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Pervaporation of tertiary butanol/water mixtures through chitosan membranes cross-linked with toluylene diisocyanate†

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Abstract: Membranes made from 84% deacetylated chitosan biopolymer were cross-linked by a novel method using 2,4-toluylene diisocyanate (TDI) and tested for the separation of *t*-butanol/water mixtures by pervaporation. The unmodified and cross-linked membranes were characterized by Fourier transform infra red (FTIR) spectroscopy, X-ray diffraction (XRD) studies and sorption studies in order to understand the polymer–liquid interactions and separation mechanisms. Thermal stability was analyzed by differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) while tensile strength measurement was carried out to assess mechanical strength. The membrane appears to have good potential for breaking the aqueous azeotrope of 88.2 wt% *t*-butanol by giving a high selectivity of 620 and substantial water flux (0.38 kg m^{-2} hr^{-1}). The effects of operating parameters such as feed composition, membrane thickness and permeate pressure on membrane performance were evaluated.

Keywords: pervaporation; chitosan membrane; 2,4-toluylene diisocyanate(TDI) cross-linker; flux; selectivity

NOTATION

A	Effective membrane surface area (m^2)
M_d	Mass of the dry polymer (g)
M_s	Mass of the swollen polymer (g)
t	Time (h)
W	Permeate weight (g)
x	Feed weight content of water (%)
y	Permeate weight content of water (%)
α	Pervaporation selectivity (dimensionless)

INTRODUCTION

Short-chain alcohols, such as tertiary butanol (*t*-butanol), are commonly-used solvents in many chemical and pharmaceutical synthesis.[1] *t*-Butanol is an important raw material in the production of synthetic perfumes, artificial musk and denatured alcohols. Like many other alcohols, *t*-butanol is also known to form an azeotropic mixture with water, a characteristic that creates difficulties in its recovery by conventional distillation.[1]

The application of pervaporation (PV) as a means of achieving the dehydration of solvents has been receiving a substantial amount of attention from the chemical, petrochemical and pharmaceutical industries. In addition, recent improvements in technology have led to the commercial development of several membrane materials for this process.[2] PV is an economical, safe and clean technique compared with conventional methods for separating azeotropic and close-boiling liquid mixtures.[3]

A number of studies reporting the successful dehydration of short-chain alcohols, including *t*-butanol/water mixtures, using both polymeric and zeolite membranes, have been published.[4] Gao *et al* prepared and used composite hydrophilic membranes, consisting of potassium A (KA), sodium A (NaA), calcium A (CaA) and sodium X (NaX) zeolites incorporated in poly(vinyl alcohol) (PVA) to examine the separation characteristics of different alcohols and water systems.[5,6] For *t*-butanol, the highest fluxes were achieved at 50 °C with a combination of PVA and NaX zeolite (0.17 kg m^{-2} h^{-1}), whilst the highest separation factors (1100–1200) were yielded by PVA containing KA, NaA and CaA zeolites. Similarly, Vankelecom *et al* found that the incorporation of zeolite Y in poly(dimethylsiloxane) membranes increased water fluxes, whilst ZSM-5 reduced both water and alcohol fluxes due to the partial retention of these

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molecules in the zeolite.[7] Takegami *et al* reported the development of composite PVA/poly(styrene sulfonic acid) ultrathin cross-linked films.[8] They were utilized for the dehydration of a 95 wt% *t*-butanol/water system by pervaporation at 60 °C, yielding fluxes of 0.21 kg m^{-2} h^{-1} and a water separation factor of 17 900. In addition, several other polymeric membranes have been investigated for their application in the dehydration of *t*-butanol mixtures: 4-vinyl pyridine,[9] polycarbonate,[10] fluorine-containing aromatic polyamides[11,12] and poly(allylamine).[13] However, studies on the usage of a biopolymer such as chitosan for dehydration of this mixture have not been reported. The present investigation attempts to test for the first time the applicability of chitosan membranes cross-linked with a new reagent, 2,4-toluylene diisocyanate (TDI), for dehydration of *t*-butanol.

EXPERIMENTAL

Materials

t-Butanol, glacial acetic acid and TDI of purities >99.9% were purchased from Loba Chemie, Mumbai, India. Chitosan flakes, purchased locally, had a degree of deacetylation of 84% (determined by the hydrogen bromide titrimetric analysis proposed by Muzzarelli *et al*).[14] Its molecular weight, determined by viscometry and gel permeation chromatography (GPC) with a TSK-gel column, was found to be 400 000. Deionized water with a conductivity of 0.02 mS cm^{-1}, which was used to make the mixtures, was generated in the laboratory itself.

