

Thermal, viscoelastic, solution and membrane properties of sodium alginate/hydroxyethylcellulose blends[☆]

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Abstract

Solution and film blend compatibility of carbohydrate polymers, viz. sodium alginate and hydroxyethylcellulose have been studied. Blend solutions were prepared in water. Films of the individual polymers and their blends were prepared by solution casting and crosslinking with glutaraldehyde and urea–formaldehyde–sulfuric acid mixture. Compatibility of blends in solution was studied by density and viscosity, while blend compatibility in solid films was evaluated by differential scanning calorimetry, dynamic mechanical thermal analyzer and scanning electron microscopy. Solution density showed a linear trend with the blend composition. The glass transition of the blends lies in between the individual polymers. The glass transition temperature of sodium alginate was lowered with the addition of HEC in the blend. These results suggested the compatibility of sodium alginate and hydroxyethylcellulose blends. Storage modulus of sodium alginate film decreased after the addition of hydroxyethylcellulose. For the crosslinked blend films, storage modulus was higher than the respective uncrosslinked blend systems. A typical blend film was chosen for the pervaporation separation of water + tetrahydrofuran mixture, while the crosslinked sodium alginate film was tested for the pervaporation separation of water + 1,4-dioxane mixture.

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1. Introduction

Carbohydrate polymers are abundant in nature. Sodium alginate (NaAlg), a polysaccharide, is available in marine algae. It is a copolymer composed of β -D-mannuronate (*M*) and α -L-guluronate (*G*) residues arranged in different *M/G* ratios. These residues are arranged in a blockwise fashion, constructed not only of homopolymer blocks of *MM* or *GG*, but also consist of alternating blocks of *M* and *G* (Fischer & Dorfel, 1955). NaAlg has been the most widely used material in pharmaceuticals (Kulkarni, Soppimath, Aminabhavi, Dave, & Mehta, 2000; Kulkarni, Soppimath, Aminabhavi, & Rudzinski, 2001; Kulkarni, Soppimath, Aralaguppi, Aminabhavi, & Rudzinski, 2000) as well as a

membrane in the separation of aqueous-organic mixtures (Aminabhavi et al., 2004; Kurkuri, Kulkarni, & Aminabhavi, 2002; Toti & Aminabhavi, 2002, 2004). Hydroxyethylcellulose (HEC) is water-soluble cellulose ether and is non-ionic carbohydrate polymer, which is compatible with a wide range of other water-soluble polymers (Chanachai et al., 2000; Nicholson & Merritt, 1985; Savage & Ethers, 1971). HEC is a commercially useful polymer that finds applications as a thickener in latex paints and paper finishes.

In the literature (Chanachai et al., 2000), blends of HEC and chitosan (CS), also a carbohydrate polymer, have been used as membranes in pervaporation (PV) separation of aqueous-alcohol mixtures. Due to the importance of membrane properties of NaAlg and HEC in separating aqueous-organic mixtures (Vijaya Kumar Naidu, Krishna Rao, & Aminabhavi, 2005), we thought of investigating their blend compatibility using a battery of techniques in solution (such as density and viscosity) and in solid (TGA, DSC, SEM and DMTA) states. Furthermore, the results are discussed to study the effect of crosslinking on the thermal and viscoelastic properties of the membranes. The

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crosslinked NaAlg and blend membranes of NaAlg with 10 mass% of HEC were used in the PV separation of water + 1,4-dioxane and water + tetrahydrofuran (THF) mixtures, respectively. PV process is environmentally cleaner process than distillation since the membrane acts as a third phase instead of an entrainer, benzene (a carcinogen!) to break the azeotrope. In addition, environmentally acceptable NaAlg and HEC carbohydrate polymers are more advantageous than the synthetic polymers.

2. Experimental

2.1. Materials

Hydroxyethylcellulose (HEC) was purchased from Polysciences, Inc., USA. Sodium alginate (NaAlg), glutaraldehyde (GA), acetone, urea, formaldehyde, sulfuric acid and hydrochloric acid were all purchased from s.d. fine Chemicals, Mumbai, India. Double distilled water was used throughout the study and its purity was checked by measuring its conductivity, which agreed well with the literature value of $0.043 \times 10^{-6} \text{ S cm}^{-1}$ within 2%.

