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Shivanand B. Teli[a]; Gavisiddappa S. Gokavi[b]; Tae-Moon Tak[a]; Tejraj M. Aminabhavi[c]
[a] Polymer Chemistry Lab, Department of Biosystems & Biomaterials Science and Engineering, College of Agriculture and Life Science (CALS), Seoul National University (SNU), South Korea [b] Kinetics and Catalysis Division, Shivaji University, Kolhapur, Maharashtra, India [c] Reliance Life Sciences Pvt. Ltd., Industrial Biotechnology Group, Dhirubhai Ambani Life Sciences Centre, Thane, Navi Mumbai, India

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Chitosan/Gelatin Blend Membranes for Pervaporation Dehydration of 1,4-Dioxane

Shivanand B. Teli,[1] Gavisiddappa S. Gokavi,[2] Tae-Moon Tak,[1] and Tejraj M. Aminabhavi[3]
[1]Polymer Chemistry Lab, Department of Biosystems & Biomaterials Science and Engineering, College of Agriculture and Life Science (CALS), Seoul National University (SNU), South Korea
[2]Kinetics and Catalysis Division, Shivaji University, Kolhapur, Maharashtra, India
[3]Reliance Life Sciences Pvt. Ltd., Industrial Biotechnology Group, Dhirubhai Ambani Life Sciences Centre, Thane, Navi Mumbai, India

Abstract: This paper deals with the development of compatible blend membranes of chitosan (CS) and gelatin (GL) by solution casting and crosslinking with glutaraldehyde. The membranes were tested in pervaporation (PV) dehydration of 1,4-dioxane. Membrane characterizations by Fourier transform infrared spectroscopy, wide-angle X-ray diffraction, and a universal testing machine were done to understand their physicochemical properties and for their suitability under PV conditions. The blend membranes were more water selective compared to pristine chitosan membrane at 30°C. Flux increased with increasing wt.% of water of the feed and also by increasing the gelatin content of the blend, but selectivity decreased. Sorption experiments gave information on the interaction between feed mixture and membrane polymers. Membranes of this study could extract nearly 97 wt.% of water from the feed mixture. Arrhenius activation parameters and diffusion coefficients estimated from a temperature dependence of PV results could explain the PV results satisfactorily.

Keywords: Activation parameter and diffusion coefficient, blend membranes, chitosan, 1,4-dioxane, gelatin, pervaporations

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Address correspondence to Shivanand B. Teli, Polymer Chemistry Lab, Department of Biosystems & Biomaterials Science and Engineering, College of Agriculture and Life Science (CALS), Seoul National University (SNU), 151-742 South Korea. Tel.: +82 2-880-4626; Fax: +82 2 873 2285. E-mail: shivateli@rediffmail.com

INTRODUCTION

Chitosan (CS) is an *N*-acylated product of chitin and is the most abundant natural polymer next to cellulose. The advantages of using chitosan as membrane have been recognized due to its high water permselectivity, solvent stability, and its soluble nature in acidic medium. Due to the presence of reactive amino and hydroxyl groups, CS can be chemically modified in acidic solutions such as acetic acid and the free amino groups can be protonated to form water-soluble chitosan-acid salts (1,2). Muzzarelli and Gooday (3) have reported the use of chemically-modified chitin and chitosan membranes for use in metal-ion separation (4), gas separation (5), reverse osmosis (6), ultrafiltration (7), evapermeation (8) etc. Particularly, in PV research, CS has been verified to have good membrane forming properties, chemical resistivity, and high permselectivity to water (9,12). Thus, due to its abundant availability, biocompatibility, and commercial viability, CS has found a widespread use in separating aqueous-organic mixtures (13,16). Gelatin (GL), on the other hand, is another carbohydrate polymer, which is a degraded product of collagen, which is a connective tissue protein present in most of the vertebraes (17). Because of its water-soluble, nontoxic, non-irritant, and good living body compatibility, GL has been extensively used in pharmacology and cosmetic applications (18). However, its usage as a membrane has not been fully explored. Chitosan has a high modulus of elasticity along with a low strain to break owing to its high *T*g and crystallinity. Its morphology and ductility can be improved by either blending or copolymerizing with other polymers. Hydrophilic biocompatible carbohydrate polymers may be ideal for such modification of CS. Several blends of CS with other synthetic polymers have been evaluated (19,20), but gelatin is of particular interest, due to its hydrophilic, biocompatible, and biodegradable nature. The compatibility of polymer blends is one of the significant factors affected by the interaction between the components of the blends that in turn affects the blends properties. Therefore, a major problem to be considered for polymer blends is compatibility. Moreover, gelatin is also a biodegradable polymer with many attractive properties, such as excellent biocompatibility, nonantigenicity, plasticity, and adhesiveness. Thus, gelatin was selected as a suitable candidate blended with chitosan (21). It is an advantage that intermolecular interactions exist between two polymer species. Utilizing both the water-soluble properties of CS and GL, we have thought of preparing the blend membranes of CS/GL for applications in PV dehydration of 1,4-dioxane, since it is a widely used industrial solvent in pharmaceutical and chemical industries, it is also miscible with water in all proportions and forms an azeotrope at 18 wt.% of water. Previously, some authors have separated 1,4-dioxane mixture using different kinds of blend and composite membranes (22,26).

