Thin Film Composite Sodium Alginate Membranes for Dehydration of Acetic Acid and Isobutanol

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ABSTRACT: Dehydration of widely used organic solvents such as acetic acid (AA) and isobutanol (IB) is challenging tasks, which form close boiling mixtures with water. Sodium alginate (SA) thin film composite membranes were prepared and crosslinked with 2,4-toluene diisocyanate (TDI) and glutaraldehyde for dehydration of IB and AA/water mixtures through pervaporation (PV). The crosslinked and uncrosslinked SA composite membranes were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction, thermogravimetric analysis, scanning electron microscopy, and universal testing machine for intermolecular interactions, crystalline nature, thermal stability, surface morphology, and tensile strength, respectively. At a feed composition of 98 wt % IB and 95 wt % AA aqueous solutions, the TDI crosslinked SA composite membrane exhibited separation factors of 3229 and 708 with reasonable fluxes of 0.021 and 0.012 kg m^{-2} h^{-1}, respectively. The results obtained in the study for IB and AA systems were compared with other SA membranes reported in the literature. The membranes appeared to have potential for commercial PV ability to dehydrate the solvents up to desirable purity levels (>99%) and feasibility of preparing them in a composite form which would enable scale-up into modular configurations. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40018.

INTRODUCTION

In recent years, membrane-based separation processes mainly pervaporation (PV) is extensively being used for dehydration of organic–water mixtures.[1] PV plays an important role in continuous removal of water from fermentation broth during production of solvents such as ethanol, propanol, butanol, acetone, etc. Usage of PV unit in bioreactors that selectively removes water, can therefore help in lowering downstream processing costs[2] and hence is used for the dehydration of industrially important solvents.[3,4]

The key to the success of PV process is fabrication of suitable membranes yielding high permeability, good separation factor and sufficient mechanical strength. It is a well-known fact that ionomeric polymer membranes possess high affinity toward water molecules, due to the presence of ionic sites in such polymers.[5,6] For the dehydration of alcohol and organic mixtures, new membrane materials contains hydrophilic groups in the polymer structure, are preferred.[7] Among various hydrophilic polymers, sodium alginate (SA) is a membrane material with potential application in dehydrating organic aqueous solutions.[8,9] Hydrophilic groups absorb water molecules preferentially, which leads to both high flux and high separation factors.

Therefore, preparation of SA membrane with high separation performance has received utmost attention in recent years. Modification in the membrane structure was felt necessary to account for the loss of membrane stability and integrity due to higher water absorption, leads to a lower separation factor. Thus, crosslinking of the SA membrane with various chemical reagents has been so far tried by many researchers to improve the membrane performance.

Yeom et al.,[10] used glutaraldehyde (GA) crosslinked SA membranes for separation of ethanol water mixtures. SA incorporated with other materials like charcoal particles,[11] silicotungstic acid (STA)[5] combined with PVA have proved to be efficient in separation for various alcohol–water mixtures.[12] Wang[13] have developed a novel method of preparing homogeneous solution of chitosan–alginate polyelectrolyte complex system. Aminabhavi et al.,[11] studied PV separation in organic water azeotropes by incorporating nanosized activated charcoal particles into the SA matrix and is crosslinked with GA to form the homogeneous membrane structures for PV applications. Kariduraganavar et al.,[14] have developed a novel PV membrane by incorporating known amount of zeolite into the SA polymer solution for the dehydration of isopropanol, ethyl alcohol, tetrahydrofuran, and

1,4-dioxane. Teli et al.[5] have studied and observed infinite separation factor for acetic acid (AA) dehydration using STA incorporated SA membrane. Wang[13] used alginate composite membranes crosslinked with 1,6-hexadiamine (HDM) or poly(vinyl alcohol) by casting an aqueous solution of SA on hydrolyzed micro porous polyacrylonitrile (PAN) was characterized for the separation of AA/water mixtures.

Based on the preceding literature survey, the emphasis in the present study is on the synthesis of thin film composite (TFC) membranes of SA on hydrophilic substrates such as cellulose triacetate (CTA) and PAN. The indigenous membranes were crosslinked with two different reagents, toluene 2,4-diisocyanate (TDI) and GA for pervaporative separation of isobutanol (IB) and AA/water mixtures, respectively. Equilibrium sorption studies were carried out in pure liquids and binary organic–water mixtures of different compositions to assess polymer–liquid interactions. The effect of feed composition on the performance of composite membrane for dehydration of IB and AA is systematically investigated and compared with the literature data.

EXPERIMENTAL

Materials

SA with an average molecular weight of 150,000 was purchased from Loba chemicals (Mumbai, India). CTA and PAN with average molecular weights of 210,000 and 150,000, respectively, were procured from Aldrich Chemicals. Chemicals such as IB, AA, GA, 1,4-dioxane, N-N-dimethyl formamide (DMF), and TDI were obtained from S.D. Fine Chemicals (Mumbai, India). All feed samples were prepared using deionized water of conductivity of 0.02 mS cm^{-1}, which was generated in the laboratory.