2.2. Preparation of blend solutions

The 0.5 weight% of NaAlg and 0.5 weight% of HEC solutions were prepared by dissolving 1 g of each polymer in 200 mL of distilled water in two separate stoppered conical flasks. Eight different blend solutions of NaAlg and HEC were prepared by mixing NaAlg with HEC in the weight ratios of 5/95, 10/90, 20/80, 30/70, 40/60, 60/40, 70/30 and 80/20. From each of these blend solutions, 0.1, 0.2, 0.3, 0.4 and 0.5% (v/v) concentrated solutions were prepared volumetrically. These solutions were used for the measurement of solution density and viscosity.

2.3. Preparation of blend films

Blend membranes of NaAlg with HEC were prepared by solution casting method. Required amount of NaAlg was dissolved in distilled water by stirring over a magnetic stirrer (Jenway, model 1103, UK) for 24 h. To this, 5, 10, 20, 30, 50 and 70 weight% (with respect to sodium alginate) of HEC were added. Films thus prepared were designated as NH-5, NH-10, NH-20, NH-30, NH-50 and NH-70, respectively, while the plain sodium alginate and hydroxyethylcellulose were designated as NaAlg and HEC, respectively. Solutions were mixed uniformly and filtered to remove any foreign 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 room temperature. The dried membranes were peeled off carefully from the glass plate.

Blend membranes required two-stage crosslinking. In the first stage, the membranes were crosslinked by immersing in 75% aqueous-acetone mixtures containing 2.5 mL HCl and 2.5 mL GA for about of 24 h. After removing the membrane from the crosslinking bath, it was washed with water repeatedly and dried in an oven at 40 °C. In the second stage, the already crosslinked membrane was further crosslinked using a mixture of 2.5 weight% urea–2.2 weight% formaldehyde–2.5 weight% sulfuric acid containing 59 weight% of aqueous ethanol at room temperature for 2 h. The crosslinked membrane was washed repeatedly with deionized water and dried at room temperature for about 24 h. The membrane thickness as measured by a micrometer screw gauge was in the range of 35–40 μm . Only three blend membranes with 5, 10 and 20 weight% of HEC along with the plain NaAlg were crosslinked by using the procedure explained above. These were designated as NHC-5, NHC-10, NHC-20 and NaAlg-cross, respectively.

2.4. Blend compatibility studies

The compatibility of NaAlg and HEC polymers was studied by determining the density and viscosity of the blend solutions at 30 °C. The solid-state film blend compatibility was investigated by differential scanning calorimetry (DSC), dynamic mechanical thermal analyzer (DMTA) and scanning electron microscopy (SEM).

2.4.1. Density measurements

Dilute solution densities of the individual polymers and their blends were measured at 30 °C using a precision vibrating tube digital densitometer (Anton Paar, DMA, model 4500/5000, Graz, Austria). Temperature of the measuring cell was controlled to an accuracy of ± 0.001 °C by an inbuilt integrated Pt 100 measuring sensor. Reproducibility in the measured density was better than five units in the fifth decimal place.

2.4.2. Viscosity measurements

Dilute solution viscosities of the plain NaAlg, plain HEC and their blend solutions were measured at 30 °C using a fully automated Scott-Gerate Viscometer (model AVS 350, Hofheim, Germany). Efflux times were measured on a digital display to an accuracy of ± 0.01 s. Temperature of the bath (Scott-Gerate, model CT 050/2, Hofheim, Germany) was maintained constant at 30 °C within an accuracy of ± 0.01 °C. The estimated error in viscosity was ± 0.001 mPa. s.

2.4.3. Differential scanning calorimetric (DSC) studies

DSC thermograms of NaAlg, HEC, uncrosslinked and crosslinked blends were recorded on a Rheometric Scientific DSC, (Model DSC-SP), UK. The DSC thermograms were recorded from 25 to 350 °C at the heating rate of 10 °C/min in an inert atmosphere. The blend samples were first heated from 25 to 150 °C to

remove the moisture present in the membranes. The sample was then cooled to 30 °C using liquid nitrogen and the second heating scans were performed from 30 to 350 °C.