The present study is an extension of our ongoing efforts to prepare such types of polymeric blend membranes used in PV separation. PV, being a membrane technology, has widespread applications in chemical industries as an effective method for the separation of azotropic mixtures and the recovery of organic compounds (27,29). In this method, the fractionation of liquid mixture is achieved by a partial vaporization of the mixture under application of high vacuum on the downstream side of the membrane. For a majority of PV dehydration studies, hydrophilic membranes have been used to completely remove water from the organics, leading to high flux and selectivity. However, the disadvantage is that their excessive swelling would result in a low selectivity due to the plasticization effect. Therefore, it is important to modify the membrane to obtain an optimal combination of flux as well as selectivity to a particular component in addition to its good mechanical strength. It is thus desirable to employ the polymeric blends in which, one component provides the desired permeability characteristics, while the other improves the mechanical properties (30). In the earlier literature, different types of hydrophilic membranes have been reported to offer the outstanding membrane performances for the PV dehydration of alcohol (31,33). The present study reports the PV separation results on water-1, 4-dioxane mixtures. It is demonstrated that gelatin and chitosan blend membranes are able to enhance the selectivity and flux to water molecules, thereby effectively dehydrating 1,4-dioxane. The membrane performance was also studied by calculating the diffusion coefficient, permeation separation index and enrichment factors. Temperature dependence of PV results has been analyzed to obtain the activation parameters.

EXPERIMENTAL

Materials

Chitosan was purchased from Aldrich Chemical Co, Milwaukee, WI, USA having an average molecular weight of 500,000 with a degree of deacetylation of 84%. Gelatin, 1,4-dioxane, isopropanol, HCl, glacial acetic acid, and glutaraldehyde (GA), all laboratory reagent (LR) grade chemicals, were purchased from s.d. Fine Chemicals, Mumbai, India. Deionized water, having a conductivity of $20\,\mu S/cm$, was produced in the laboratory itself from the Permionics pilot plant (Vadodara, India) using a nanofiltration membrane module.

Preparation of Chitosan/Gelatin Blend Membrane

Blend membranes of CS with gelatin were prepared by the solution casting method. The required amount of CS was dissolved in 2% (v/v) aqueous acetic acid solution by stirring over a magnetic stirrer for 12 h. After the CS flakes were fully dissolved, the solution was filtered to remove any undissolved suspended articles. To this, 10 and 20 wt.% (with respect to chitosan) gently heated gelatin solution were added. Membranes prepared were designated as CS/GL-10 and CS/GL-20, respectively, while the pristine CS membrane was prepared in the absence of gelatin. Blend polymer solutions were mixed uniformly and filtered to remove any floating or suspended particles. The respective solution was poured onto a clean glass plate, leveled perfectly on a tabletop kept in a dust-free atmosphere, and dried at the ambient temperature. The dried membranes were peeled off carefully from the glass plate. After removing the dried membrane, it was crosslinked using isopropanol water (90/10 vol%) mixture containing 1 vol% of HCl as a catalyst and 4 vol% of GA as the crosslinker. After crosslinking for about 120 min, the membranes were washed with deionized water and dried at ambient temperature for 24 h. The membrane thickness as measured by a micrometer screw gauge, was found to be in the range of 40–45 μm. The CS and GL blends formed were clear with a homogeneous solution, indicating the good miscibility of the polymers.

MEMBRANE CHARACTERIZATION

Pristine CS, uncrosslinked CS/GL blend, crosslinked blend, and pristine gelatin were scanned using Nicolet-740, Perkin-Elmer-283B FTIR spectrometer, Milwaukee, WI, USA. Membrane samples were ground well with KBr and pellets were prepared by applying a hydraulic pressure of 400–450 kg/cm^2. Spectra were scanned in the range of 500–4000 cm^{-1}. Siemens D 5000 powder X-ray diffractometer was used to study the solid state morphology in a powder form. X-rays of 1.5406 Å wavelength was generated by a CuKα source. The angle of diffraction (θ) was varied from 20 to 50° to identify the changes in crystal structure.

Sorption Experiment

Sorption of pristine CS and crosslinked blend membranes of CS/GL was measured at 30°C gravimetrically in 10, 15, 20, 25, and 30 wt.% water-containing feed mixtures. Interactions of the blend membrane with both the liquids of feed mixture were determined by calculating % sorption values. Initial weights of the circularly cut (dia = 2.5 cm) pristine CS and blend membranes were taken on a single-pan digital microbalance (Model AE 240, Mettler, Switzerland) sensitive to ±0.01 mg. Samples were placed inside the specially designed airtight test bottles containing 20 cm^3 of the test solvent. Test bottles were transferred to an oven maintained at the constant desired temperature. Dry membranes were equilibrated by soaking in different feed mixtures in a sealed vessel at 30°C for 48 h. Sorbed membranes were weighed immediately after careful blotting on a digital microbalance. The % sorption was calculated as:

$$\%\,\text{Sorption} = (W_0 - W_\infty)/W_\infty \times 100 \tag{1}$$

where W_∞ and W_0 are the weights of completely sorbed and dry membranes, respectively.