Membrane Preparation

TFC membranes were synthesized by coating SA over the CTA (8%, w/v) and PAN (15%, w/v) porous substrates, by phase inversion technique. The 8 g of CTA in 1,4-dioxane and 15 g of PAN in DMF were dissolved with constant stirring for about 2 h and the bubble free solutions were cast on nonwoven fabric supports with the thickness of 100 μm fixed on glass plates. The glass plates were immersed in ice-chilled water as a nonsolvent bath. This method of casting the membrane is known as phase inversion technique. The supports were then removed and air dried at room temperature. Simultaneously, 8% (w/v) SA solution was prepared by dissolving 8 g SA in 100 mL of distilled water with constant stirring for 6–8 h. The homogeneous bubble free solution of SA was then cast onto CTA and PANS supports under ambient conditions followed by evaporation of water at room temperature for about 4–5 h. To obtain uniform thickness of the SA dense skin layer as well as the substrates CTA and PAN (50 μm), the knobs provided at the either ends of the knife edge of casting machine (Aquaplus, Pune, India) were fixed accurately at an adjustable height using doctor's blade. The pictorial representation of automatic flat sheet casting machine is shown in Figure 1. The resultant membranes were peeled off from the glass plate and modified chemically using 2% TDI in hexane[15] and 5% GA in isopropyl alcohol[16] crosslinking baths for about 4 h. The thickness of the SA dense skin layer was found to be 3 μm which was arrived at
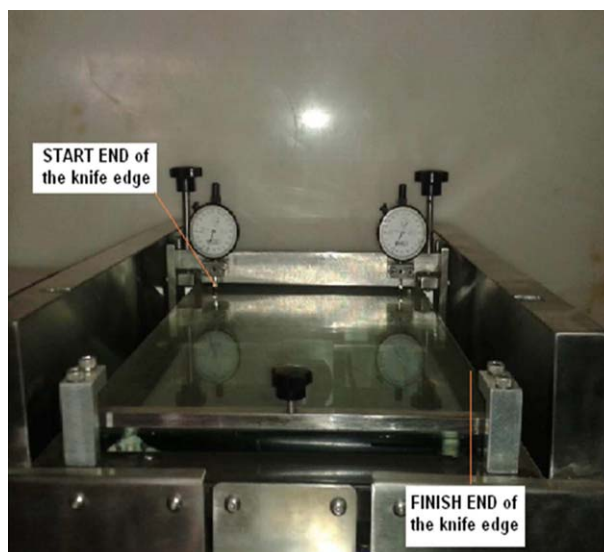

Figure 1. Pictorial representation of automatic flat sheet casting machine. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

by peeling off the top layer from the substrate and finding the difference between the total thickness of top two layers and substrate thickness using an accurate digital microguage (Mitutoyo, Japan). The dried SA-TFC membranes were utilized in PV experiments. The stability of the membranes was analyzed by bending test before and after PV studies.

Experimental Procedure

Experiments were carried out according to the procedure reported by Rao et al.[17] Figure 2 shows the schematic representation of indigenously constructed PV manifold. The feed consisting of either aqueous IB or AA mixture was charged into the PV unit cell at upstream side of the membrane and stirred vigorously at a speed of 150 rpm throughout the experiment to minimize concentration polarization. The effective area of the membrane in contact with the feed stream was 20 cm^2 and the upstream side of the membrane was maintained at ambient
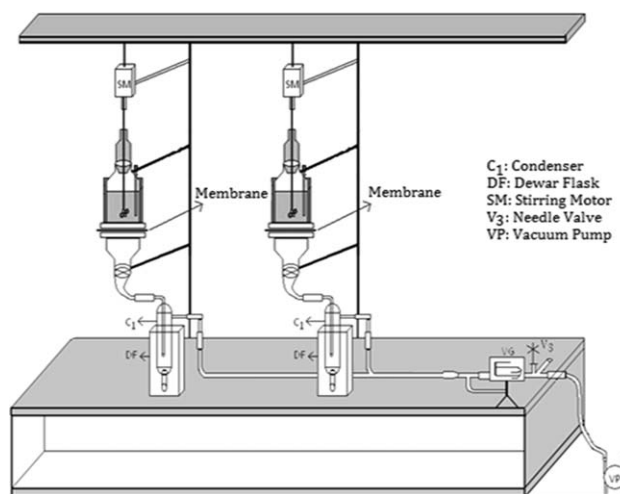

Figure 2. Schematic representation of laboratory pervaporation set up.

temperature and atmospheric pressure (1 atm = 760 mmHg), whereas the downstream side was maintained under vacuum, i.e., 0.5 mmHg. Therefore, the pressure gradient across the membrane was approximately 759.5 mmHg. Permeate vapors were condensed in a trap using liquid nitrogen and collected for a duration of 6–8 h. Experiments were repeated twice using fresh feed solution to check for reproducibility. The collected permeate was weighed by using Sartorius electronic balance having an accuracy of 10^{-4} g to determine the flux. Permeate samples were analyzed by refractive index and gas chromatography for IB/water and AA/water, respectively, to evaluate the membrane separation factor.

Flux and Separation Factor Calculations

As reported in PV studies,[6] the flux J for the faster permeating molecules 'i' of the two liquid mixture comprising of i (water) and j (organic) is given by:

$$Ji = \frac{Wi}{At} \qquad (1)$$

where W_i represents the mass of permeate in kg, A is the membrane area m^2, and t represents the evaluation time in hours. The membrane separation factor is defined as the ratio of permeability of water to that of organic (IB and AA), which can also be calculated from the respective concentrations in the feed and permeate as follows:

$$\alpha = \frac{y(1-x)}{x(1-y)} \qquad (2)$$

where x and y represent the feed and permeate concentrations, respectively, of the faster permeating molecule i water in present case, $(1-x)$ and $(1-y)$ represent the organic in feed and permeate, respectively.

