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Dehydration of 1,4-dioxane by pervaporation using modified blend membranes of chitosan and nylon 66

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Abstract

The pervaporation separation of 1,4-dioxane/water mixtures was carried out using crosslinked blend membranes of chitosan (CS) and nylon 66 (NYL). These membranes were characterized by FTIR, TGA, XRD, and tensile strength to assess intermolecular interactions, thermal stability, crystallinity and mechanical strength, respectively. Sorption studies were carried out in pure liquids and binary mixtures of different compositions to evaluate polymer–liquid interactions. The effects of CS/NYL ratio, membrane thickness, feed concentration on the transmembrane permeation rate and separation factor were investigated. Optimum CS/NYL ratio was determined as 90/10 (w/w) for 4.3 wt.% feed water concentration at 40 °C. Increasing barrier from 30 to 120 μm improved the separation factor from 767 to 1123 at the cost of flux, which lowered from 0.118 to 0.028 kg/m^2 h. The membrane performance was also investigated for the separation of various feed compositions of 1,4-dioxane–water mixtures and permeate pressures. The azeotrope formed at 82-wt.% dioxane was easily broken with a selectivity of 865 and water flux of 0.089 kg/m^2 h.

Keywords: Pervaporation; CS/NYL blend; 1,4-Dioxane–water mixture; Membrane characterization

1. Introduction

Pervaporation, a promising membrane technology, is used to separate a liquid mixture by partly vaporizing it through a nonporous permselective membrane (Nunes & Peinemann, 2001). The "feed" mixture is allowed to flow along one side of the membrane and a fraction of it (the permeate) is evolved in the vapor state from the opposite side, which is kept under vacuum (Fleming & Slater, 1992; Noble & Stern, 1995; Schaetzel, Gref, Clement, Tarjus, & Nguyen, 1995a; Schucker, 1995). Mass transport by pervaporation across permselective membranes involves three successive steps: (i) upstream partitioning of the feed components between the flowing liquid mixture and the swollen upstream surface layer of the membrane, (ii) diffusion of the components through the membrane thickness and (iii) desorption of these components at the downstream surface of the membrane (Heintz & Stephan, 1994; Schaetzel et al., 1995a; Schaetzel, Favre, Nguyen, & N'eel, 1993; Schaetzel, Gref, Clement, Tarjus, & Nguyen, 1995b). Pervaporation is of interest in cases where conventional separation processes either fail or result in a specific energy consumption and/or high investment costs (Baker et al., 1991; Bravo et al., 1986; Koops & Smolders, 1991; Rhim, Sohn, & Lee, 1994).

The most important category of separation problems which pervaporation can solve are mixtures such as dioxane–water which form an azeotrope or exhibit small differences in boiling characteristics (Baker et al., 1991; Huang, 1991; Hwang & Kammermeyer, 1975). 1,4-Dioxane is a well-known organic compound primarily used as an industrial solvent and as a stabilizer for chlorinated solvents. It is widely used in pharmaceutical and chemical industries, and is miscible with water in all proportions. Dioxane forms an azeotrope with water at 82-wt.% concentration, which cannot be concentrated by simple distillation. Moreover

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dioxane boils at a temperature (101 °C) close to water and forms close boiling mixtures at other compositions (Sridhar, Smitha, Madhavi Latha, & Rama Krishna, 2004).

Chitosan, (1 → 4)-2-amino-2-deoxy-β-D-glucan, is a polysaccharide biomacromolecule, which is generally used for dehydrating solvents owing to its hydrophilic nature. The presence of a potentially reactive amino and hydroxyl functional group have given chitosan unique possibilities for utilization in different fields. In particular, the ability of chitosan to form films has found application in various fields (Kubota, Ohga, & Moriguchi, 1991; Majeti & Ravikumar, 2000). Chitosan is expected to make exclusively strong hydrogen bond interactions with water, owing to the close proximity of its solubility parameter value to that of water (Ravindra, Krovvidi, & Khan, 1998; Qurashi, Blair, & Allen, 1992), resulting in the loss of mechanical strength through excessive swelling in wet state. Great efforts have therefore been made to improve the stability and mechanical properties of chitosan-based membranes, such as bringing crosslinked structure to membranes (Ge, Cui, Yan, & Jiang, 2000; Liu, Su, & Lai, 2004), and blending chitosan with other polymers (Chanachai et al., 2000; Shieh & Huang, 1998; Smitha, Sridhar, & Khan, 2004).

Nylons are also called polyamides because of the characteristic amide groups in the backbone chain. These amide groups are moderately polar, and can hydrogen bond with one another. Nylons are often crystalline due to polar groups present in the molecule, leading to the formation of hydrogen bonds, which thereby enables tighter packing. Nylon 66 is usually synthesized by reacting adipic acid with hexamethylene diamine (Brandrup, Immergut, & Grulke, 1999; Deanin, 1972; Gowariker et al., 1999; Meares, 1965).

In the present study, the highly hydrophilic chitosan was blended with nylon 66, followed by crosslinking with sulfuric acid to reduce its excessive swelling for the enhancement of separation properties. These membranes were characterized substantially for their physico-mechanical properties and were then evaluated for their efficacy in dehydrating dioxane–water mixtures. The effect of different feed composition, varying membrane thickness and pressure on pervaporation performance have also been dealt with.