Membrane preparation

Membranes were prepared by a solution casting and solvent evaporation technique. A 3% (w/v) solution of chitosan in 2% (v/v) aqueous acetic acid was prepared, stirred and filtered to remove undissolved matter. A bubble-free solution was cast onto a clean glass plate to the desired thickness and initially dried in the atmosphere at room temperature followed by vacuum-drying for a period of 5 h at elevated temperature (50 °C) in a closed oven to remove remaining traces of solvent. The membranes thus obtained were further modified by cross-linking them using TDI as cross-linking agent in a hexane bath containing two or three drops of dibutyl tin dilaurate as a catalyst. A solution of 2% (w/v) TDI in hexane and a cross-linking time of 6 h was found to be optimum whereas higher concentrations of TDI produced brittle membranes. The cross-linked membranes were washed in a methanol bath to remove traces of residual TDI and finally vacuum-dried for a period of 12 h.

Membrane characterization

Fourier transform infra red (FTIR) studies

Chitosan and its cross-linked version were scanned using a Nicolet-740, Perkin-Elmer-283B FTIR Spectrometer (Perkin Elmer, Massachusetts, USA).

Ion exchange capacity (IEC)

To determine the total number of interacting groups present in the membranes, unmodified and cross-linked chitosan of similar weight were soaked in 50 mL of 0.01 M sodium hydroxide solution for 12 h at ambient temperature. Then, 10 mL of solution was titrated against 0.005 M sulfuric acid. The sample was regenerated with 1 M hydrochloric acid, washed free of acid with water and dried to a constant weight. The IEC was calculated according to the equation:

$$\mathrm{IEC} = \frac{B - P \times M_{\mathrm{NaOH}} \times 5}{m}$$

where:

IEC : Ion exchange capacity
B: amount of 0.005M sulfuric acid used to neutralize unmodified chitosan
P: amount of 0.005M sulfuric acid used to neutralize the cross-linked membranes
5 : factor corresponding to the ratio of the amount of NaOH taken to dissolve the polymer to the amount used for titration
m: sample mass in g

X-ray diffraction (XRD) analysis

A Siemens D 5000 powder X-ray diffractometer (Siemens, Wultzberg, Germany) was used to study the solid state morphology of cross-linked chitosan in powdered form. X-rays of 1.5406 wavelength 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 cross-linking.

Thermal analysis by differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA)

The DSC spectra of unmodified and cross-linked chitosan membranes were obtained on Perkin-Elmer DSC Model 7 instrument. Measurements were performed over the temperature range of 30• to 200 °C at a heating rate of 5 °C min^{-1} in hermetically-sealed aluminum pans. Membrane samples were allowed to attain steady state with the solvents and the sample pan conditioned in the instrument before running the experiment.

Thermal stability of the polymer films was examined, using a TGA/SDTA 851^{e} analyzer (Metler Toledo, Grelfensee, Switzerland) from 25 to 700 °C heated at 10 °C min^{-1} and flushed with nitrogen at 200 mL min^{-1}. The samples were subjected to TGA both before and after sulfonation to determine the thermal stability and decomposition characteristics.

Mechanical properties

The equipment used for carrying out the test was a universal testing machine (UTM) with an operating head load of 5kN. The 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 5cm 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:

$$\text{Tensile strength} = \frac{\text{Load at break}}{\text{Cross-sectional area}}$$

Sorption studies

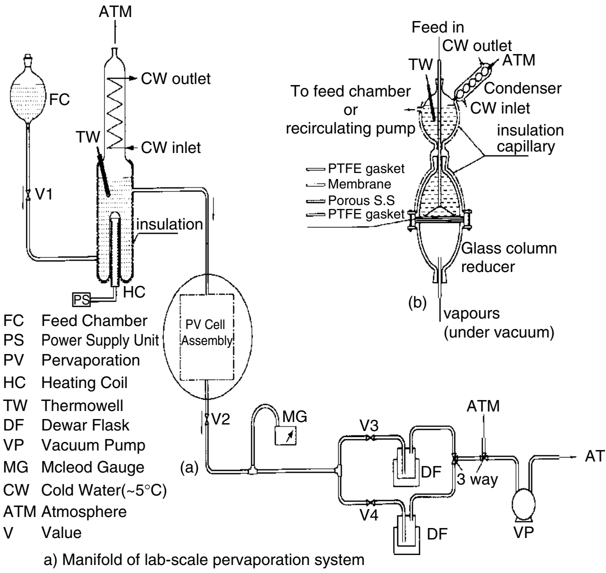
Weighed samples of circular pieces of cross-linked chitosan films (3 cm diameter) were soaked in pure water and *t*-butanol as well as in their binary mixtures. The films were taken out after different soaking periods and quickly weighed, after carefully wiping off excess liquid, to determine the amount absorbed at the particular time *t*. The film was then quickly placed back in the solvent. The process was repeated until the films attained steady state as indicated by constant weight after a certain period of soaking time. The amount of sorption was calculated from the equation:

