithmic selectivity [Figs. 4(b) and 5(b)] at 30°C for water + isopropanol and water + THF feed mixtures, respectively. For all membranes and both feed mixtures, water flux increased with an increasing concentration of water in the feed. Flux values were generally higher for water + isopropanol mixtures than for water + THF mixtures. The CS/PVA-60 blend membrane exhibited a higher water flux than other membranes for both feed mixtures. In general, blend membranes exhibited higher flux for both feed mixtures than for the plain CS membrane. This could have been because of the hydrophilic nature of the PVA in the blend. With an increasing amount of PVA in the blend, polymer chains became more flexible, thereby increasing the free-volume space of the blend matrix and increasing the flux. Enrichment factor (β) for different weight percents of water in the feed mixtures of isopropanol and THF presented in Tables II and III, respectively, decreased with an increasing concentration of water in the feed.

According to the Flory and Rehner theory,[37] polymer swelling depends on the crosslink density of the matrix in addition to free volume. In the present work, a somewhat less hydrophilic CS when blended with a more hydrophilic PVA was able to produce membranes with better mechanical strength than individual polymers to withstand the conditions of the PV experiments. Moreover, blend membranes have increased flux and selectivity compared to the plain CS membrane. Notice that flux increased linearly with increasing concentration of water in the feed; these values were higher for blend systems than for the plain CS membrane because of the preferential interaction of water molecules with the hydrophilic PVA portion of the blend matrix. There have been many studies of PV dehydration of organic mixtures using either plain CS or plain PVA or their chemical modifications.[10,38–40] However, even though blends of PVA and CS have been used in biomedical applications,[15] their usage in PV separation has been somewhat limited. In this respect, the present study is novel, as for the first time, a crosslinking agent (UFS) was used to increase membrane performance. The highest selectivity, 17,991, was observed for the CS/PVA-20 membrane when tested for water–isopropanol feeds, with removal of 99.9% of the water on the permeate side. Thus, the present combination of membranes improved selectivity much better than that reported previously (see comparison in Table IV). Similarly, the highest selectivity, 4203, observed for the water + THF mixtures with the CS/PVA-20 membrane, with removal of 99.6% of the water on the permeate side, appears to have superseded the previous results reported in the literature (see Table V).

CONCLUSIONS

Naturally available chitosan was used to prepare blend membranes by adding different amounts of PVA (20, 40, and 60 wt %). Membranes were crosslinked with a urea-formaldehyde/sulfuric acid mixture, which acted as a unique compound to impart good strength and membrane performance to water in terms of flux and selectivity. Blend compatibility was confirmed by DSC, whereas membrane crosslinking was confirmed by FTIR. Pervaporation dehydration of the membranes was tested for water + isopropanol and water + THF mixtures at 30°C. Results of this study indicated superiority over those of previous reports for both the feed mixtures containing either PVA or CS in blend form. The blend membrane of CS containing 60 wt % PVA showed higher permeation flux for both the water + isopropanol and water + THF feed mixtures, whereas higher selectivity, up to 17,991 and 4203, were observed for the blend membrane containing 20 wt % PVA for dehydrating isopropanol or THF from their aqueous streams. Of all the membranes tested, the blend membrane of CS containing 20 wt % PVA (CS/PVA-20) was found to be a better candidate for dehydration of either isopropanol or THF because it produced optimum water selectivity for both feed mixtures containing 10 wt % water.

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