2. Experimental

2.1. Materials

Nylon 66 of molecular weight 25,000 was purchased from BDH Chemicals Ltd., Poole, England and chitosan having average molecular weight 500,000 were purchased from Chempol (India) Ltd, Nellore, India. The degree of deacetylation of chitosan as supplied by the vendor was 84%. Formic acid and sulfuric acid were purchased from Loba Chemie, Mumbai, India. Demineralized water (conductivity = 0.02 S/cm) used for the preparation of feed solutions was generated in the laboratory itself.

2.2. Membrane preparation

Solutions of nylon 66 (1 wt.%) and chitosan (1 wt.%) in formic acid were mixed in different proportions as listed in Table 1. Sample blends were designated CS/NYL (chitosan wt.%) (nylon wt.%). For example, CS/NYL 70/30 represents the membrane containing 70 wt.% chitosan and 30 wt.% nylon 66. The solutions were cast on clean glass plates and dried at 30 °C in a convection oven for over 24 h. The membranes were then washed with water for 24–30 h. The membranes were then crosslinked in sulfuric acid bath for a period of 120 min followed by drying.

2.3. Pervaporation procedure

Experiments were carried out with an indigenously constructed pervaporation manifold (Fig. 1) operated at a vacuum as low as 0.05 mmHg in the permeate line. The test cell itself was made of glass and the membrane was generally supported by a sintered (stainless steel) disc. The volume of the liquid feed was approximately 100 ml and the membrane area about 20 cm^2. The permeate was alternatively collected in a cold trap after attaining the stabilization period of 24 h, in which it condensed totally. The experimental procedure is described in detail elsewhere (Sridhar, Susheela, Jayasimha Reddy, & Khan, 2001). The liquid thus recovered was weighed after allowing it to attain room temperature in a Sartorius electronic balance (accuracy: 10^{-4} g) to determine the flux and then analyzed by gas chromatography to evaluate separation factor. Tests were carried out at room temperature (30 ± 2 °C) and repeated twice using fresh feed solution to check for reproducibility.

2.3.1. Analytical procedure

The feed and permeate samples were analyzed using a Nucon Gas Chromatograph (Model 5765) installed with Thermal Conductivity Detector (TCD) and packed column of 10% DEGS on 80/100 Supelco port of 1/8″ ID and 2 m length. The oven temperature was maintained at 70 °C (isothermal) while the injector and detector temperatures were maintained at 150 °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 dioxane–water mixtures and the calibration factors were fed into the software to obtain correct analysis for unknown samples.

2.3.2. Flux and selectivity equations

The behaviour of a pervaporation membrane used to separate a binary liquid mixture (components A and B) of given composition is characterized by two experimental parameters namely, the permeate flux ‘J_A’ expressed in kg/m^2 h and the selectivity. The flux of faster permeating

Table 1
Typical sample preparation and designation of polymer blend membranes

S1.no	Blending information	Composition of blend
1.	CS/NYL (9:1)	90 wt% of chitosan and 10 wt% of nylon 66
2.	CS/NYL (8:2)	80 wt% of chitosan and 20 wt% of nylon 66
3.	CS/NYL (7:3)	70 wt% of chitosan and 30 wt% of nylon 66
4.	CS/NYL (6:4)	60 wt% of chitosan and 40 wt% of nylon 66
5.	CS/NYL (1:1)	50 wt% of chitosan and 50 wt% of nylon 66