Pervaporation separation index (PSI) is a measure of the separation capability of a membrane and is expressed as a product of separation factor and flux.[18]

$$PSI = Ji \times \alpha \qquad (3)$$

Membrane Characterization

Fourier Transform Infrared. TFC membranes of SA both uncrosslinked and crosslinked with GA and TDI have been characterized for their intermolecular behavior. The membranes were scanned in the range 400–4000 cm^{-1} wave numbers using Thermo Nicolet Nexus 670 spectrometer (resolution 4 cm^{-1}).[19]

X-ray Diffraction. A Siemens D 5000 powder X-ray diffractometer was used to assess the solid-state morphology of both uncrosslinked and crosslinked SA membranes.

Thermogravimetric Analysis. Thermal stability of SA uncrosslinked and crosslinked membranes was examined to determine the thermal stability.[20]

Scanning Electron Microscopy. The surface and cross-sectional morphologies of the SA-TFC membranes were studied by scanning electron microscopy (SEM; model JEOL JSM-6380LA) with the help of National Institute of Technology

(Surathkal, Karnataka, India). In preparing the specimens, the fracture surface of the cross-section of the TFC three layered membrane inclusive of nonwoven fabric polyester support, ultraporous substrate, and dense skin layer were obtained by cutting the membrane in liquid nitrogen to ensure smooth morphology.

Mechanical Properties

Mechanical properties of the membranes were evaluated by universal testing machine (UTM; model AGS-10 kNG, Shimadzu, Japan) with an operating head load of 5 kN, following the procedure outlined in ASTM D-638 test method. The test length was 5 cm while the speed of testing was set at the rate of 10 mm min^{-1}. Tensile strength was calculated using the following equation:

$$\text{tensile strengh} = \frac{\text{maximum load}}{\text{cross-sectional area}} \text{N/mm}^2 \qquad (4)$$

Ion Exchange Capacity

The total number of interacting groups presents in the uncrosslinked and crosslinked SA membranes can be determined by soaking similar weights in 50 mL of 0.01 N NaOH solutions for 24 h at ambient temperature.[21] The 10 mL of solution was then titrated against with 0.01 N sulfuric acid. The ion exchange capacity (IEC) was calculated according to the following equation:

$$IEC = \frac{(B-S) \times N \times 5}{Wt} \qquad (5)$$

where B and S are the amounts of 0.01 N sulfuric acid used for neutralization the blank (without membrane) and S (with uncrosslinked and crosslinked membrane separately), and $Eq.$ 5 represents the factor corresponding to the ratio of the amount of NaOH taken to dissolve the polymer to the amount used for titration, and W_t is the weight of the sample taken in grams.

Extent of crosslinking has been calculated as,

$$\text{Extent of Crosslinking} = \frac{\left(IEC_{SA,\ unmodified} - IEC_{SA,crosslinked}\right)}{IEC_{SA,\ unmodified}} \times 100 \qquad (6)$$

Sorption Studies

As reported by Sridhar et al.,[6] weights of samples of crosslinked SA films were soaked in pure IB, AA, water, and binary mixtures of different compositions as well. The films have been taken out after 48 h of soaking and weighed immediately after carefully wiping out the excess liquid to determine the amount of liquid sorbed by the films. The degree of swelling was calculated from the following equation:

$$\text{Degree of Swelling} = Ms/Md \qquad (7)$$

where Ms is the mass of the swollen polymer in grams and Md is the mass of the dry polymer in grams. The % sorption was calculated from the equation:
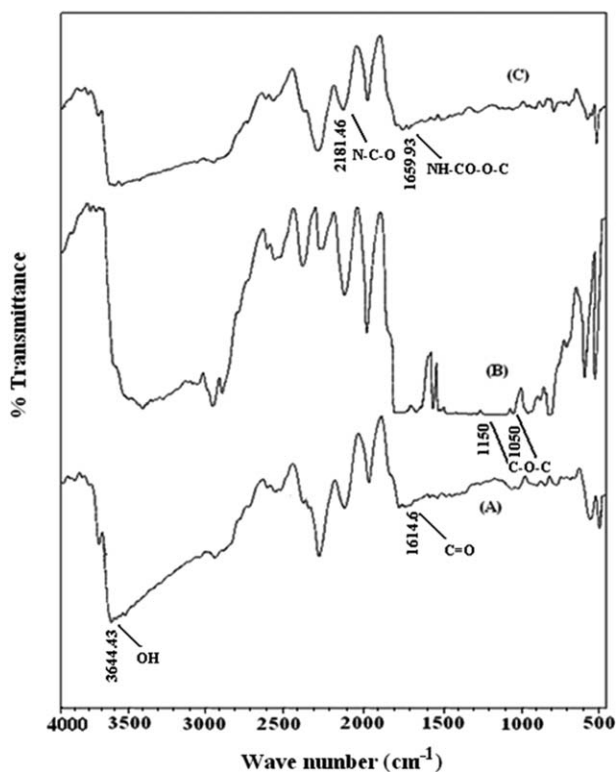
Figure 3. FTIR spectra of (A) uncrosslinked, (B) GA crosslinked, and (C) TDI crosslinked SA composite membrane.

$$\% \, Sorption = \frac{(Ms - Md)}{Md} \qquad (8)$$

Analytical Procedure

The concentration of each component in feed and permeate samples obtained from the experimental results of IB/water was accurately measured by refractive index method (Schmidt-Haensch digital refractometer) because there is large difference between the values of refractive indices for IB (1.39615) and water (1.33314).[22] The AA/water feed and permeate samples were analyzed using Nucon gas chromatography (model 5765) installed with thermal conductivity detector (TCD) and Tenax (commercial porous polymer resin made up of 2,6-diphenylene-oxide-based column) packed column of 2 m length. The oven temperature was initially maintained at 80°C for 3 min followed by an increase at the rate of 10°C min^{-1} up to 220°C through temperature programming. The injector and detector temperatures were maintained at 220°C each. The sample injection size was 1 μL and pure hydrogen was used as the carrier gas at a pressure of 3 kg cm^{-2}. The GC response was calibrated for this particular column and conditions with known compositions of AA–water mixtures and the calibration factors were fed into the software to obtain correct analysis for unknown samples.