2.4.4. Dynamic mechanical thermal analyzer (DMTA) studies

Dynamic mechanical properties (storage modulus, loss modulus and $\tan \delta$) of the uncrosslinked and crosslinked NaAlg and its blends with HEC were measured using Rheometric Scientific, USA, DMTA IV instrument operated in tensile mode at a frequency of 1 Hz at the heating rate of 6 °C/min to determine the glass transition temperature (T_g) and thermal behavior of the blends over the temperature range of –50 to 200 °C.

2.4.5. Scanning electron microscopic (SEM) studies

The plain NaAlg and NaAlg-HEC-10 films were gold-coated to a thickness of about 15 nm. Then SEM photographs were taken on a Leica 400, Cambridge, UK, scanning electron microscope.

2.5. Pervaporation experiments

The procedure used in PV experiments was described earlier (Aminabhavi & Naik, 2002a,b). The effective membrane area was 32.43 cm². Weight of the feed mixture taken in the PV cell was 50 g. Temperature of the feed mixture was maintained constant by a thermostatic water jacket. Downstream pressure was maintained below 10 Torr using a vacuum pump (Toshniwal, Mumbai, India). Before the actual experiment, the test membrane was equilibrated for about 2 h with the feed mixture. After establishment of a steady state, permeate vapors were collected in traps immersed in liquid nitrogen. PV experiments were performed using different feed mixtures of water+organic component (1,4-dioxane or THF). Adding the required amount of solvent enriched the depleted solvent mixture in the feed compartment. The weight of permeate collected in the trap was noted and permeate composition was determined by measuring refractive index and comparing it with the established graph of refractive index vs. mixture composition.

For mixtures having lower amount of permeate, analysis was done using a Nucon Gas Chromatograph (model 5765) provided with a Thermal Conductivity Detector (TCD) equipped with a DEGS packed column of 1/8" ID having 2 m length. Oven temperature was maintained at 70 °C (isothermal), while the injector and detector temperatures were maintained at 150 °C. The sample injection volume was 1 µL. Pure hydrogen was used as a carrier gas at a pressure of 1 kg/cm². The GC response was calibrated for the column and for known compositions of water+1,4 dioxane or THF mixture. Calibration factors were fed into the GC software to obtain the analysis for unknown samples.

Pervaporation selectivity, α_{PV} was calculated as,

$$\alpha_{PV} = \left(\frac{P_A}{1 - P_A} \right) \left(\frac{1 - F_A}{F_A} \right)$$

where F_A is mass% of water in the feed and P_A is mass% of water in the permeate. The flux, J (kg m⁻²h⁻¹), was calculated using the weight of liquids permeated, W (kg), effective membrane area, A (m²) and measurement time, t (h) as

$$J = \frac{W}{At}$$

At least three independent measurements of flux and α_{PV} were taken under the same conditions of temperature and feed composition to confirm the steady-state pervaporation.

3. Results and discussion

3.1. Blend compatibility

3.1.1. Solution property studies

From the measured viscosity values, reduced viscosities of the plain polymers and the blend polymer solutions were calculated. The miscibility of polymer blends in solution was studied by plotting the reduced viscosity vs concentration of the blend solutions (data displayed in Fig. 1). Slopes of the straight lines were calculated for individual polymers and blends. Then, by using these data and following the procedure published earlier (Kurkuri, Kulkarni, & Aminabhavi, 2002), we have calculated the interaction parameter, Δb (see Table 1). Positive Δb values for all the compositions of the blend confirmed the