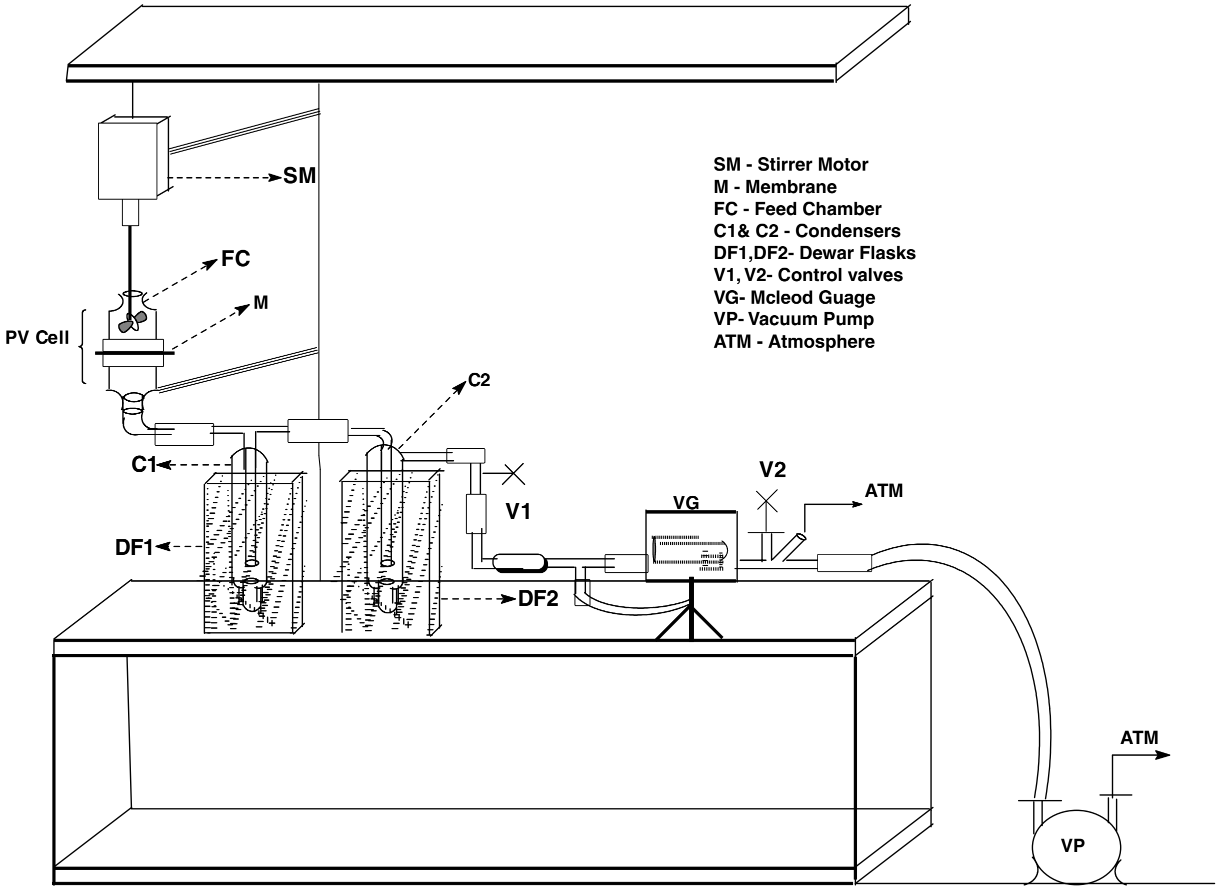


Fig. 1. Schematic of pervaporation experimental set-up.

component A of a binary liquid mixture comprising of A (water) and B (1,4-dioxane) is given by

$$J_A = \frac{W_A}{A \cdot t} \tag{1}$$

where W_A represents the mass of water in permeate (kg), A is the membrane area (m^2) and t represents the evaluation time (h). In the present study, normalized flux (for 10 μm thickness) is reported in case of varying feed composition whereas actual flux was reported for the experiments with varying barrier thickness.

The Separation factor (Wijmans & Baker, 1993) which may be quantified by the dimensionless ratio, α, is defined as follows

$$\alpha = \frac{C_{A'}/C_{B'}}{C_A/C_B} \tag{2}$$

where $C'_{A'}$, $C_{B'}$ represents the permeate concentrations and C_A, C_B are the feed concentrations of both components in the feed mixture.

2.4. Membrane characterization

2.4.1. FTIR studies

The FTIR spectra of unmodified and crosslinked CS/NYL blend membranes were scanned using Nicolet-740, Perkin-Elmer-283B FTIR Spectrometer.

2.4.2. XRD studies

A Siemens D 5000 powder X-ray diffractometer was used to study the solid state morphology of membranes in powdered form. X-rays of 1.54 Å wavelengths were generated by a CuK source. The angle of diffraction was varied from 0° to 65° to identify the change in the crystal structure and intermolecular distances between the intersegmental chains after crosslinking.

2.4.3. Thermal analysis: TGA studies

Thermal stability of the polymer films was examined, using Seiko 220TG/DTA analyzer, from 25 to 700 °C with heating at the rate 10 °C/min and flushing with N_2 gas flowing at 200 ml/min.

2.4.4. Mechanical properties

The equipment used for carrying out the test was Instron Universal Testing Machine (UTM) operating with a head load of 5 kN. 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^{-1}. Tensile strength was calculated in N/mm^2 using the equation:

$$\text{Tensile strength} = \frac{\text{load at break}}{\text{Cross-sectional area}} \tag{3}$$

2.4.5. Determination of ion exchange capacity

In order to determine the effect of sulfuric acid on the blend, ion exchange capacity (IEC) was estimated. IEC indicates the number of groups present before and after crosslinking, which gives an idea about the extent of crosslinking. Thus, IEC gives the number of milli-equivalents of ions in 1 g of dry polymer. To determineIEC, the specimens of identical weights were soaked in 50 mL of 0.01 N NaOH solution for about 12 h at ambient temperature. Then, 10 mL of sample was titrated against 0.01 N H_2SO_4. The sample was regenerated with 1 M HCl, washed with water and dried to constant weight. IEC was then calculated as:

$$\text{IEC} = \frac{(B-P)\times 0.01\times 5}{m} \tag{4}$$

where B is sulfuric acid used to neutralize the blank sample, P is sulfuric acid used to neutralize the PV membrane, 0.01 is the normality of sulfuric acid, the number 5 represents the factor corresponding to ratio of the amount of NaOH taken to dissolve the polymer to the amount used for titration and m represents the sample mass (g).

2.4.6. Sorption studies

Weighed samples of circular pieces of crosslinked CS/NYL films (3 cm diameter) were soaked in pure water and dioxane as well as their binary mixtures. The films were taken out after different soaking periods and quickly weighed (after carefully wiping out excess liquid) to determine the amount absorbed at the particular time t. The film was then immediately placed back in the liquid. The process was repeated until the films attained steady state as indicated by constant weight after a certain period of soaking time. The degree of swelling was calculated from the equation:

$$\%Sorption = \frac{(W_s - W_d)}{W_d}\times 100 \tag{5}$$

where

W_s = weight of the swollen polymer in grams
W_d = weight of the dry polymer in grams

3. Results and discussion

Chitosan membrane was chosen for dehydrating dioxane/water mixtures based on the close proximity of its Hansen's solubility parameter value (43.04 $\text{J}^{1/2}/\text{cm}^{3/2}$) (Qurashi et al., 1992) to that of water (47.9 $\text{J}^{1/2}/\text{cm}^{3/2}$) (Ravindra et al., 1998) as well as high chemical resistance to organic solvents. However, in the wet state, chitosan tends to lose its mechanical stability. This was balanced by blending it with a partially hydrophilic but tough polymer such as nylon, which would prevent of the loss of strength in the swollen state without altering the polarity to a greater extent. It was observed that all the homopolymer solutions and the blend solutions of CS/NYL were optically clear to the naked eye. There was not any separation into two layers or precipitation when the blends were allowed to stand for one month at room temperature.