$$\%\text{Sorption} = \frac{(M_s - M_d)}{M_d} \times 100$$

M_s- mass of the swollen polymer
M_d- mass of the dry polymer

Pervaporation procedure

Experiments were carried out on a 100 mL batch level with an indigenously constructed pervaporation manifold (Fig 1) operated at a vacuum as low as 0.05 mmHg in the permeate line. The membrane area in the pervaporation cell assembly (Fig 1(b)) was approximately 20 cm^2. The experimental procedure is described in detail elsewhere.[15] Permeate was collected for a duration of 8–10 h. Tests were carried out at room temperature (30 ± 2 °C) and repeated twice using fresh feed solution to check for reproducibility. The collected permeate was weighed after allowing it to attain room temperature in an electronic balance (accuracy: 10^{-4} g) (Satorius, Meilingenstadt, Germany) to determine the flux and then analyzed by gas chromatography to evaluate the membrane selectivity.



a) Manifold of lab-scale pervaporation system
b) Blow-up of the pervaporation cell assembly

Figure 1. Schematic of laboratory pervaporation set up.

Flux and selectivity equations

In pervaporation the flux *J* of a given species, say faster permeating component *i* of a binary liquid mixture comprising of *i* (water) and *j* (*t*-butanol) is given by:

$$J_i = \frac{W_i}{At}$$

where W_i 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, though different membrane thickness were utilized, the flux has been normalized and reported for thickness of 10 μm.

The membrane selectivity (α) is the ratio of permeability coefficients of water and *t*-butanol and can be calculated from their respective concentrations in feed and permeate as given below:

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

where x and y are the concentrations of ethanol and water in permeate respectively.

Analytical procedure

The feed and permeate samples were analyzed using a Nucon Gas Chromatograph (GC Model 5765) installed with a thermal conductivity detector (TCD) (Nucon, Huntley Road Columbus, Ohio, USA), and packed column of 10% diethylene glycol sebacate (DEGS) on 80/100 Supelcoport of 1/8 inch 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 ethanol–water mixtures and the calibration factors were fed into the software to obtain correct analysis for unknown samples. Figure 6 shows (see next section) sample chromatograms for feed and permeate.

RESULTS AND DISCUSSION

A chitosan membrane was chosen for dehydrating a *t*-butanol/water mixture on the basis of the close proximity of its Hansen's solubility parameter value[16] (43.04 $\text{J}^{1/2}\,\text{cm}^{-3/2}$) to that of water[17] (47.9 $\text{J}^{1/2}\,\text{cm}^{-3/2}$) as well as its good mechanical strength and chemical resistance. It was then cross-linked with TDI to reduce the extent of swelling. During the cross-linking reaction, the amino group of chitosan interacts with the carbonyl group of TDI resulting in the formation of urea linkages. However, the possibility of formation of homolinks between the isocyanate group of TDI and the hydroxyl group of chitosan. cannot be overlooked.[18] An estimation of the number of groups present before and after cross-linking gives an idea of the extent of cross-linking.

The amount of residual amine and hydroxyl groups present after cross-linking was estimated from the IEC studies. It was noted that unmodified chitosan showed an IEC of 0.42 meq g^{-1} whereas the cross-linked polymer exhibited an IEC of 0.2 meq g^{-1}. The IEC, which is equivalent to the total number of free amino groups (considering the fact that amino groups are more interactive when compared with hydroxyl groups), $R{-}NH_2$ present in the membrane decreased upon cross-linking because some amino groups were consumed with the reaction of the cross-linker during the preparation of the cross-linked membrane.[19] This shows that almost 50% of the amine groups present in the unmodified chitosan have now formed cross-links with TDI and there are still a few amine and hydroxyl groups left for the formation of homolinks. Scheme 1 represents the cross-linking reaction occurring between chitosan and TDI and also shows the possible homolinks formed. IEC and FTIR studies proved the occurrence of cross-linking.

Membrane characterization

Fourier transform infra red spectroscopy

Fig 2 shows the FTIR spectra of the plain and cross-linked chitosan. The spectrum of the cross-linked polymer shows peaks in the range from 700 to 850 cm^{-1}, which indicates the presence of the benzene ring. The reduced number of peaks in the range from 1000 to 1200 cm^{-1} as compared with the spectra of uncross-linked chitosan is due to the vibration of the C–O bond formed by urethane linkage. The new peak at 1650 cm^{-1} shows the presence of a urea linkage. The spectrum of uncross-linked chitosan shows a broad peak at wavenumbers 1570–1655 cm^{-1} which indicates the presence of amides I and II.