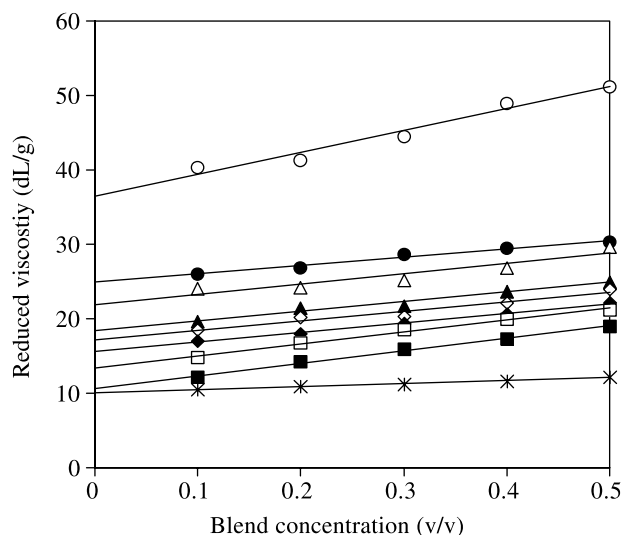


Fig. 1. Plots of reduced viscosity vs. concentration for (○) for pure NaAlg, (●) 5% HEC, (△) 10% HEC, (▲) 20% HEC, (◇) 30% HEC, (◆) 50% HEC, (□) 70% HEC, (■) 90% HEC and (✕) pure HEC.

Table 1
Interaction parameter, Δb values for different blend compositions

Percentage of HEC in NaAlg/HEC blend	Interaction parameter (Δb)
5	0.23
10	2.73
20	1.82
30	1.69
50	4.81
70	1.73
90	5.63

compatibility of NaAlg and HEC polymers (Kurkuri, Kulkarni, & Aminabhavi, 2002; Singh & Singh, 1983; Chee, 1990). Compatibility of the blends was also confirmed from the linear dependency of density (see Fig. 2) with weight% of HEC in the blend (Subha et al., 1999).

3.1.2. DSC analysis of the films

One of the most commonly used methods to estimate compatibility of the films of polymer blends is the determination of T_g of the blend compared to T_g of the individual polymers. For blends, where one component is crystalline, the observation of melting point (T_m) depression can be used as an evidence to support their compatibility (Miura, Kimura, Suzuki, Miyashita, & Nishio, 1999; Nishi & Wang, 1975; Imken et al., 1976). Sodium alginate is known to form semitransparent films having good mechanical strength, while HEC can form transparent and highly flexible films. The films were found to be moisture sensitive since both the polymers are water-soluble. The compatibility of NaAlg and HEC can be explained on the basis of the shift in T_g of the blend compared to T_g of the homopolymers. DSC thermograms of the plain NaAlg and HEC are presented in Fig. 3, whereas their blends are displayed in Fig. 4. For NaAlg, T_g was reported to be around

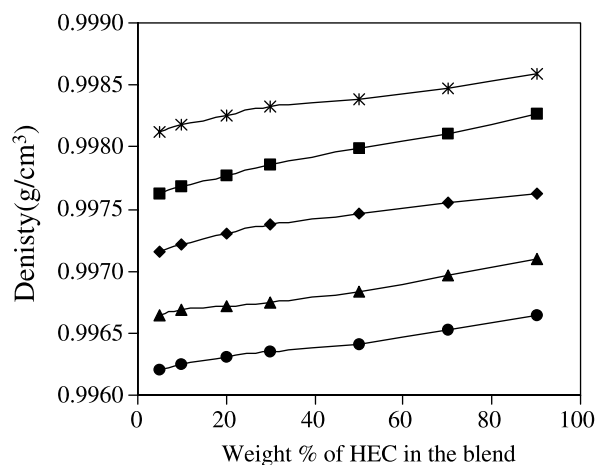


Fig. 2. Plots of density vs. mass% of HEC in blend for different concentrations: (●) 0.1%, (▲) 0.2%, (◆) 0.3%, (■) 0.4% and (✱) 0.5%.