Determination of Ion Exchange Capacity [IEC]

In order to determine the crosslinking reaction of CS with GA in the blend form, ion exchange capacity (IEC) of the blend was estimated. IEC indicates the number of groups present before and after crosslinking, which gives an idea about the extent of crosslinking. IEC indicates the number of milli-equivalents of ions in 1 g of dry polymer. To determine IEC, specimens of similar weight were soaked in 50 mL of 0.01 N NaOH solution for 12 h at the ambient temperature. Then, a 5 mL sample was titrated against 0.01 N H_2SO_4. The sample was regenerated with 1 M HCl, washed with water, and dried to a constant weight. IEC was then calculated as:

$$\text{IEC} = [B - P \times 0.01 \times 5/m] \tag{2}$$

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, number 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 m represents the sample mass (g).

PERVAPORATION EXPERIMENTS

Pervaporation experiments were performed in an apparatus indigenously designed; detailed protocols have been described elsewhere (34). An effective area of the membrane in the PV cell was 28.27 cm^2 and the volume capacity was 200 cm^3. The PV apparatus consists of a stirred stainless steel cell in which feed stock solution was maintained at the required temperature by a thermostatically controlled water jacket. The PV cell has an efficient three blade stirrer powered by a DC motor in the feed compartment and the feed mixture was stirred at 200-rpm rotation speed. The downstream side of the pressure was maintained below 13.332×10^2 Pa (10 Torr) using a vacuum pump. Before starting the PV experiment, the test membrane was equilibrated for 1 h with the feed mixture and after the establishment of a steady state, the liquid permeate was collected in traps immersed in liquid nitrogen and condensed in traps using liquid nitrogen. Experiments were repeated in triplicate with the feed mixtures ranging from 10 to 30 wt.% water. The weight of the permeate in the trap was collected and its composition was determined by measuring the refractive index using an Abbe refractometer (Atago, Model 3T, Tokyo, Japan). Alternatively, the condensed permeate as well as the feeds were warmed up to ambient temperature, weighed, and analyzed by gas chromatograph (Nucon GC model, 5765, Mumbai, India) equipped with a thermal conductivity detector (TCD) and a DEGS or a Tenax packed column of 1/8" ID having 2 m length. The oven temperature was maintained at 70°C (isothermal), while the injector and the detector temperatures were maintained at 150°C. Pure hydrogen was used as a carrier gas at the pressure of 0.75 kg/cm^2. The sample injection volume was 1 μL and the GC response was calibrated for the column and for known compositions of water + 1,4-dioxane mixtures. Calibration factors were fed into GC software to obtain the analysis for the unknown sample. From the PV experiments, the total pervaporation fluxes (*J*), the selectivity (α), the pervaporation separation index (*PSI*), and the enrichment factor (β) were computed, respectively using the following equations.

$$J = W/At \tag{3}$$

$$\alpha = (P\text{w}/P\text{org})/(F\text{w}/F\text{org}) \tag{4}$$

$$PSI = J(\alpha - 1) \tag{5}$$

$$\beta = \mathrm{C}_w^P/\mathrm{C}_w^F \tag{6}$$

Here, *W* is the weight of the permeate (kg), *A* is the effective membrane area (m^2) and *t* the measurement time (h); *P* and *F* are weight fractions of the permeate and the feed, respectively. Subscript *w* stands for water, org stands for 1,4-dioxane, and *C* is the concentration. A minimum of three independent readings were taken under identical conditions of temperature and feed compositions to confirm the steady-state pervaporation. The

% error values in computing different mixture compositions were less than 3%, since all weight measurements were done within ±0.01 mg.

RESULTS AND DISCUSSION

Membrane Characterization

FTIR

The FTIR spectra of pristine chitosan (curve a), uncrosslinked blend (curve b) and crosslinked blend (curve c) and pristine gelatin (curve d) are shown in Fig. 1. The curve (a) shows characteristic absorption bands

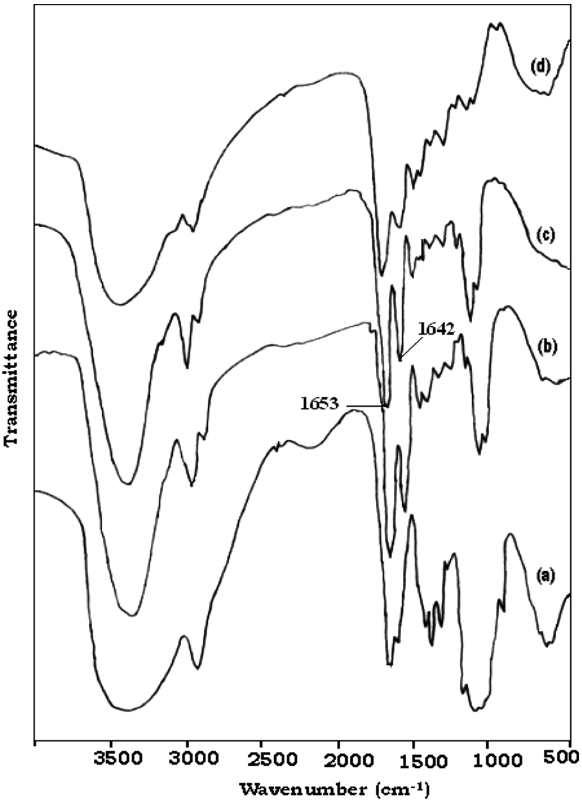


Figure 1. FTIR spectra of (a) pristine chitosan (b) uncrosslinked blend, (c) crosslinked blend and (d) pristine gelatin.