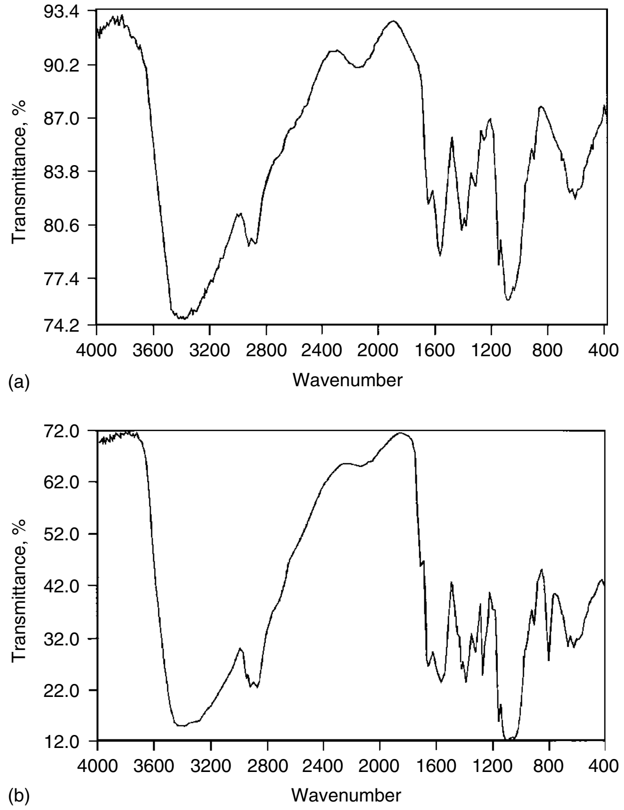
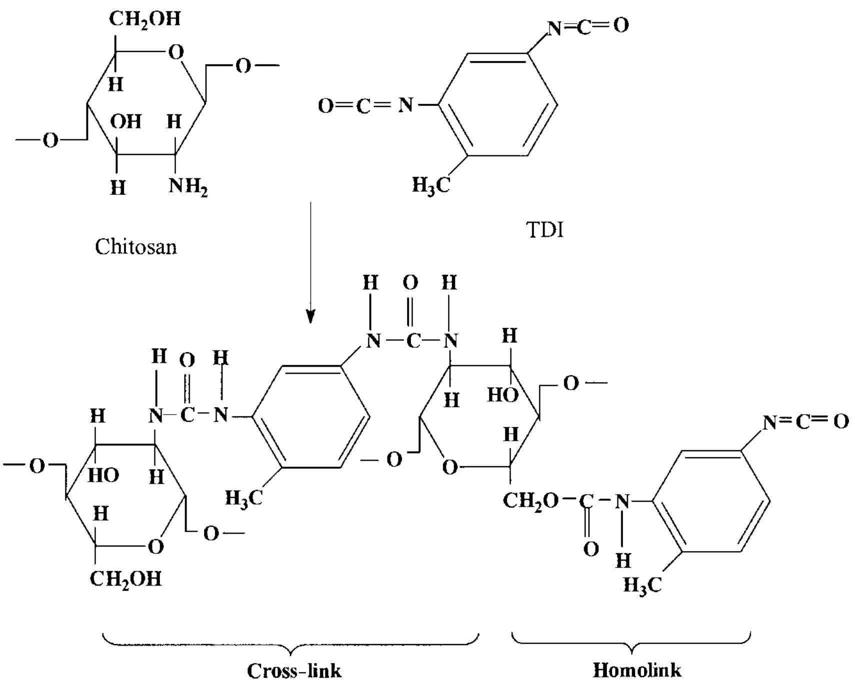


Figure 2. FTIR spectra of (a) unmodified and (b) cross-linked chitosan membranes.



Scheme 1. Structural representation of cross-linking of chitosan with 2,4-toluylene diisocyanate resulting in the formation of cross-links and homolinks.

The wavenumber corresponding to CH_2 stretching is at 2833 cm^{-1} whereas that of free hydroxyl group is at 3450 cm^{-1}. The FTIR analysis of modified chitosan confirms that cross-linking has taken place by the reaction of hydroxyl group of chitosan with the carbonyl group of toluylene-2,4-diisocyanate.

X-ray diffraction studies

From the spectra of unmodified and cross-linked chitosan (Fig 3) it can be noted that the XRD patterns of both plain and cross-linked chitosan membranes appear to be semi-crystalline. The XRD patterns showed broad peaks at around 10° of 2θ, indicating the average intermolecular distance of the amorphous part and relatively sharp semi-crystalline peaks centered at around 20° of 2θ. From these results, it can be said that the average intermolecular distances in unmodified chitosan and cross-linked chitosan are the same. It can also 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.[20] Crystal 1, which corresponds to the peak at 9°, is responsible for separation as it comprises functional groups such as $-NH_2$ and $-OH$ and has undergone significant change after cross-linking.[21] A reduction in effective d-spacing value from 12.07 for uncross-linked to 7.8 in cross-linked polymer gives an indication of shrinkage in cell size or intersegmental spacing, which would improve the selective permeation property of the membrane.[22]

Thermal and mechanical analysis

Thermal properties of the unmodified and cross-linked chitosan polymer were examined by DSC and TGA. It was of particular interest to estimate how the thermal transition of chitosan varied with cross-linking. The DSC spectra of chitosan and its cross-linked form are shown in Fig 4. From the spectra it can be noticed that there are no significant transitions in the temperature range of the DSC scan. Thus it can be said that cross-linking with TDI does not greatly affect the glass transition temperature ('T_g') or melting temperature ('T_M') of chitosan.