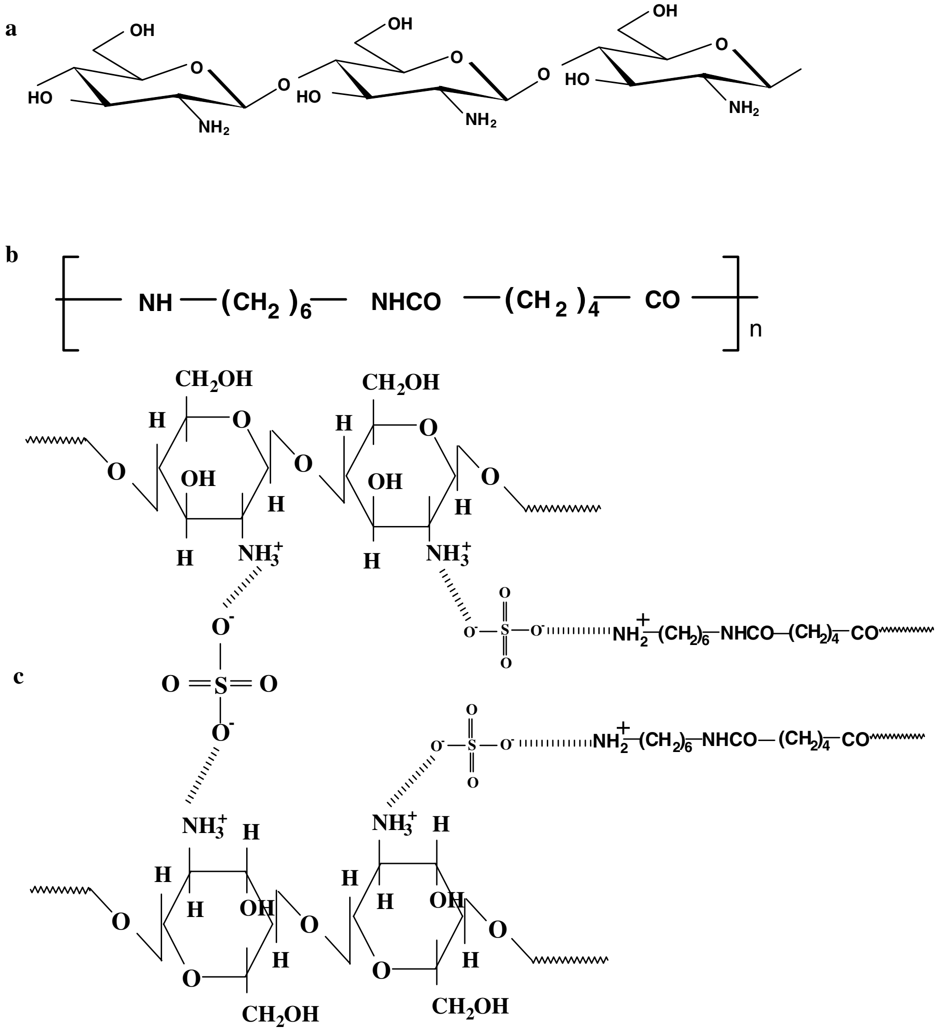
3.1. Membrane characterization

3.1.1. Interaction of the crosslinking agent

The blend was crosslinked with sulfuric acid to further reduce the extent of swelling. Interaction between sulfuric acid and chitosan/nylon blend is likely through the amine groups of chitosan and nylon. To analyze the extent of crosslinking, IEC (which is equivalent to the total number of free amino groups (considering the fact that amino groups are more interactive when compared to hydroxyl groups), R–NH_2 present in the membrane) studies were conducted. A model scheme depicting the possible interaction is shown in Scheme 1. The microstructural representation of the interaction of the crosslinked polymer blend with water is given in Scheme 2. On blending, the entanglements of chains of chitosan and nylon can be visualized as shown in Scheme 2a. The interaction of sulfuric acid moieties with chitosan can be represented as shown in Scheme 2b. These SO_3^- groups attract the oppositely charged hydronium ions (Scheme 2c), which aid in the transport of water through the cross-section of the membrane thereby resulting in an enhanced selectivity. These interactions can be confirmed by FTIR.

3.1.2. IEC studies

The amount of residual amine and hydroxyl groups of chitosan present after crosslinking was estimated from the Ion Exchange Capacity (IEC) studies. It was noted that unmodified CS/NYL showed an IEC of 0.94 meq/g whereas the crosslinked CS/NYL (9:1) blend exhibited a decreased IEC of 0.63 meq/g. The amino groups are generally more interactive than hydroxyl groups, and it was



Scheme 1. Chemical structures of (a) chitosan, (b) nylon 66 and (c) crosslinked chitosan.

assumed that –OH groups would react only after the entire $-NH_2$ groups get crosslinked (Keiji Igarashi & Yoshio Nakano, 2002). This shows that 67% of the amine groups present in the unmodified blend have now formed crosslinks with sulfuric acid leaving 33% of $-NH_2$ groups and all the hydroxyl groups available interaction with water thereby enabling its transport.