RESULTS AND DISCUSSIONS

Membrane Characterization

Fourier Transforms Infrared Studies. The Fourier transform infrared spectroscopy (FTIR) spectra of uncrosslinked and crosslinked SA are shown in Figure 3. The prominent peaks at 1614.6 cm^{-1} and 3644.43 cm^{-1} are attributed to strong —C=O
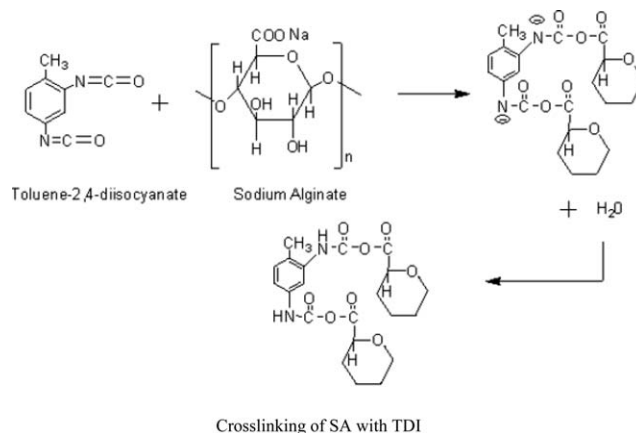
Scheme 1. Structural representation of SA membrane crosslinked with TDI.

stretching vibration of carboxylic group and free —OH group of uncrosslinked membrane, respectively (Curve 3A). The characteristic peaks at 2181.46 cm^{-1} corresponds to —N—C—O— groups of TDI which is intact and does not participate in the crosslinking. The formation of a new peak at 1659.93 cm^{-1} corresponding to (—HN—CO—O—C—) urethane linkage which confirms the crosslinking of TDI with SA (Curve 3C). Scheme 1 represents the possible crosslinking structure of SA with TDI as confirmed by FTIR.

On the other hand, a comparison of the FTIR spectrum of uncrosslinked SA membranes with that of GA crosslinked one exhibited a peak in the range 1050–1150 cm^{-1}, corresponding to –C–O–C (acetal) linkage is formed by –OH group of SA with –CHO group of GA (Curve 3B).[16]

X-ray Diffraction Studies. X-ray diffraction (XRD) studies not only indicate the nature of the compounds but also enable the identification of the space between the clusters of the polymer chains. It is a well known fact that on crosslinking the polymer chains are close to one another, and thus, a reduction in the cluster space may be encountered. The d-spacing (d) value gives an indication of cluster space existing in the polymer before and after crosslinking. The X-ray diffractograms of crosslinked and uncrosslinked SA composite membranes are shown in Figure 4.

The XRD pattern of uncrosslinked SA composite membrane appears to be amorphous in nature (Curve 4A), whereas the XRD pattern of TDI crosslinked membrane appears to be semi-crystalline in nature with little sharp peaks at 17, 24, and 26° of 2θ (Curve 4C), which might have imparted better separation factor to the membrane. On the other hand, enhancement in d-spacing at 17, 24, and 26° of 2θ for GA crosslinked SA composite membrane shows higher crystalline in nature (Curve 4B) than their corresponding ones. It can also be inferred that the crystalline nature makes the membrane more brittle, decrease the separation factor and might get damaged soon.

Thermogravimetric Analysis Studies. Thermal stability of uncrosslinked and crosslinked SA composite membranes are shown in Figure 5(A–C). Thermogravimetric analysis (TGA)
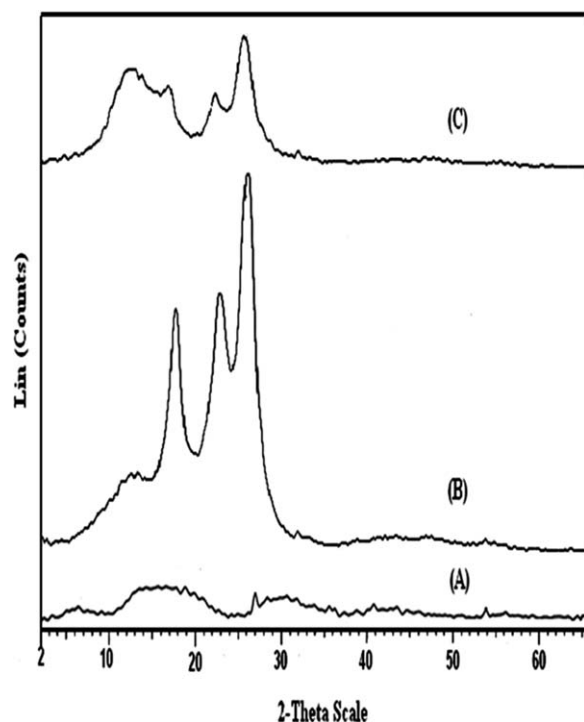
Figure 4. XRD diffractograms of (A) uncrosslinked, (B) GA crosslinked, and (C) TDI crosslinked SA composite membranes.