The thermal degradation behavior of the polymer was examined by TGA, the spectra are shown in Fig 5 for unmodified and cross-linked chitosan respectively. From the spectra it can be seen that the first weight loss of chitosan takes place with a maximum rate at 270 °C, followed by the second degradation process at 560 °C. In the case of cross-linked chitosan a shift in the first weight loss can be noticed. This shift may be due to the formation of urea linkages upon cross-linking of chitosan polymer. This is also confirmed by the tensile strength of the polymer before and after cross-linking. The tensile strength of cross-linked chitosan (278.4 $N\,mm^{-2}$) is higher than the unmodified one (212.7 $N\,mm^{-2}$). It can thus be said that cross-linked chitosan can be safely used for application in the temperature range of 30 to 200 °C.

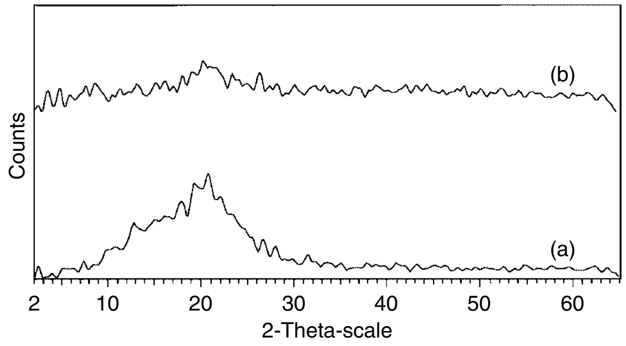


Figure 3. XRD spectra unmodified (a) and cross-linked (b) chitosan membranes.

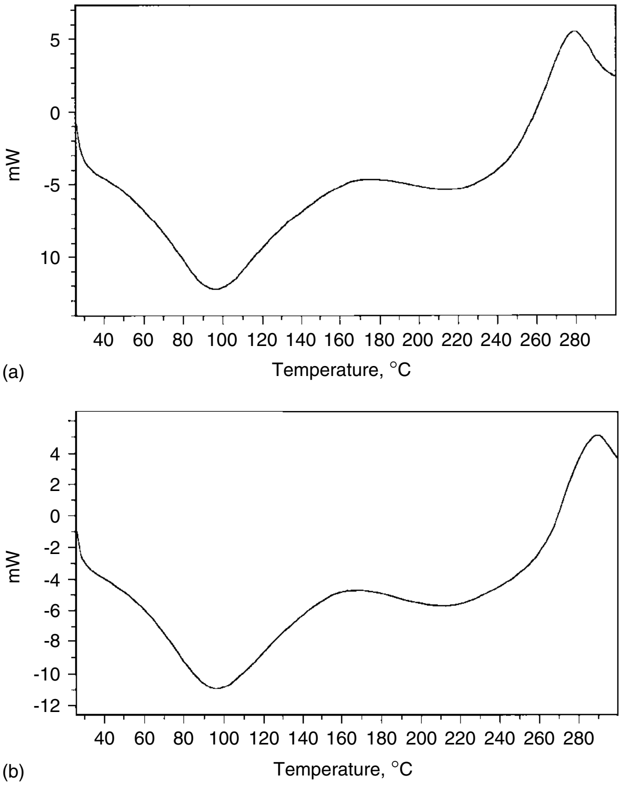


Figure 4. DSC spectra of unmodified (a) and cross-linked (b) chitosan membranes.

Swelling characteristics

The swelling behavior of the cross-linked chitosan membrane in *t*-butanol/water mixtures of different compositions is shown in Table 1. The degree of swelling in feed composition at azeotropic composition containing approximately 11.5% (w/w) water was found to be low, ie 22.6% but the value increased steadily with increasing concentration. This shows that the membrane interacts extensively with water and is capable of being highly selective towards the same during separation. However, absorption of large amounts of water at high feed concentrations could cause enhanced swelling and subsequently a fall in membrane selectivity due to plasticization of the polymer chains.