at 1653 cm^{-1} (amide I), 1604 cm^{-1} (amide II) and 1381 cm^{-1} ($-CH_2$ bending). Absorption bands at 1160 cm^{-1} due to anti-symmetric stretching of C$-$O$-$C bridge and 1075 and 1024 cm^{-1} due to skeletal vibrations involving C-O stretching are representative of the saccharide structure. Curve (b) for the uncrosslinked blend membrane suggests the presence of amide groups at 1651 cm^{-1} of chitosan. Curve (c) shows the crosslinked blend polymer network formed via imine ($-C{=}N-$) formation at 1542 and 1652 cm^{-1} due to amino groups reacting with ($-CHO$) of glutaraldehylde. The hydrogen bond formed between CS and GL networks in the blend polymer might have disturbed the crystallization of CS in the blend matrix. Curve (d) for gelatin shows a strong absorption band at 3413 cm^{-1} due to (NH-stretching); characteristic peaks at 1646 and 1535 cm^{-1} are attributed, respectively to carbonyl and amino groups of gelatin.

X-RD

The X-ray diffractogram for pristine gelatin (curve a), blend (curve b), and pristine CS membrane (curve c) shown in Fig. 2 suggests that membranes are semicrystalline. Curve (a) indicates that for gelatin, two peaks i.e., one small peak at 8° and a broad peak at 20^0 of 2θ indicates

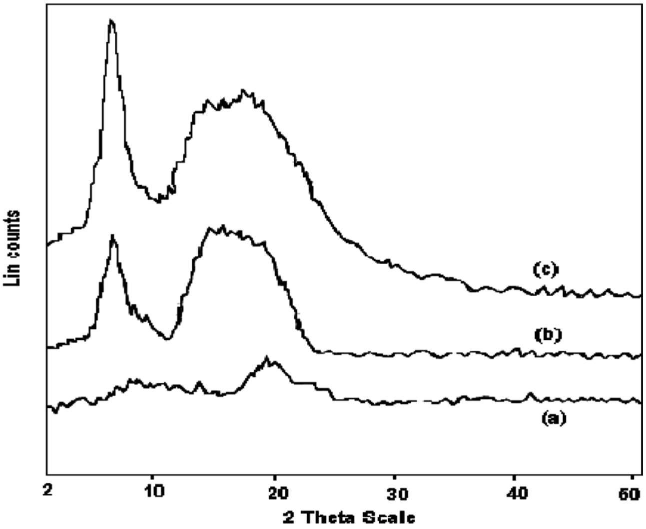


Figure 2. X-RD spectra of (a) pristine gelatin, (b) crosslinked CS/GL blend and (c) pristine chitosan membrane.

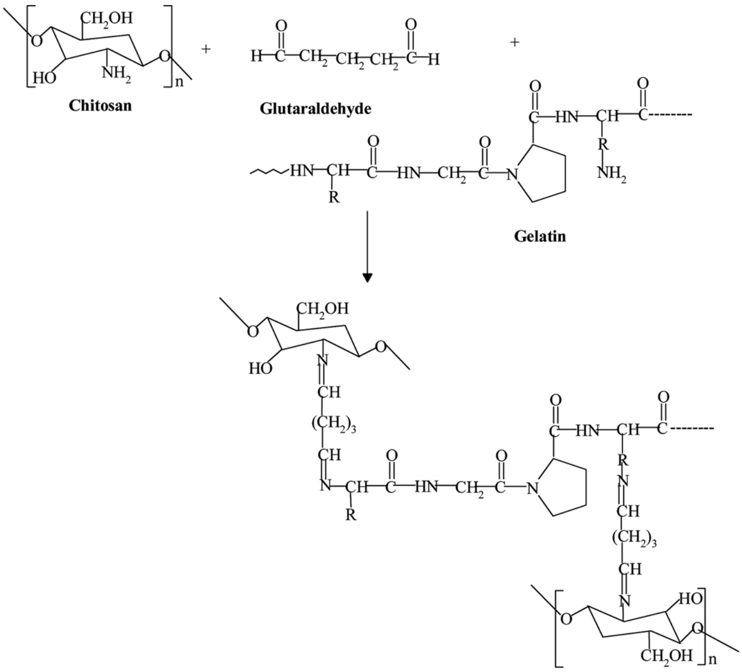
the average intermolecular distance of the amorphous part; relatively, a sharp semicrystalline peak is seen around 20° of 2θ (35). Curve (b) of the blend membrane has a decreased intensity at 2θ of 7.60. X-RD results suggest the good miscible nature of the polymers in a blend form. In the case of pristine CS, curve (c) shows two distinct bands with maxima around 2θ of 9° to 10° and at 2θ of 19.7°; these are related to two types of crystals: crystal 1 and crystal 2. Of these, crystal 1, which corresponds to the peak at 2θ of 9°, is responsible for the separation, since it comprises functional groups like $-NH_2$ and $-OH$.