curve of uncrosslinked (Curve 5A) one shows it first minor weight loss occurring at 80°C, followed by major weight loss around 240°C. The rapid drop in weight at 240°C can be attributed to the decomposition of the uncrosslinked membrane. The TGA curves of crosslinked SA composite membranes with GA
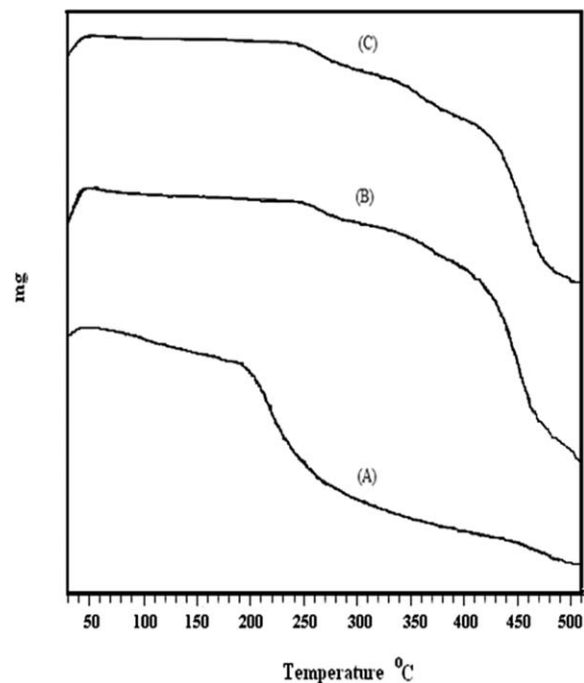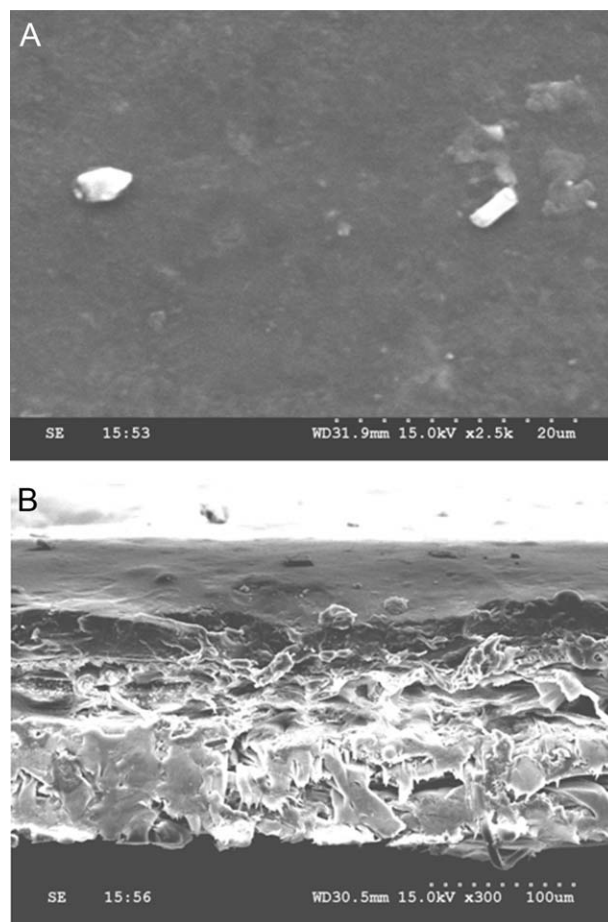

Figure 6. SEM images of (A) surface and (B) cross-sectional view of SA composite membranes.

and TDI (Curves 5B and C) found to be stable up to 300°C and later there was a gradual decrease in weight of the membrane. Greater loss in polymer weight was observed beyond 450°C for crosslinked SA membranes. These observations provided evidence that the membrane exhibited high thermal stability after crosslinking.

SEM Studies. Figure 6(A,B) shows surface and cross-sectional morphology of SA-TFC membrane. Figure 6(A) reveals the defect-free nature of the SA surface and there are no visible pores depicting the dense nature of the membrane with uniform surface morphology. Figure 6(B) shows the cross-section view of composite SA membrane, which reveals the existence of a dense skin layer atop an ultraporous substrate which is in turn supported on a nonwoven polyester fabric with adequate interpenetration of the two upper layers. No agglomerations or cluster formation of any of the polymers can be observed.

Mechanical Properties

Composite membranes of unmodified SA and those crosslinked with TDI and GA exhibited tensile strengths of 1.06, 36.32, and 30.51 N mm^{-2}, respectively, as determined from the stress–strain curves. The percent elongation at break for TDI and GA crosslinked SA composites were also higher than those of uncrosslinked SA polymer (2.60). Table I reveals that the

Figure 5. TGA curves of (A) uncrosslinked, (B) GA crosslinked, and (C) TDI crosslinked SA composite membranes.