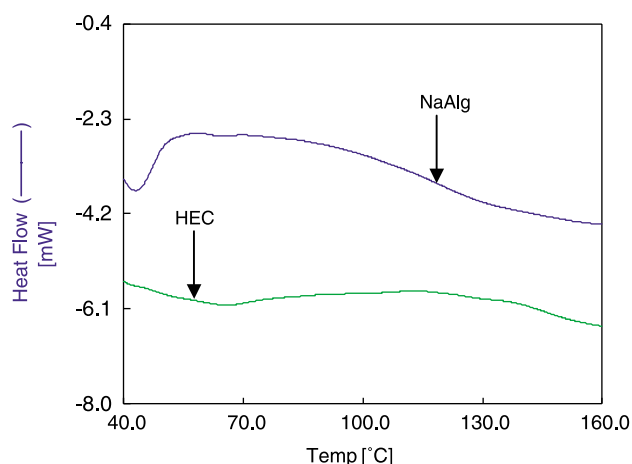


Fig. 3. DSC thermograms of NaAlg and HEC.

119 °C (Miura et al., 1999), while for HEC, T_g is around 65 °C. T_g of the blend systems is in between the T_g of individual polymers.

DSC thermograms of the crosslinked blend membranes along with the crosslinked plain NaAlg membrane are displayed in Fig. 5. NaAlg-crosslinked membrane has shown a sharp endothermic peak around 188 °C. The crosslinked blend membranes have shown endothermic transitions at 186, 183 and 165 °C, respectively, for NHC-5, NHC-10 and NHC-20 membranes. A systematic decrease in temperature of the endothermic peak from 188 to 165 °C with increasing HEC content in the blend suggests the compatibility of the blend at these compositions.

3.1.3. DMTA analysis of the films

The change in loss modulus (E'') measured as a function of temperature for plain NaAlg and HEC are shown in Fig. 6. For NaAlg/HEC blends, E'' vs temperature plots are shown in Fig. 7. For NaAlg, a dispersion peak around 130 °C was reported (Nisho & Manley, 1988) for the NaAlg/PVA blends, which was attributed to the amorphous phase

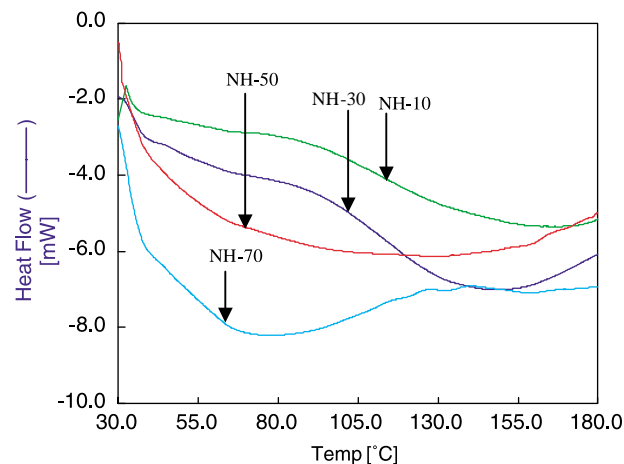


Fig. 4. DSC thermograms of uncrosslinked NaAlg/HEC blends.

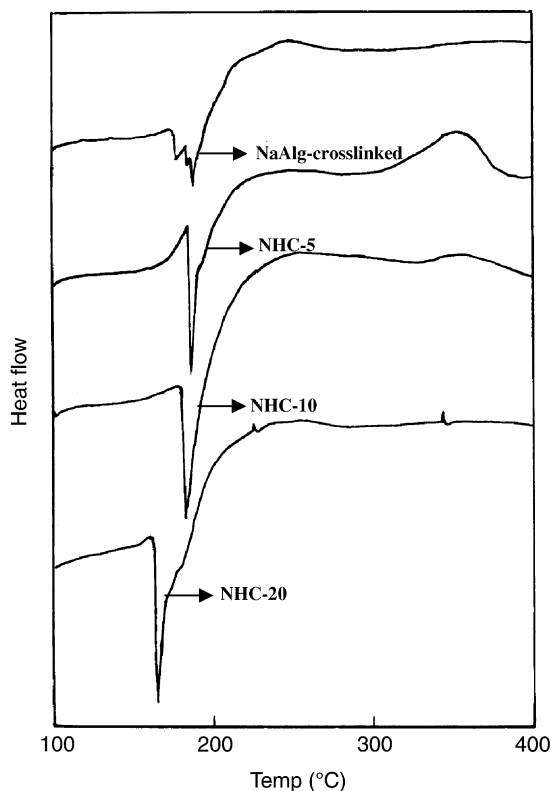


Fig. 5. DSC thermograms of crosslinked NaAlg/HEC blends along with NaAlg.