Table 1. Effect of feed composition on separation performance of the cross-linked chitosan membrane (permeate pressure: 1mm Hg, membrane thickness: 45 μm)

	Feed composition			Permeate composition			
Sample number	Water (x)	t-butanol (1-x)	Sorption in feed (%)	Water (y)	t-Butanol (1-y)	Selectivity $\alpha = \frac{y(1-x)}{x(1-y)}$	Flux (kg m^{-2} h^{-1})
1	4.31	94.69	6.7	99.18	0.82	2657.4	0.21
2	11.46	88.54	22.6	98.77	1.23	620.4	0.38
3	26.46	73.54	83.3	94.70	5.30	49.7	0.89
4	34.57	65.43	114.0	86.50	13.5	12.1	1.13
5.	50.70	49.30	134.0	81.70	18.3	4.3	1.43

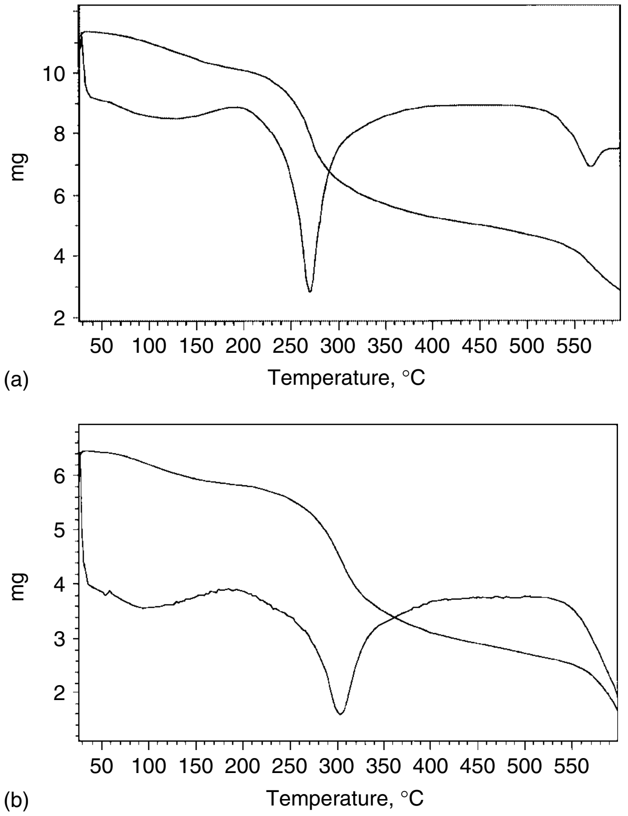


Figure 5. TGA spectra of unmodified (a) and cross-linked (b) chitosan membranes.

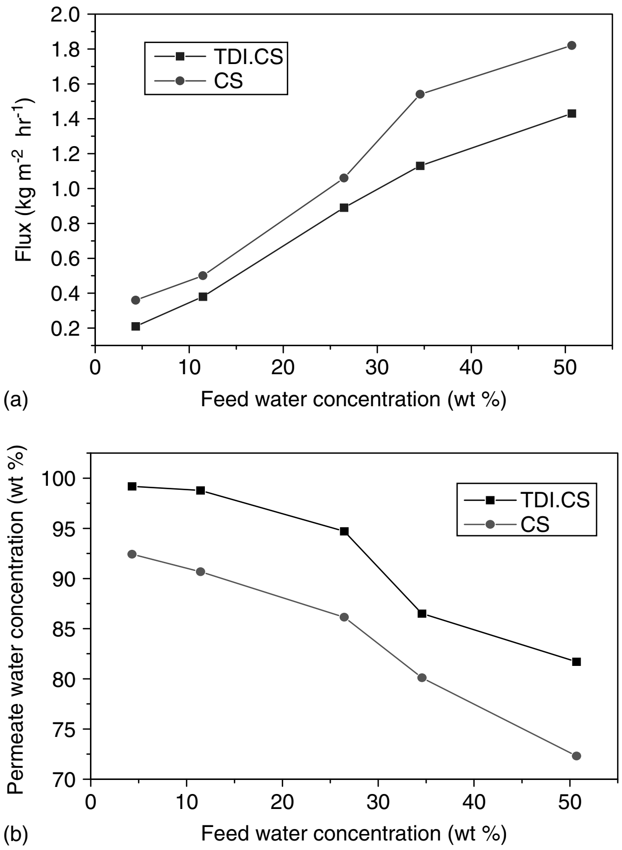


Figure 6. Effect of feed composition on (a) flux and (b) selectivity of unmodified (CS) and cross-linked chitosan (TDI.CS) membranes (membrane thickness: 45 μm, permeate pressure: 1 mmHg).