3.1.3. FTIR studies

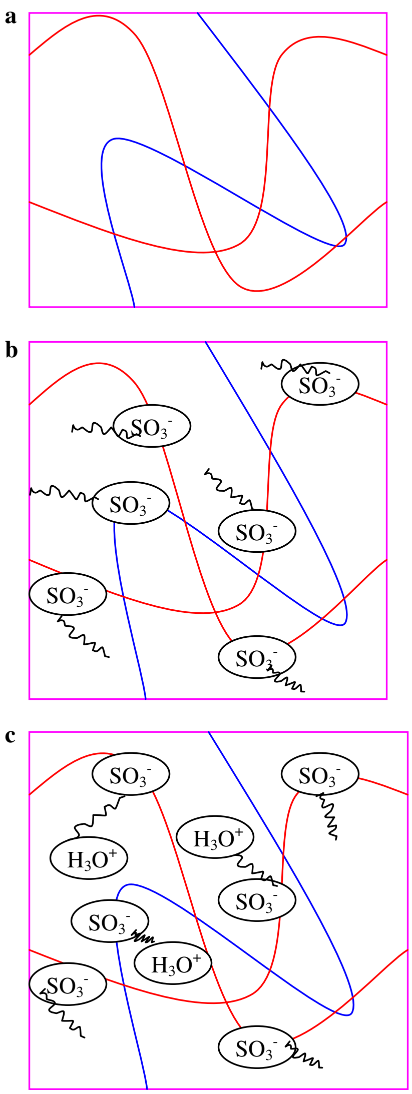
The occurrence of crosslinking is confirmed by FTIR (Fig. 2). The characteristic peaks of chitosan (Fig. 2a) are located at 1650 and 1550 cm^{-1} representing amides I and II, respectively. The characteristic amide group of nylon (not shown) also exhibits a peak at 1550 cm^{-1}. On crosslinking (Fig. 2b), amides I and II bands shift to the lower wave numbers caused by the crosslinking of chitosan chains. Shifting of the amide II peak to 1530 cm^{-1} in the spectra of the crosslinked blend membrane is evident. This may be assigned to the symmetric $-NH^{3+}$ deformation resulting on due to the crosslinking reaction occurring between the amino groups of chitosan and nylon with the sulfate ions of sulfuric acid.

3.1.4. XRD studies

From the spectra of unmodified and crosslinked blend (Fig. 3) it can be seen that there are two distinct bands having their maxima at $2\theta = 7°$ to 9° and 2θ at 20°. These two peaks are related to two types of crystals: crystal 1 and crystal 2. Crystal 1, which corresponds to the peak at 20°, comprises functional groups such as $-NH_2$ and –OH and has undergone significant change after crosslinking (Ravindra et al., 1998). A reduction in effective d-spacing value from 4.6 Å for uncrosslinked to 4.3 Å in crosslinked polymer gives an indication of shrinkage in cell size or intersegmental spacing, which would improve the selective permeation property of the membrane.

3.1.5. TGA studies

The TGA curve of chitosan (Fig. 4a) and nylon (Fig. 4b) reveals a single weight loss stage ranging from 250 to 340 °C and 250 to 300 °C depicting the main chain degradation of the polymer followed by final decomposition at 350 and 310 °C, respectively. The TGA curve of crosslinked CS-NYL (Fig. 4c) blend shows three weight loss stages at 210–240 °C, 260–310 °C and 450–480 °C followed



Scheme 2. Schematic representation of microstructures of (a) CS-NYL blend, (b) CS-NYL blend crosslinked with sulfuric acid and (c) interaction of crosslinked polymer matrix with water (red lines – chitosan chains; blue line – nylon chain). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)

by a final decomposition at 480 °C. The first weight loss may be attributed to degradation of the main chain of CS, the second one may be due to the decomposition of nylon and the last stage because of the cleavage of the main polymer chain.

Thus, from the TGA studies it is clear that the crosslinked membranes synthesized in the study are thermally very stable and can be used for pervaporation.

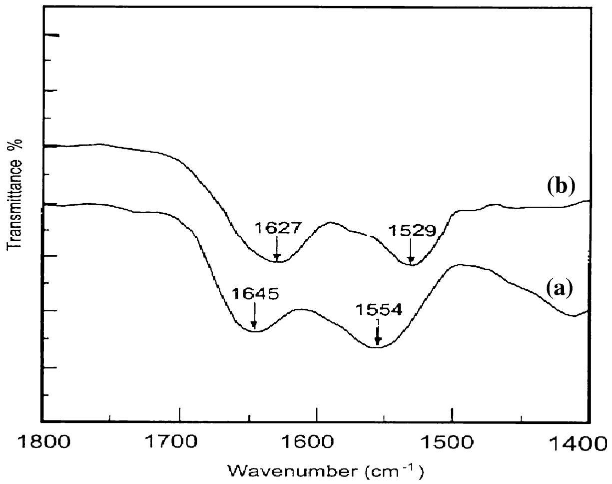


Fig. 2. FTIR spectra of (a) CS and (b) crosslinked CS/NYL blend membrane.