Table I. Comparison of Tensile Strength and % Elongation of Composite SA Membranes with Literature Data

Membrane type	Tensile strength (N mm^{-2})	Elongation (%)	Reference
SA-uncrosslinked	01.08	02.60	Present study
TDI-SA-TFC membrane	36.32	12.21	
GA-SA-TFC membrane	30.51	10.15	
CaCl$_2$ crosslinked SA dry film	43.68	05.23	23
CaCl$_2$ crosslinked SA wet film	10.42	44.45	
0.08 g of CaCl$_2$ mixing SA film	43.50	09.10	24
SA and pectin composite edible films (50% alginate + 50% pectin)	42.30	14.90	25
Photocured SA with 2% EHA in 10% silane monomer	49.67	21.50	26
SA/GO-6 wt % composite membrane	113	–	27
SA/Electrospun PEO nanofibers	20.90	05.10	28

SA, sodium alginate; EHA, 2-ethylhexylacrylate; PEO: poly(ethylene oxide).

crosslinked SA composites membranes display higher mechanical strength and % elongation property compared to unmodified one which is in agreement with data reported earlier in the literature.[23–28]

IEC Studies

IEC plays an important role in PV parameters such as flux and separation factor. The amount of residual hydroxyl and acetate groups present in crosslinked and uncrosslinked SA composite membranes and the extent of crosslinking are also estimated from IEC studies. Table II represents the IEC and extent of crosslinking values of SA composite membranes before and after crosslinking. The higher extent of crosslinking was found to be 78.6% at 4 h, which imply most of the ions of SA crosslinked with TDI.

On the other hand, GA crosslinked SA membranes exhibited IEC of 10.75 meq g^{-1}, whereas, the uncrosslinked SA shows IEC of 18.11 meq g^{-1}, representing the 40% of hydroxyl groups in SA crosslinked with aldehyde groups of GA (Table I). From the results it can be observed that the extent of crosslinking was better in case of TDI in comparison with GA. Hence, the TDI crosslinked composite membrane exhibited high flux and separation factor.

Sorption Studies

The SA layer was peeled off from the nonwoven polyester fabric support before subjecting it to sorption experiments. The effect of varying composition of IB/water and AA/water mixtures on

sorption of the SA membrane crosslinked with TDI and GA is shown in Figure 7. From the graph, it can be inferred that % water uptake of the IB binary feed mixtures increased from 2.4 to 14.85% for TDI–SA and from 6.6 to 21.28% for GA–SA membranes with increase in feed water concentration from 1.9 to 5.5 wt %, whereas for AA/water system the feed water concentration increases from 4.89 to 30 wt % the corresponding % sorption decreases from 5.1 to 23.76% and 8.9 to 30.2% for TDI and GA-SA membranes, respectively, signifying the possibility of attaining enhanced flux using these composite membranes. Therefore, the amount of water sorbed into the membrane increases with a rise in feed water concentration, resulting in swelling of the membrane and subsequent fall in membrane separation factor, due to plasticization of the polymer chains which have preferential affinity for water.

PV Experimental Results

Effect of TDI Crosslinking Time. The effect of crosslinking time of TDI for 2, 4, and 6 h at constant feed water concentration of IB/water (98/2) and AA/water (95/5) mixtures are given in Table III. It can be observed that the SA-TFC membrane crosslinked with TDI for 4 h shows optimum separation factor. The possible explanation for the above observation could be as

Table II. Effect of Ion Exchange Capacity and Extent of Crosslinking on SA Composite Membranes Before and After Crosslinking

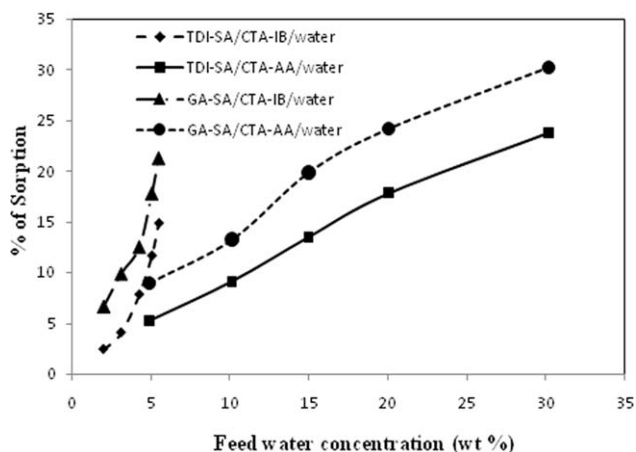| Type of membrane	IEC (meq g^{-1})	Extent of crosslinking (%)
SA-uncrosslinked	3.508	–
SA-TDI-2 h crosslinked	2.315	34.0
SA-TDI-4 h crosslinked	0.748	78.6
SA-TDI-6 h crosslinked	1.248	64.4
SA-GA crosslinked	2.080	40.7

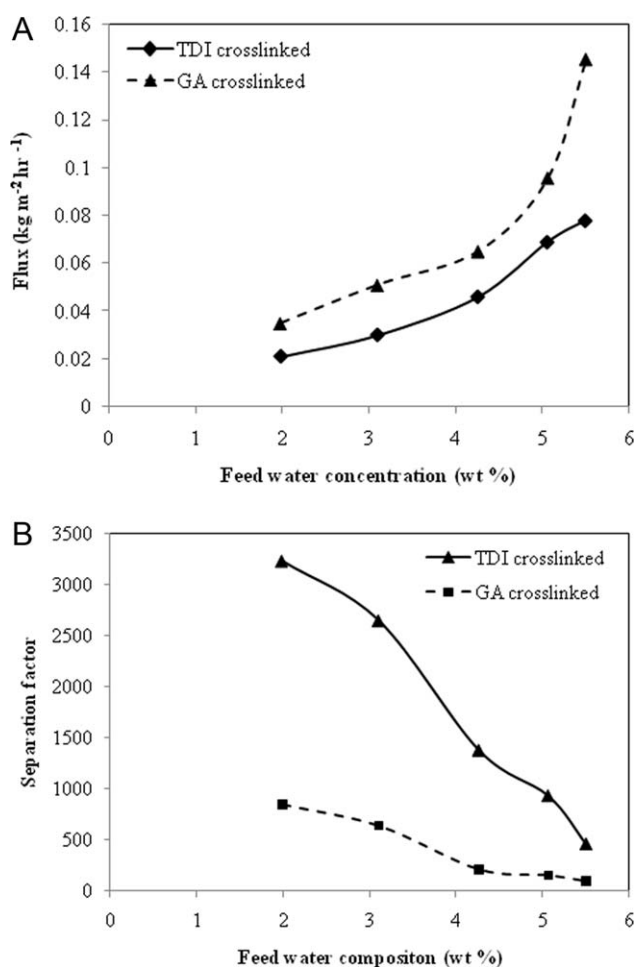**Figure 7.** Effect of feed water concentration on % sorption.