relaxation corresponding to T_g i.e. transition, α_a of NaAlg. In the present case, NaAlg film cast from the aqueous solution exhibited a dispersion signal centered around 125 °C (see Fig. 6) corresponding to T_g of NaAlg. The E'' curve of the plain HEC film showed a dispersion signal around 68 °C (see Fig. 6), which corresponds to T_g of the polymer. The DMTA data of NaAlg/HEC blends (Fig. 7) showed a general trend of depression in the position of α_a transition peak of NaAlg with increasing HEC content in the blend membranes. The T_g of the crosslinked blends was

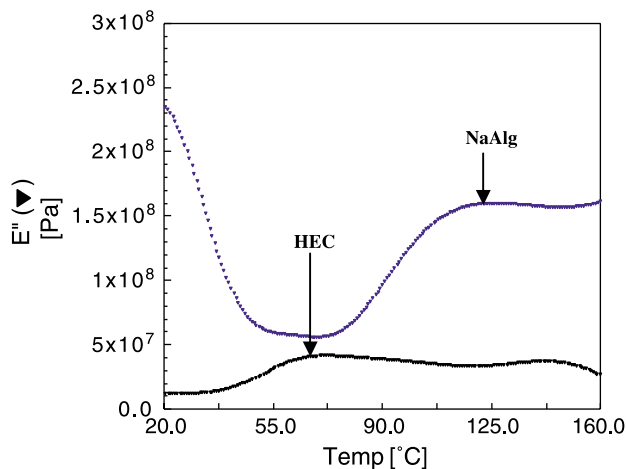


Fig. 6. Temperature dependence of loss modulus (E'') for NaAlg and HEC.

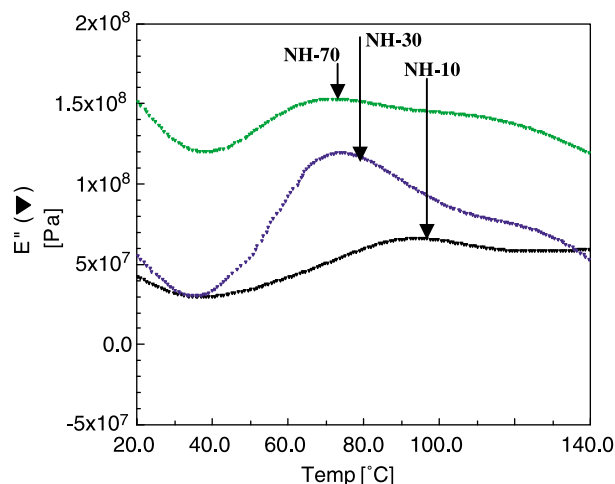


Fig. 7. Temperature dependence of loss modulus (E'') for NaAlg/HEC blends.

situated at the higher temperature than the respective uncrosslinked blends as shown typically in Fig. 8 for 20 weight% of HEC containing NaAlg blend.

The tensile storage modulus, E' is a measure of stiffness of the material. The E' vs temperature plots for the plain polymers (NaAlg and HEC) and NaAlg/HEC blends are shown, respectively (Figs. 9 and 10). A sharp fall in E' was observed for both uncrosslinked and crosslinked NaAlg films up to 55 °C (see Fig. 9). The fall in E' was shifted to lower temperature due to the addition of HEC into NaAlg, and the shift continued with increasing amount of HEC in the blend (see Fig. 10). This may be due to the more flexible nature of HEC chains than NaAlg. The extent of decrease in storage modulus is less in the crosslinked blends compared to their respective uncrosslinked counterparts. The E' of the plain NaAlg film (4.64×10^8 Pa) decreased by one order of magnitude after the introduction of HEC (NH-10), which