Ion Exchange Capacity (*IEC*)

The amount of residual amine and hydroxyl groups present after the crosslinking reaction was estimated from *IEC* studies. It may be noted that the unmodified CS showed an *IEC* of 0.45 mequiv/g, whereas the crosslinked CS exhibited an IEC of 0.23 mequiv/g. *IEC* is equivalent to the total number of free amino groups (considering the fact that amino groups are more interactive than hydroxyl groups) present in the membrane, which tend to decrease upon crosslinking (36). This indicates that almost 60% of amine groups present in the unmodified CS are engaged in crosslinking with GA. Scheme 1 displays the crosslinking reaction occurring between CS and GL in the presence of GA as confirmed by *IEC* and FTIR studies. Notice that GA is responsible for forming a linkage with CS through the imine formation as confirmed by FTIR.

Sorption Studies

Sorption of the membranes has an effect on their PV characteristics. Figure 3 displays the % sorption of crosslinked CS, CS/GL-10, and CS/GL-20 membranes as a function of wt.% of water in the feed. It can be seen that both the CS/GL blend membranes show a higher extent of sorption than the pristine CS membrane. Sorption increased with increasing amount of gelatin of the blend. An increase in the gelatin content of the blend would lead to increased flexibility of the polymer network. Thus, the membrane may have higher free volume space for liquid sorption to take place. Gelatin is more hydrophilic than CS, since it has a greater number of amide groups that would exhibit a strong hydrogen bonding interaction with water, resulting in a higher hydrophilicity of CS/GL blend membranes. For the blend membrane containing 20 wt.% of gelatin, we could observe an excessive water sorption, along



Scheme 1. Crosslinking reaction between chitosan and gelatin in the presence of glutraldehylde.

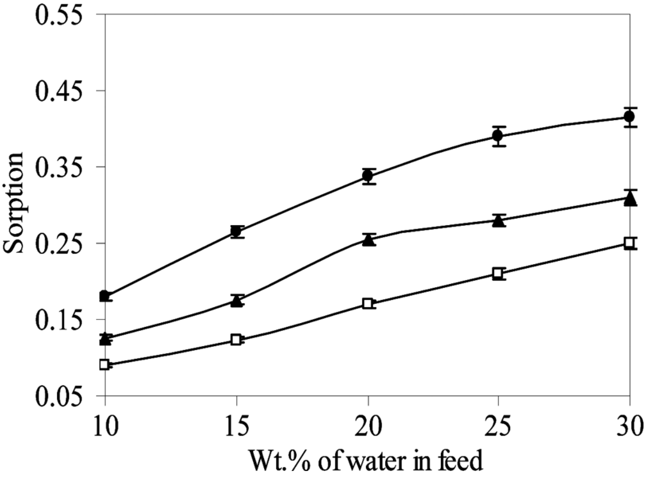


Figure 3. Degree of sorption of water-1,4-dioxane vs. wt.% of water in the feed mixtures at 30°C for pristine CS (□), 10% blend (▲) and 20% blend (●) membranes.

with an increased flexibility of the polymer network, making the membrane to sorb more.

PERVAPORATION RESULTS

Pervaporation Performance

The pervaporation performance of the pristine CS and blend membranes of CS/GL was investigated for 10, 15, 20, 25, and 30 wt.% water containing feed at 30°C. The calculated values of flux, selectivity, *PSI,* and enrichment factor for all the membranes are presented in Table 1. It is observed that water flux of all the membranes increased with increasing the wt.% of water in the feed as well as with increasing the amount of gelatin of the blend membrane. Total flux values of the blend membranes are higher than those of the pristine CS membrane due to strong hydrophilic interactions between the polymers, which caused a high swelling of

Table 1. Pervaporation results of water-1,4-dioxane mixtures at 30°C temperature

Wt.% of water in feed	Wt.% of water in permeate	J (kg/m$^2\cdot$h)	Selectivity (α)	*PSI*	β
30°C					
Pristine chitosan					
10	89.63	0.102	78	8	15.6
15	87.63	0.155	40	6	5.3
20	84.58	0.208	22	4	2.2
25	82.65	0.263	14	4	1.1
30	78.38	0.319	8	2	0.6
CS/GL-10					
10	97.11	0.118	302	33	55.2
15	95.36	0.180	116	21	15.5
20	93.12	0.240	54	13	5.4
25	91.35	0.302	32	9	2.5
30	87.01	0.365	16	5	1.0
CS/GL-20					
10	93.67	0.124	133	16	26.6
15	91.18	0.193	59	11	7.8
20	88.23	0.260	30	8	3.0
25	86.43	0.334	19	6	1.5
30	83.15	0.415	12	4	0.8

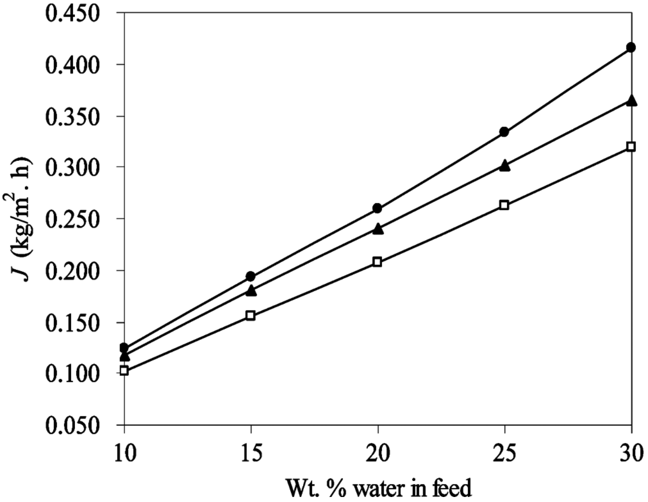


Figure 4. Water fluxes vs. wt.% of water in feed mixtures of water + 1,4-dioxane at 30°C for pristine CS (□), 10% blend (▲) and 20% blend (●) membranes.