Table III. Effect of Crosslinking Time of TDI on Flux and Separation Factor of the SA Composite Membranes

Feed system	Feed composition (wt %)	Crosslinking time (h)	Permeate composition (wt %)		Flux (kg m^{-2} h^{-1})	Separation factor (α)
			Organic	Water		
IB/water	98.02/1.98	2	2.63	97.37	0.036	1832.8
		4	1.51	98.49	0.021	3229.0
		6	3.152	96.85	0.045	1521.1
AA/water	95.10/4.90	2	4.29	95.71	0.025	433.4
		4	2.674	97.32	0.012	707.7
		6	4.99	95.01	0.031	369.9

follows: the crosslinking time of 2 h is perhaps not sufficient for the completion of interaction occurring between functional groups of SA (–COONa) and TDI (–N=C=O–). This explanation can be supported by the IEC values for the same membrane given in Table II. The IEC value decreases when the crosslinking time is increased to 4 h, indicating extensive interaction between the functional groups. Initially, the reaction between SA and TDI progresses quickly due to availability of more number of free polymer functional groups for crosslinking. However, the reaction becomes retarded with time owing to increasing unavailability of reactive groups in SA. When the crosslinking time is increased to 6 h, accumulation of excess TDI molecules within the membrane matrix occurs due to diffusion phenomenon, which increases the IEC as revealed in Table II. As a consequence, flux increases due to interaction of the preferentially permeating water molecules with more number of polar moieties now available within the membrane. However, there is always a tradeoff phenomenon with respect to flux and separation factor in polymer membranes. The separation factor reduces due to increasing membrane swelling which causes dragging of more number of organic solvent molecules through the barrier along with water due to momentum transfer (Table III). Moreover, exposure to TDI for prolonged durations, especially beyond 4 h, also causes brittleness in membranes, as seen in the present case, which limits their feasibility for scale-up in commercial applications.

Effect of Feed Water Concentration. The relation between liquid feed composition and PV performance over a wide range of compositions of feed mixtures at room temperature is investigated using TDI and GA crosslinked SA membranes keeping other operating parameters such as permeate pressure (0.5 mmHg) and membrane thickness (top layer 5 μm) constant. The effect of feed water concentration on flux and separation factor of the TDI and GA crosslinked SA composite membranes in aqueous IB and AA are graphically illustrated in Figures 8(A,B) and 9(A,B), respectively. As expected, a rise in the mass percentage of water in feed produces an increase in the flux from 0.021 to 0.078 kg m^{-2} h^{-1} (TDI-SA-TFC) and from 0.035 to 0.145 kg m^{-2} h^{-1} (GA-SA-TFC) and a drop of separation factor from 3229 to 458 and from 851 to 98.5 for IB/water feed composition [Figure 8(A,B)] and correspondingly a flux enhancement from 0.012 to 0.064 kg m^{-2} h^{-1} (TDI-SA-

TFC) and from 0.045 to 0.168 kg m^{-2} h^{-1} (GA-SA-TFC) and separation factor reduction from 707 to 32.8 and from 517 to 68.7 for AA/water mixture [Figure 9(A,B)]. Mass transport through the hydrophilic polymer membrane occurs by solution diffusion mechanism,[29] in which the molecular transport of liquids as embodied due to the interactions between the liquid molecules (water) and the polymer chain. The membranes developed in the present study have more affinity for water molecules than IB or AA.