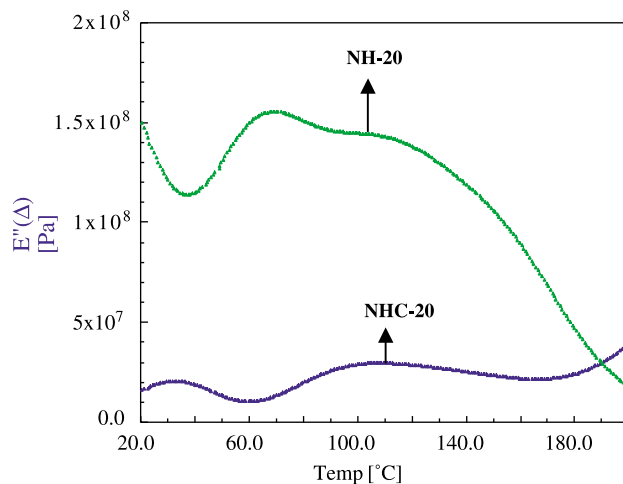


Fig. 8. Temperature dependence of loss modulus (E'') for NH-20 and NHC-20 blend membranes.

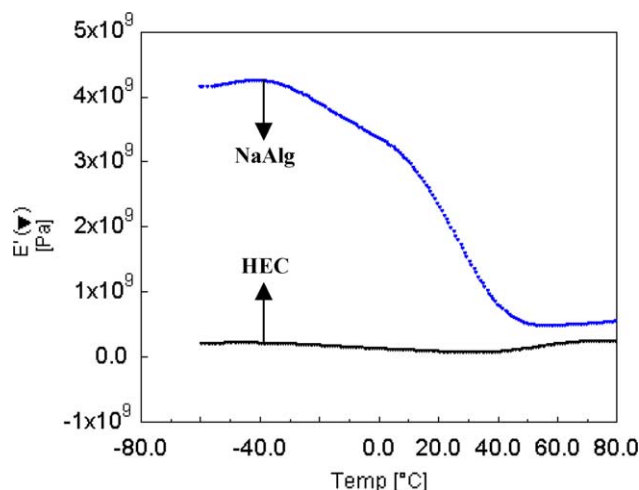


Fig. 9. Temperature dependence of dynamic storage modulus (E') for NaAlg and HEC.

continued at the higher loadings of HEC into NaAlg film. However, the E' values have the same order for the crosslinked NaAlg and NaAlg/HEC blends as shown in Fig. 11. This observation confirmed the crosslinking of HEC in the blends.

The molar mass between crosslinks, M_c calculated from the DMTA data are presented in Table 2. The M_c values increased with the addition of HEC to NaAlg. Generally, higher the crosslink density lower will be the M_c and more harder the film becomes. But, the chain flexibility will be higher in the uncrosslinked films. In the present case, an increase in M_c with the addition of HEC into NaAlg is possibly due to the introduction of higher flexibility to the blend polymer, since HEC is more flexible than NaAlg. The composition dependent shift in T_g of the blends after the addition of HEC followed the same trends as observed in the crystalline/amorphous portion of the polymer blends that are capable of forming miscible phases (MacKnight,

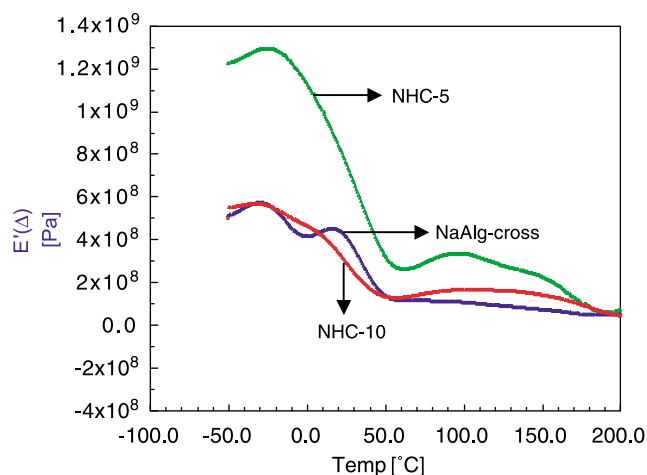


Fig. 11. Temperature dependence of dynamic storage modulus (E') for crosslinked membranes.