Pervaporation results

Effect of feed composition

The pervaporation performance of the chitosan membrane cross-linked with TDI was investigated for varying feed compositions comprising 4.5% (w/w) to 50.7% (w/w) water keeping other operating parameters such as permeate pressure and membrane thickness constant at 1 mmHg and 45 μm respectively. As expected, a rise in the feed concentration of water produced an increase in the water flux from 0.21 to 1.43 kg m^{-2} h^{-1} (Fig 6). Mass transport through the hydrophilic blend membrane occurs by solution diffusion mechanism.[23] Scheme 1 shows the structure of a cross-linked chitosan membrane having urea linkages, which are polar in nature. Moreover residual –OH and $-NH_2$ groups will also be available for interaction with water molecules through hydrogen bonding. The effect of feed composition on flux and selectivity of both unmodified and cross-linked chitosan membranes is shown in Fig 6 and the sorption data for binary feed mixtures are presented in Table 1. From Fig 6, it can be seen that the unmodified chitosan yields a higher flux but offers poor selectivity. In pervaporation, it is essential to obtain reasonably good flux but higher selectivity in order to attain a permeate free of the organic component. Hence, the usage of unmodified chitosan does not prove worthy in the separation of *t*-butanol/water mixtures. Hence studies relating to other parameters are restricted to cross-linked chitosan membranes only.

From Table 1 it was also found that the cross-linked membrane showed a high degree of sorption in pure water (424%) but relatively negligible sorption (1.2%) in pure *t*-butanol. The preferential affinity of the membrane towards water causes swelling which allows rapid permeation of feed molecules. The amount of sorption correspondingly rises with an increase in the feed water concentration, resulting in enhanced flux. However, increased swelling has a negative impact on membrane selectivity since the swollen and plasticized upstream membrane layer allows some *t*-butanol molecules also to escape into the permeate side along with water. Therefore the permeate water concentration was found to reduce from 99.2% to 94.7%, indicating a drop in selectivity from 2657.4 to as low as 49.7 over the same feed concentration range of 4.5–26.46% water. With a further increase in the feed water concentration from 26.46% to 50.7% (as shown in the fourth and fifth rows of Table 1) a further drop in selectivity to a value as low as 4.3 can be seen. Hence it is worth mentioning that the membrane yields promising results for dehydrating feeds having 5–25% water. Moreover, the azeotropic composition (of 88.2% (w/w) *t*-butanol) was easily broken by pervaporation. About 98.7% water was obtained in permeate with a selectivity of 620 and flux of 0.38 $\mathrm{kg\,m^{-2}\,h^{-1}}$.

Table 2 provides the comparison of pervaporation performance of cross-linked chitosan membrane with literature data. From the table, it can be seen that the flux and selectivity offered by the cross-linked membrane is higher than the block copolymers but is a little lower when compared with the blend. However, the high separation factor and relatively high flux in association with the cost-effectiveness and simple synthesis procedure makes the applicability of TDI cross-linked chitosan for pervaporation dehydration of *t*-butanol/water more feasible.

Effect of membrane thickness

The effect of varying membrane thickness on separation performance was studied at constant feed composition (azeotropic) and permeate pressure (1 mmHg) by synthesizing membranes of thickness in the range 45 µm to 153 µm. Figure 7 shows that there was a gradual decrease in the flux from 0.38 to 0.10 $\mathrm{kg\,m^{-2}\,h^{-1}}$. Though the number of polar groups increases with an increase in the thickness, flux decreases since diffusion becomes increasingly retarded as the feed molecules have to travel a greater distance to reach the permeate side. The permeate concentration of water varied from 98.77 to 99.26% (w/w) which meant that the selectivity increased from 620 to 1039. In the pervaporation process, the upstream layer of the membrane is swollen and plasticized due to absorption of feed liquid and allows unrestricted transport of feed components. In contrast the downstream layer is virtually dry due to continuous evacuation on the permeate side and therefore this layer forms the restrictive barrier which allows only interacting and smaller sized molecules such as water to pass through.[3] It is expected that the thickness of the dry layer would increase with an increase in the overall membrane thickness resulting in improved selectivity as observed in the present case.

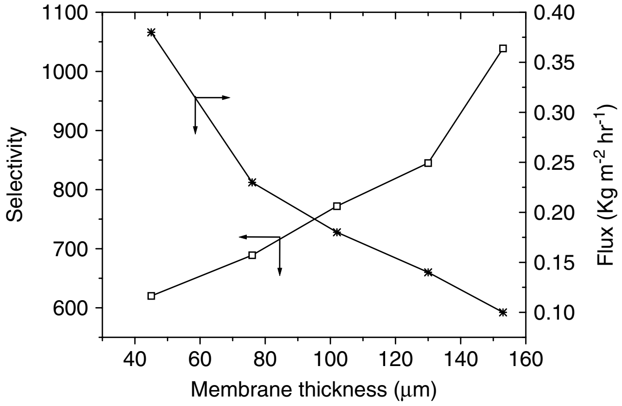


Figure 7. Influence of membrane thickness on pervaporation performance of cross-linked chitosan membranes (feed composition: azeotropic, permeate pressure: 1 mmHg).