Figure 8. Effect of feed water concentratin on (A) flux and (B) separation factor of SA composite membranes for aqueous IB mixture.
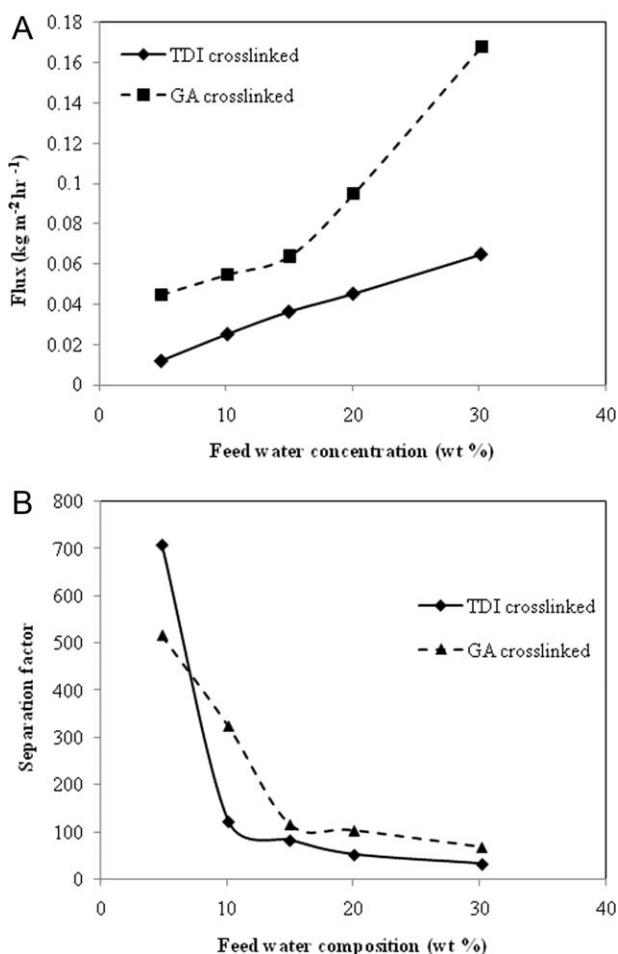
Figure 9. Effect of feed water concentration on (A) flux and (B) separation factor of SA composite membranes for aqueous AA mixture.

Comparison of Present Work with Literature

Data reported in the literature[6,13,29–31] on PV-based separation of organic/water systems are summarized in Table IV for comparison with TDI and GA crosslinked SA-TFC membranes used in the present work. The data in the table indicates that the performance of TDI and GA crosslinked SA-TFC membranes are comparable with other membranes, especially for dehydration of IB/water, where a separation factor of 3229 was observed. However, the membrane used was not a TFC like the one used in the present study which enhances feasibility of scale-up. Moreover, IB/water separation using SA in dense or composite form is not available in literature. Some of the membranes reported in literature have shown high flux but low values of separation factor. To optimize the flux and bring it within comparable range, the TDI-SA-TFC membrane could be cast with finer thickness of 5 μm or lower on the CTA substrate. The ease in fabrication of these membranes associated with their low cost render them more attractive for PV of aqueous IB and AA mixtures.

CONCLUSIONS

Hydrophilic PV process using composite SA membranes has exhibited immense potential as a commercially viable technique for separation of water from its close boiling mixtures with *iso*-butanol and AA. FTIR confirmed modification of the polymer and illustrated its intermolecular interactions with the more efficient 2,4-toluene diisocyanate (TDI) crosslinker. XRD studies revealed decrease in amorphous nature, along with a reduction in *d*-spacing value which is an indication of shrinkage in the cell size that improves the selective nature of the membrane. The membranes showed adequate thermal stability to withstand PV experimental conditions as revealed by thermal gravimetric analysis. IEC and extent of crosslinking were found

Table IV. Comparison of Flux and Separation Factor of Composite SA Membranes with Values Reported in the Literature

Membrane type	Feed composition (wt %)	Flux (kg m^{-2} h^{-1})	Separation factor (α)	Reference
STA (1 wt %) – SA	90% acetic acid	NA	820	6
SA on PAN crosslinked with HDM	85% acetic acid	0.262	161	13
Aluminum-rich zeolite beta-filled SA	90% acetic acid	0.109	12,848	29
SA + 5 wt % PVA + 10% wt % PEG + GA crosslinked	90% acetic acid	0.071	40	30
Cobolt (III) (3-acetylpyri-dine-*o*-aminobenzoyl hydrazine)-filled SA	90% acetic acid	0.123	174	31
SA composite membrane crosslinked with TDI	95.1% acetic acid	0.012	707	Present work
	98% isobutylalcohol	0.021	3229	
SA composite membrane crosslinked with GA	95.1% acetic acid	0.045	517	Present work
	98% isobutylalcohol	0.035	851	

SA, sodium alginate; PAN, poly(acrylonitrile); PVA, poly(vinylalcohol); PEG, poly(ethylene glycol); HDM, 1,6-haxanediamine; GA, gluteraldehyde; TDI, 2,4-toluene diisocyanate.

to be 0.784 and 78.6% for 4 h crosslinking duration, which meant that most of the functional groups of the polymer were crosslinked. Sorption studies revealed the membrane to possess greater affinity toward water than organic solvents. With an increase in feed water concentration, the membrane performance was found to be substantially influenced by enhanced swelling which caused an enhancement in flux at the expense of separation factor. Membrane treated with TDI exhibited promising separation factors of 3229 and 707 for dehydration of isobutanol/water and AA/water mixtures, respectively, proving to be more competent than GA as a crosslinking agent. SA membranes crosslinked with diisocyanates have not been explored extensively as per the literature and appear to be promising materials for dehydration of organic solvents due to the high flux that could be achieved with considerable separation factors. Moreover, their TFC structure makes the membranes easy to scale up due to the strength, adhesion, and defect-free nature of active layer rendered by using ultraporous substrates and nonwoven polyester during membrane preparation.

Economic estimation of the present process and constitution of a hybrid process combining PV with distillation to achieve desired purity levels of IB and AA solvents form the future plan of work. The potential of these membranes would be extended to the recovery of polar aprotic solvents of great importance in pharmaceutical industry, such as dimethyl formamide, dimethyl sulfoxide, and *n*-methyl pyrrolidone, because SA has sufficient chemical resistance in such harsh media. Another future prospect envisaged is the scale-up of these composite membranes into spiral wound or plate and frame configuration for evaluating their performance in downstream processing such as continuous removal of water from fermentation broths to enhance yield of *iso*-butanol and AA products.

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