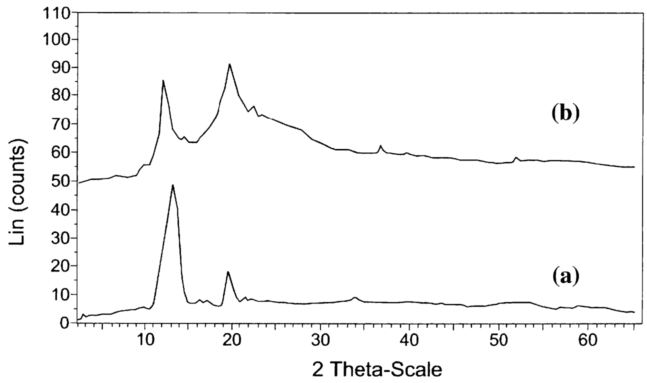


Fig. 3. XRD spectra of (a) unmodified CS/NYL membrane and (b) crosslinked CS/NYL membrane.

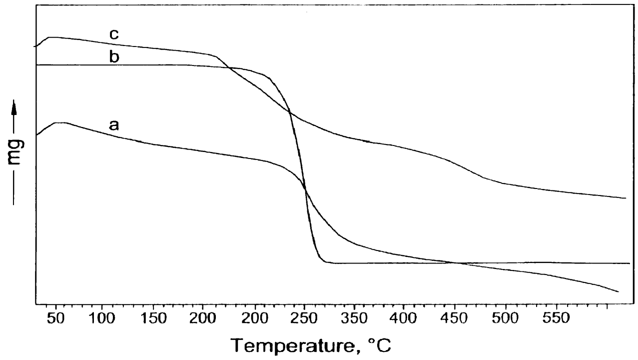


Fig. 4. TGA curves for (a) CS, (b) NYL and (c) crosslinked blend membranes.

3.1.6. Mechanical properties

The tensile strength at break and % elongation of the unmodified and crosslinked blends are given in Table 3. From the results, it can be observed that there is a decrease in the tensile strength and elongation of all the blends after crosslinking. This reduction may be attributed to the modification occurring due to the crosslinking of the blend, which causes the polymer matrix to contract. This contraction renders a reduction in the free volume, thereby decreasing chain movement, that which make the plastic material glassy (Brandrup, 1985). This reduced chain movement implies that the material changes partially from rubbery state (flexible and soft) to glassy state (hard and brittle), thereby causing a reduction in the tensile strength at break and a corresponding reduction in the elongation (Smitha, Sridhar, & Khan, 2003).

Amongst all the blends synthesized, the 9:1 (CS/NYL) blend showed a tensile strength of 8.92 N/mm^2, whereas its crosslinked form yielded a tensile strength of 6.87 N/mm^2. The unmodified and crosslinked 1:1 (CS/NYL) blends exhibited the highest tensile strengths of 11.0 and 9.5 N/mm^2, respectively.

3.1.7. Sorption studies

From the sorption data for binary feed mixtures presented in Table 2 it can be observed that the crosslinked CS/NYL (9:1) membrane showed a high degree of sorption in pure water (98.72%), with a relatively negligible sorption (0.012%) for pure 1,4-dioxane. The % water uptake correspondingly decreased from 98.72 for CS/NYL (9:1) to 56.28 for CS/NYL (1:1) signifying the possibility of attaining enhanced separation characteristics without compromising on dimensional stability. One can also notice that an increase in the nylon content from 0% to 50% in the blend matrix caused a threefold drop in the water uptake.

3.2. Pervaporation studies

3.2.1. Effect of nylon content in the blend membranes

Fig. 5 shows the separation factor ‘α’ and the total permeation flux as a function of the nylon content in the membrane. As the nylon content increases from 10 to 50 wt.%, the flux declined from 0.09045 to 0.00598 kg/m^2 h, and a corresponding reduction in the selectivity from 865 to 31.8 can be evidenced. The rigid backbone in association with the absence of polar groups renders nylon a tough, partially hydrophilic polymer that causes a reduction in flux and selectivity with a rise in nylon concentration in the blend.

3.2.2. Effect of feed water composition

The relationship between liquid feed composition and PV data was investigated at 30 °C over a feed composition ranging from 4.3 to 50 wt% of water for 9:1 Cs/NYL blend. For this study, the membrane thickness and permeate pressure were kept constant at 50 μm and 0.5 mmHg, respectively. Flux and selectivity data as a function of feed composition are displayed in Table 4, Fig. 6. The permeation rate of 1,4-dioxane was much lower as compared to water, showing that the membrane is permselective to latter. As expected, a rise in feed composition of water produced an increase in water flux from 0.05 to 1.75 kg/m^2 h. Mass transport through hydrophilic blend membranes occurs by the solution-diffusion mechanism (Wijmans & Baker, 1995; US Department of Energy, 1990).

From the sorption data for the binary feed mixtures presented in Table 2, it can be observed that the crosslinked membrane showed a high degree of sorption with increasing feed water concentrations resulting in an enhanced flux. The increased swelling has a negative impact on separation factor since the swollen and plasticized upstream membrane layer allows some dioxane molecules to escape into the permeate side along with water molecules. Therefore, permeate water composition was reduced from 99.53 to 97.43 wt.% indicating a drop in selectivity from 4789 to as low as 37.9, respectively. It is worth mentioning that the blend membrane used is promising for dehydrating feed mixtures containing 0–30 wt.% water. The azeotropic composition viz., 82 wt.% of 1,4-dioxane was broken by PV membrane which acting as a third phase (Fig. 7).