Table 2. Comparison of pervaporation performance of the cross-linked chitosan membrane with literature data for t-butanol/water mixtures

Sample number	Membrane	Feed composition Water (%)	*t*-Butanol (%)	Selectivity	Flux ($\mathrm{kg\,m^{-2}\,h^{-1}}$)	Reference
1	Present work	4.31	94.69	2657.4	0.21	
2[a]	PVA/PVS blend	3	97	3200	0.31	24
3[b]	T-PDMS	3.2	96.8	12	0.63	25
4[b]	T-PDMS-T-BFCH	3.2	96.8	12	0.57	25
5[b]	T-PDMS-T-BFH	3.2	96.8	11	0.43	25
6[b]	TX-PDMS	3.2	96.8	12	0.56	25
7[b]	TX-PDMS-T-BFCH	3.2	96.8	11	0.58	25
8[b]	IP-PDMS	3.2	96.8	12	0.39	25
9[b]	IP-PDMS-IP-BFCH	3.2	96.8	11	0.59	25

[a] PVA/PVS: Poly(vinyl alcohol)/poly(vinyl sulfate).

[b] Siloxane–urea block copolymers.

PDMS — polydimethylsiloxane, T — 1, methyl-2,4 (6) isocyanato-benzene, TX — 1,3-bis-(1-isocyanato-1-methylethyl)-benzene, IP — isophorone disiocyanate, BFH — 2,2-3,3-4,4-5,5-octa-fluoro-hexane-1,6-diol, BFCH — 1,4-bis-(2-hydroxy-hexafluoro)-cumene.

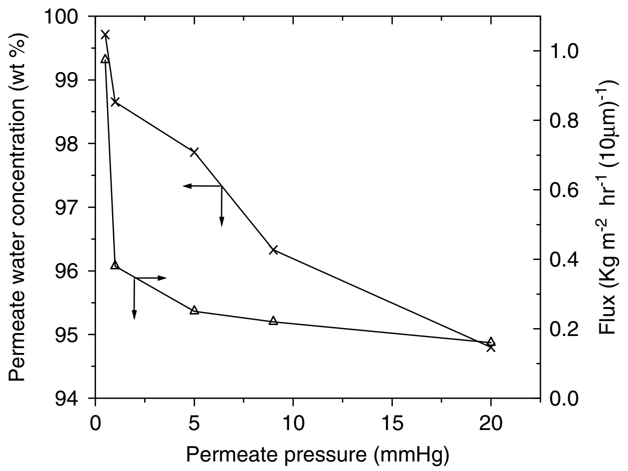


Figure 8. Effect of downstream pressure on pervaporation performance of cross-linked chitosan membrane (feed composition: azeotropic, membrane thickness: 45 μm).

Effect of permeate pressure

The permeate pressure was varied from 0.5 to 20 mm of Hg to study the permeation characteristics at a constant thickness of 45 μm and azeotropic feed composition. At lower pressures (high vacuum) the influence of the driving force for the diffusing molecules in the membrane is high and will result in the components being swept out immediately from the permeate side, resulting in high mass transfer rates. Figure 8 shows that the membrane exhibits a considerable lowering of flux from 0.97 to 0.16 $\mathrm{kg\,m^{-2}\,h^{-1}}$ while the permeate water concentration reduced from 99.7 to 94.8% (w/w), resulting in a decrease in selectivity from 2686 to 141. Under high vacuum conditions (lower pressures) diffusion through the membrane is the rate-determining step of the pervaporation process and the diffusing water molecules experience a larger driving force, which enhances the desorption rate at the downstream side.[3] Lower vacuums reduce the driving force, thus slowing the desorption of molecules. In such cases the relative volatilities of the two components of the mixture govern the separation factor of the membrane. *t*-Butanol, being more volatile (boiling point: 83 °C) than water, permeates competitively with the latter, thus lowering its concentration in the permeate.

CONCLUSIONS

Hydrophilic pervaporation has shown immense potential as a viable process for the separation of water from mixtures with *t*-butanol. A cross-linked chitosan membrane easily broke the azeotrope, indicating that the membrane acts as a third phase and selectively allows water molecules to pass through due to the preferential affinity. TDI appears to be a useful and novel cross-linker by rendering the membrane highly selective without compromising heavily on flux.

Characterization of membranes by FTIR confirmed cross-linking. On the other hand the XRD results of cross-linked chitosan showed reduction in the effective d-spacing value which is an indication of shrinkage in the cell size which would in turn improve the selective permeation property of membrane. Cross-linking did not bring about major changes in thermal and mechanical stability.

With increasing feed water concentration, the membrane performance was found to be affected substantially by an increase in the extent of swelling of the polymer, which resulted in the rise in flux but a reduction in selectivity. Increasing membrane thickness decreased the flux but improved selectivity. Higher permeate pressure caused a reduction in both flux and selectivity.

Pervaporation could be effectively combined with distillation to constitute an economical hybrid process to achieve the desired purity levels of *t*-butanol.

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