the membrane. Figures 4 and 5 show the PV characteristics in terms of the selectivity and flux of the pristine CS and CS/GL blend membranes. Selectivity decreased with increasing the amount of gelatin in the blend as well as with increasing the amount of water in the feed. This may be

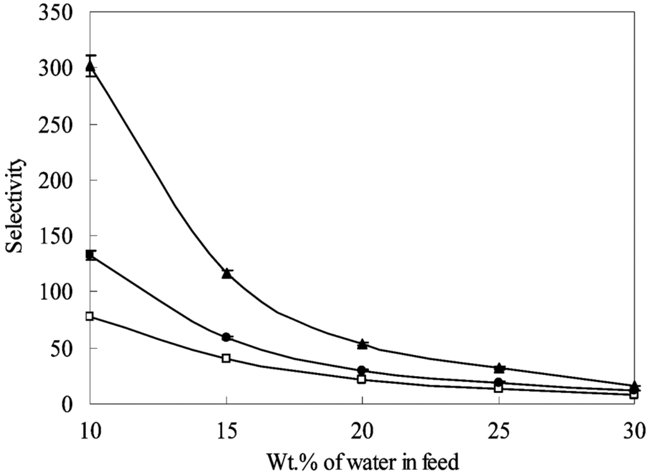


Figure 5. Selectivity vs. wt.% of water in feed mixtures of water + 1,4-dioxane at 30°C for pristine CS (□), 10% blend (▲) and 20% blend (●) membranes.

attributed to the hydrophilic nature of gelatin. However, the blend membranes exhibited a much-improved selectivity than the pristine CS membrane. For instance, with CS/GL-10 (10 wt.% gelatin) blend membrane, a highest selectivity of 302 at 10 wt.% of water in the feed was obtained, whereas for CS/GL-20 (20 wt.% gelatin) blend membrane had a selectivity of 133 at 30°C. This difference in the selectivity data can be explained as due to varying thermodynamic interactions between 1,4-dioxane and water, leading to differences in membrane performances. Flux of the pristine CS membrane is in the range of 0.102 to 0.319 $kg/m^2 \cdot h$, while for the blend membrane of CS/GL-10, the flux varied in the range of 0.0118 to 0.365 $kg/m^2 \cdot h$. On the other hand, for the CS/GL-20 membrane, the flux increased and varied from 0.124 to 0.415 $kg/m^2 \cdot h$. Thus, the higher the gelatin content of the blend membrane the higher will be the flux for water. Increasing the water content of the feed, the blend membranes showed a higher flux with a lower selectivity; this can be explained in terms of the plasticizing effect due to the presence of water. At a higher water concentration of the feed mixture, the amorphous regions of the membrane are more swollen and the polymer chains would become more flexible. This makes both the water and the 1,4-dioxane molecules to penetrate easily through the membranes; thus the PV flux has increased, but selectivity has decreased. The results of the pristine CS membrane at 40° and 50°C as well as those of the blend membranes are shown in Table 2. Membrane performance was also studied by computing *PSI* and the enrichment factor (β) values (see data given in Tables 1 and 2). It is observed that both *PSI* and β values for 10 wt.% gelatin containing the blend membrane are highest for 10 wt.% water containing feed mixture. However, a systematic

Table 2. Pervaporation results of water + 1,4-dioxane mixtures at different temperatures for different membranes at 10 wt.% of water in the feed mixtures

Membranes	Wt.% of water in permeate	J ($kg/m^2 \cdot h$)	Selectivity (α)	*PSI*	β
30°C					
Pristine	86.70	0.115	59	7	11.8
CS/GL-10	94.56	0.129	156	20	31.2
CS-GL-20	89.23	0.138	75	10	15.0
50°C					
Pristine	83.02	0.123	43	5	8.2
CS/GL-10	91.06	0.135	92	12	18.3
CS-GL-20	87.21	0.151	61	9	12.2

decrease is observed with increasing water in the feed as well as with increasing the amount of gelatin in the blend membrane. Overall, the blend membranes of this study showed better PV performances in separating water-1,4-dioxane mixtures than the pristine CS membrane.