3.2.3. Effect of permeate pressure

Permeate pressure was varied from 0.5 to 9 mmHg in the case of crosslinked CS/NYL blend membrane at the constant thickness of 50 μm and at azeotropic feed composition. At lower pressures (high vacuum), the influence of driving force on the diffusing molecules inside the membrane is high. This could result in the components being swept away immediately from the permeate side, resulting in high mass transfer rates. From Fig. 8, we observe that the membrane exhibited a considerable lowering of flux from 0.09045 to 0.0123 kg/m^2 h as well as a reduction in selectivity from 865 to 37 with increasing permeate pressure from 0.5 to 10 mmHg. This variation in flux and selectivity can be explained on the basis of Fick’s Law. An increase in the permeate pressure results in an increase of the activities of both permeants dissolved in the downstream layer of the working membrane. Activity gradients across the thickness of the membrane consequently decline and permeation fluxes drop (Sheldon & Thompson, 1984). The change in permeate pressure also affects the selectivity. The selectivity can increase or decrease with increasing permeate pressure, depending on the relative volatility of the permeating components. Beyond a certain pressure threshold, the desorption can slow down due to the swollen membrane layer on the downstream side leading to both the penetrants easily, and caused a steep decline in selectivity.

In such cases, vapor pressures of the two components of the mixture govern the separation factor of the membrane. Dioxane, which has a higher vapor pressure (37 mmHg at

Table 2
Sorption characteristics of crosslinked membranes of different blending ratios in pure water, 1,4-dioxane and azeotropic mixture

Sl. no	Polymer blend	Sorption (%) in pure water	Sorption (%) in 1,4-dioxane	Sorption (%) in azeotropic mixture
1.	Chitosan	216	0.21	10.1
2.	CS/NYL (9:1)	98.72	0.012	37.78
3.	CS/NYL (8:2)	89.12	0.023	31.22
4.	CS/NYL (7:3)	76.33	0.017	27.68
5.	CS/NYL (6:4)	65.21	0.021	21.35
6.	CS/NYL (1:1)	56.89	0.011	18.89

Table 3
Tensile strength and elongation of modified CS/NYL blend membranes

Sample code	Tensile strength (N/mm^2)	Elongation (mm)
9:1 Uncrosslinked	8.92	20.44
9:1 Crosslinked	6.87	7.37
7:3 Uncrosslinked	9.79	16.9
7:3 Crosslinked	8.23	13.2
1:1 Uncrosslinked	10.99	10.2
1:1 Crosslinked	9.5	5.0

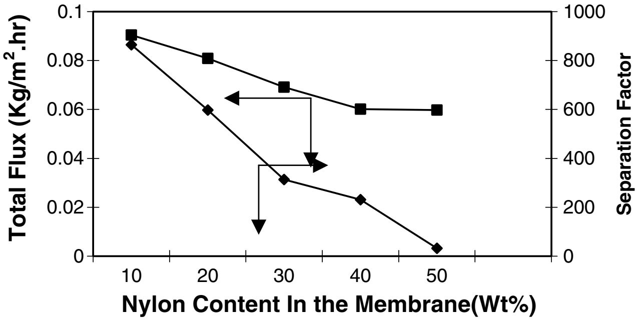


Fig. 5. Effect of nylon 66 content in the membrane on pervaporation performance after crosslinking (azeotropic concentration, thickness 50 μm, pressure 0.5 mmHg, temperature 40 °C).

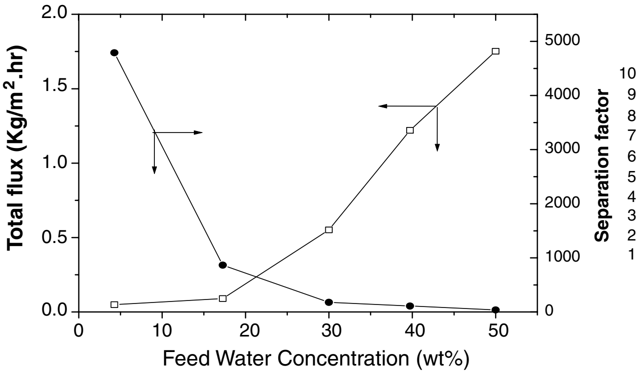


Fig. 6. Effect of feed water concentration on pervaporation performance of 9:1 CS/NYL membrane (thickness 50 μm, pressure 0.5 mmHg, temperature 40 °C).

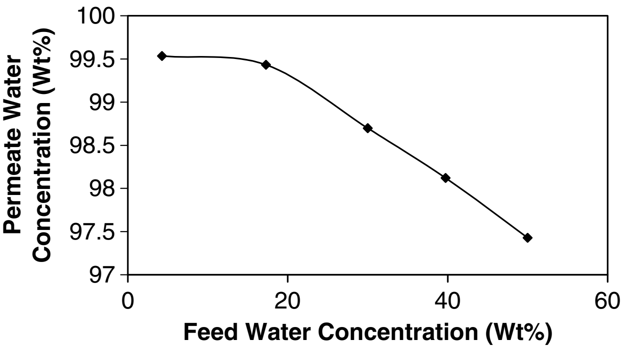


Fig. 7. Feed water concentration V_s permeate water concentration of 9:1 membrane (thickness 50 μm, pressure 0.5 mmHg, temperature 40 °C).

25 °C), permeates competitively with water, thus lowering the concentration of water in permeate.

3.2.4. *Effect of membrane thickness*

Effect of varying membrane thickness on PV performance was investigated at a constant feed composition (azeotropic) and permeate pressure (0.5 mmHg) by fabricating membranes of thickness ranging from 35 to 120 μm. By increasing the membrane thickness, a gradual reduction in flux from 0.1184 to 0.0279 kg/m^2 h was observed (Fig. 9). In pervaporation, diffusion being the rate-determining step decreases with increasing membrane thickness due to increase in resistance to mass transfer. Even though the availability of polar groups of the membrane was enhanced with increasing membrane thickness, the flux decreased because diffusion would be increasingly retarded as the feed molecules move through a longer tortuous distance to reach the permeate side. So flux reduced consequently. The selectivity increased from 767 to 1123 over the same thickness range. The downstream membrane layer is virtually dry due to the continuous evacuation, which makes it the restrictive barrier layer, which allows only the interacting and smaller sized water molecules to pass through. It is expected that thickness of the dry layer would increase with increasing the overall membrane thickness, which resulted in an improved selectivity.

4. Conclusions

Crosslinked blend membranes were prepared from chitosan and nylon 66 by mixing the respective polymer solutions in different weight ratios. FTIR characterization confirmed the crosslinking between sulfate ions of sulfuric acid and amine groups of chitosan. The blends were found to possess adequate thermal stability after the occurrence of crosslinking. Moderate water sorption (50–90%) of the

Table 4
Pervaporation data of 1,4-dioxane and water mixtures at 30 °C (permeate pressure 0.5 mmHg, membrane thickness 50 μm)

Feed composition		Sorption in feed (%)	Permeate composition		Separation factor for the process	Flux (kg/m^2 h)
Water (x)	1,4-Dioxane ($1 - x$)		Water (y)	1,4-Dioxane ($1 - y$)		
4.28	95.72	24.73	99.53	0.46	4789	0.049
17.27	82.73	31.72	99.43	0.57	865	0.09
30.00	70.00	52.44	98.69	1.30	176.9	0.55
39.74	79.26	82.74	98.12	1.88	104.22	1.22
50.00	50.00	93.97	97.43	2.57	37.9	1.75

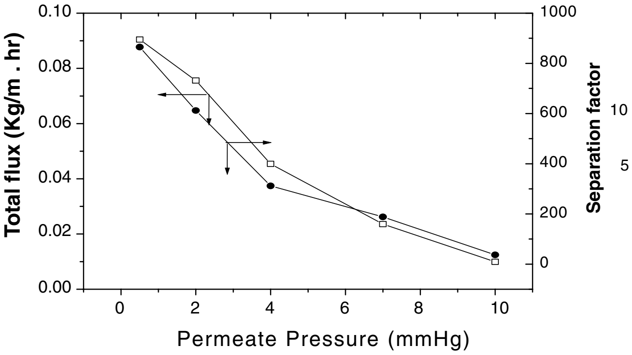


Fig. 8. Effect of downstream pressure on flux and selectivity of 9:1 CS/NYL membrane (thickness 50 μm, azeotropic composition, temperature 40 °C).

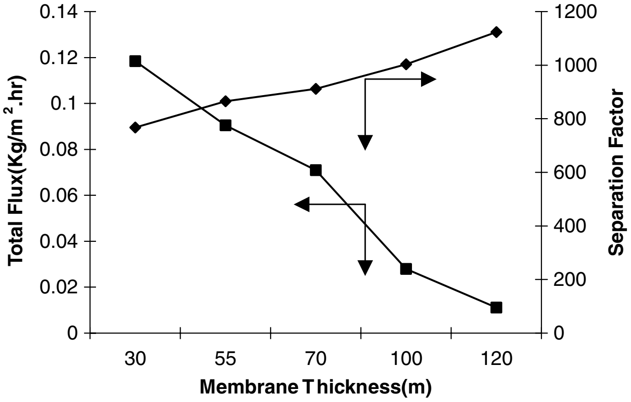


Fig. 9. Effect of membrane thickness on flux and selectivity of 9:1 CS/NYL membrane (pressure 0.5 mmHg, azeotropic composition, temperature 40 °C).

blends with no significant effect on mechanical stability was attained on blending the two polymers. Though chitosan finds extensive application for alcohol dehydration, its blend with nylon 66 appears to be better candidates for dehydration of dioxane due to the enhanced stability in aqueous solutions.

Among the blends synthesized in this study, crosslinked CS/NYL (9:1) appears more suitable for dioxane dehydration considering its optimum physico-mechanical properties and pervaporation characteristics. The blend exhibited a selectivity of 865 and moderately good flux of 9.045×10^{-2} (kg/m^2 h) for azeotropic composition of 18 wt% water at 0.5 mmHg. Increasing water concentration in feed brought about enhanced membrane swelling and thereby improved flux at reduced selectivity due to plasticization effect. Varying thickness caused a considerable lowering of the flux with marginal improvement in selectivity. Higher permeate pressures resulted in a reduction in both the flux and selectivity.

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