Effect of Temperature on Membrane Performance

The effect of operating temperature on PV performance for 10 wt.% water in the feed has been studied (see data in Table 2). It is observed that the permeation rate increased from 30° to 50°C, whereas the selectivity decreased, due to a decreased interaction of the membrane with water with increasing temperature. As the temperature increases, the chain dynamics also increases, resulting in a large free volume, thereby accommodating more of the solvent molecules. This type of increase in free volume of the membrane matrix will result in an easy transport of 1,4-dioxane. Therefore, membrane selectivity to water will be reduced, but flux will increase. The temperature dependence of permeation can be expressed by an Arrhenius type relationship (37):

$$J = J_0\, exp(-E_J/RT) \tag{7}$$

From Eq. (7), the permeation activation energy (i.e., energy barrier required for the species to transport across the membrane) was calculated from the least squares method. If activation energy is positive, then the permeation flux will increase with increasing temperature. Using the respective water fluxes obtained at 30°, 40°, and 50°C, the E_J values of water were obtained from the slopes of ln J vs 1/T linear plots. The E_J values calculated from the least squares estimations of Eq. (7) are displayed in Table 3. According to the free volume theory (38), an increase in temperature will increase the thermal mobility of the polymer chains, which would generate extra free volume spaces within the polymer matrix; this will further increase the sorption and diffusion rates of the permeating molecules. The apparent activation energy for transport was calculated from the slopes of the Arrhenius plots of ln J vs $1/T$ as displayed in Fig. 6. The permeation activation energy thus calculated from the flux values are shown in Tables 1 and 2, respectively. For all the membranes, linear trends were observed; with an increasing water content of the feed mixture the selectivity values decreased. The E_J values for pristine CS and CS/GL-10 and CS/GL-20 blend membranes are respectively 13.71, 9.84, and 11.96 kJ/mol for a feed mixture containing 10 wt.% of water in the feed. The increases in E_J values are more considerable for

Table 3. Diffusion coefficients (water-1,4-dioxane) at different wt% of water in feed mixture at 30°C

Wt.% of water in feed	$D_w \times 10^{11}\ m^2/s$	$D_w \times 10^{11}\ m^2/s$
Pristine CS		
10	2.84	0.31
15	4.43	0.61
20	5.81	1.05
25	7.34	1.52
30	8.91	2.44
CS/GL-10		
10	3.29	0.10
15	5.33	0.25
20	6.73	0.50
25	8.44	0.80
30	9.98	1.40
CS/GL-20		
10	3.46	0.22
15	5.40	0.52
20	7.27	0.97
25	9.34	0.47
30	11.56	2.33

water + 1,4-dioxane feed. This suggests that membranes with higher selectivity to water will have lower E_J; this is indeed observed in the present systems.

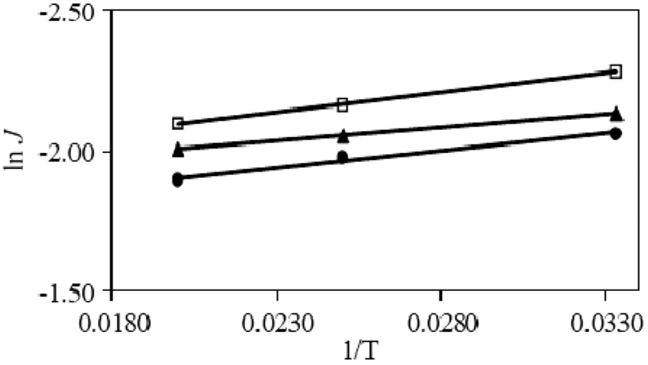


Figure 6. ln *J* vs. 1/T plots for pristine CS (□), CS/GL-10 (▲) and CS/GL-20 (●) membranes at 10 wt.% of water in feed mixtures at different temperatures.

Diffusion Coefficients

Diffusion occurs as a result of the concentration gradient existing between the feed and the permeate mixtures (39). Diffusion coefficients, D*i* of solvent molecules were calculated using Eq. (8):

$$J_i = P_i\,[p_i(\text{feed}) - p_i(\text{permeate})] = D_i/(h)\,[C_i\,(\text{feed}) - C_i\,(\text{permeate})] \tag{8}$$

Here, D_i is assumed to be constant across the effective membrane thickness, h; *C*i (feed) and C_i (permeate) are, respectively the composition of liquids in feed and permeate sides. The calculated values of D_i (where the subscript i stands for water or organic component) at 30°C are displayed in Table 4, whereas calculated values of D_i at 40°C and 50°C are presented in Table 5. The D_i of water + 1,4-dioxane mixture increased systematically for the pristine CS membrane as well as with the blend membranes. The values of *Dw* for water in case of CS/GL-20 membrane are higher than those observed for CS/GL-10; these followed the same trends as those of D_{dio} for 1,4-dioxane (see Tables 4 and 5) as well as the flux data given in Table 1. The values of D_i for 1,4-dioxane are smaller by an order of magnitude than for water, but their dependencies on the gelatin content are different i.e., CS/GL-10 and CS/GL-20 blend membranes exhibit higher *Dw* values for 1,4-dioxane than pristine CS membrane. Even though the diffusion coefficients of 1,4-dioxane are smaller than water, these results have shown a considerable increase with increasing the water content of the feed mixture. In case of 1,4-dioxane, with the pristine CS and CS/GL-20 membranes, the diffusion coefficient (D_{dio}) values are smaller than those found for the CS/GL-10 membrane; notice that membrane selectivity to water is also higher at 10 wt.% gelatin

Table 4. Diffusion coefficients (water-1,4-dioxane) at different temperatures for 10 wt.% of water in feed mixture

Membranes	$D_w \times 10^{11}\,m^2/s$	$D_w \times 10^{11}\,m^2/s$
40°C		
Pristine	3.21	0.33
CS/GL-10	3.60	0.13
CS-GL-20	3.86	1.10
50°C		
Pristine	3.43	0.55
CS/GL-10	3.77	0.21
CS-GL-20	4.22	1.39

Table 5. Permeation and diffusion activation energy, heat of sorption for water and energy difference value of the membranes for 10 wt.% of water in feed mixture

Arrhenius parameter	Membranes		
	Pristine CS	CS/GL-10	CS/GL-20
E_J (kJ/mol)	13.71	9.84	11.96
E_D (kJ/mol)	14.21	10.27	13.37
ΔH_S (kJ/mol)	−0.50	−0.43	−1.79

content of the blend. The temperature dependence of diffusion was also analyzed using a similar type of equation as that of Eq. (9):

$$D = D_{io} \exp -(E_D/RT) \tag{9}$$

where E_D is the activation energy for the diffusion, D_{io} is the diffusion rate constants, R is the molar gas constant, and T is the temperature in Kelvin. The E_D values were calculated from the slopes of the linear lines of the Arrhenius plots by the method of least squares as shown in Fig. 7. If the activation energies (E_0) are positive, then the permeation flux increases with increasing temperature, but the selectivity decreases. The negative values of the heat of sorption ΔH_S as calculated from the relationship: $\Delta H_S = E_J - E_D$, the results are shown in Table 3. The

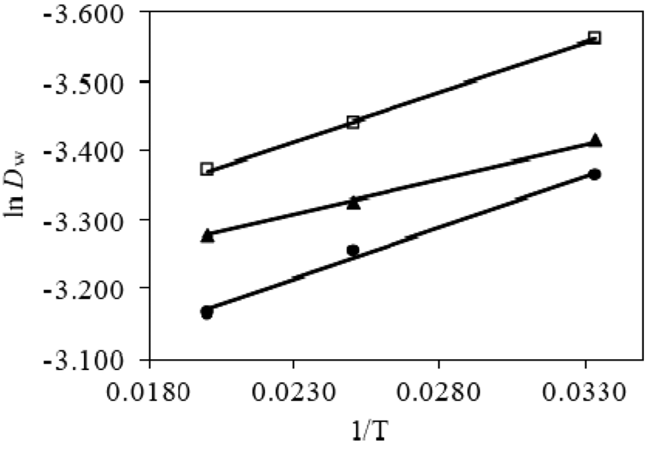


Figure 7. ln D_w vs. 1/T plots for plain CS (□), CS/GL-10 (▲) and CS/GL-20 (●) membranes at 10 wt.% of water in feed mixtures at different temperatures.

Table 6. Comparision of the present data with the reported literature data for water + 1,4-dioxane mixtures

Membranes	Wt.% of water in feed	J (kg/m^2 · h)	Selectivity (α)	References
Chitosan/gelatin (90:10)	10	0.118	302	Present work
DMDES/TMOS = 10/1	20	0.200	23	21
PVA crosslinked TDI	18	0.098	16	23
NaAlg-grafted- poly (acryl amide)	18	0.523	58	24
PVA chitosan crosslinked with GA	18	0.108	117	25
PVA/PMMA (95:5)	10	0.097	104	26
PVA/NaAg (5:95)	10	0.200	60	40
PVA/NaAg (10:90)	10	0.250	50	
PVA/NaAg (20:80)	10	0.270	48	
NaAlg (GA + UFS crosslinked 40–50 μm)	10	0.575	268	41
PVA/PEI	10	0.200	33	42
PVA-zeolite T composite (PVA-3)	10	0.213	1681	43
Chitosan and Nylon 66 blend	4.28	0.049	4789	44
PVA/PEI (5:1)	18	0.733	44	45

DMDS, dimethyldiethoxysilane; TMOS, tetramethoxysilane; PVA, poly(vinyl alchol); NaAlg, Sodium alginate; TDI, tolylene-2,4-diisocyanate, GA, glutaradehyde; PEI, polyethyleneimine.

calculated ΔH_S values for Pristine CS, Blend CS/CL-10, and CS/CL-20 membranes are −0.50, −0.43, and −1.79 kJ/mol, respectively. The negative values of ΔH_S suggest the exothermic sorption process.

Comparison of the Present PV Results with the Reported Data

A comparison of the present PV data (flux and selectivity) with the previously published results is given in Table 6. It is observed that the selectivity values of the present data are much superior to the published results for water-1,4-dioxane mixtures at 30°C. However, the flux values are slightly lower than the published reports.

CONCLUSIONS

The study demonstrates the applicability of two well-known carbohydrate polymers viz., chitosan and gelatin, from which blend membranes can be prepared in different ratios and membranes which were tested for PV dehydration of 1,4-dioxane. It was found that the membranes are selective to water over the entire feed mixture compositions; however, the separation capability of the membranes was affected by changes in the water feed composition, temperature, and the extent of membrane swelling. At 30°C for 10 wt.% gelatin containing blend membrane, the PV flux was $0.118\,\mathrm{kg/m^2 \cdot h}$ with selectivity 302 for 10 wt.% water containing the feed mixture. These results demonstrate the superiority of the blend membranes over that of the plain CS membrane for the effective dehydration of 1,4-dioxane. Arrhenius parameters and diffusion coefficients data seemed to vary depending upon the thermodynamic nature of the mixed feed media as well as the type of membrane polymers used. The temperature dependence of the PV results indicated a linear relationship for flux and diffusion coefficients, suggesting the Arrhenius trends.

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