Karasz, & Fried, 1978; Olabishi, Robeson, & Shaw, 1979). The composition dependent shift in the T_g of NaAlg/HEC blend membranes studied by DSC and the observed linear variation of density with blend composition supports that NaAlg and HEC are compatible.

3.1.4. SEM analysis

Blend compatibility of NaAlg/HEC polymers was also confirmed by the identical morphology exhibited by NaAlg-cross and NHC-10 membranes as seen from the SEM micrographs shown in Fig. 12 (Kressler, Higashida, Inoue, Hecman, & Seitz, 1993).

3.2. Membrane performance

PV membranes are quite useful in separating mixtures at the azeotropic compositions. Water+1,4-dioxane and water+THF mixtures are known to form azeotropes at 18.1 and 6.7 mass% of water, respectively. Near the azeotropic feed compositions of these mixtures, we have experimented from 5 weight% of water to 15 weight% for the crosslinked NaAlg membrane in case of water+1,4-dioxane mixture and for the NHC-10 blend membrane in case of water+THF mixture. It was found that NHC-10 blend membrane was better for the PV separation of water+THF mixture, whereas the crosslinked NaAlg membrane was better for water+1,4-dioxane mixture (Vijaya Kumar Naidu et al., in press). These results are compiled in Table 3 and displayed in Fig. 13. Water flux has

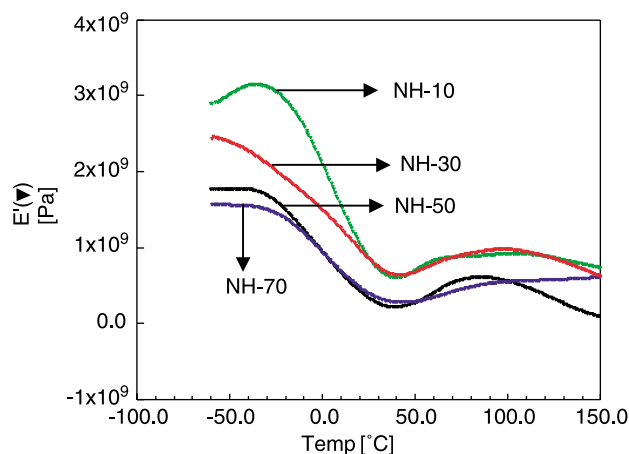


Fig. 10. Temperature dependence of dynamic storage modulus (E') for NaAlg/HEC blends.

Table 2
Molar mass between crosslinks (M_c) of the membranes

Membrane	$M_c \times 10^{-5}$ (kg/mol)
NaAlg-crosslinked	193
NHC-5	5079
NHC-10	9096

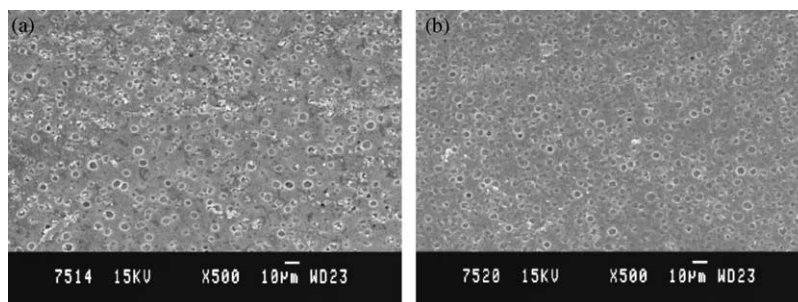


Fig. 12. Scanning electron micrographs of (a) NaAlg-cross and (b) NHC-20.

Table 3

Pervaporation results of water + 1,4-dioxane and water + THF mixtures for crosslinked NaAlg and blend membrane at 30 °C

Weight% of water		α_{pV}	J_w (kg/m ² h)	Weight% water		α_{pV}	J_w (kg/m ² h)
Feed	Permeate			Feed	Permeate		
Water + 1,4-dioxane				Water + THF			
NaAlg-crosslinked							
10	96.75	268	0.112	10	97.12	304	0.178
20	92.42	49	0.168	20	94.29	66	0.217
NHC-10							
10	93.37	127	0.135	10	99.41	1516	0.183
20	88.40	30	0.260	20	98.59	280	0.258
NaAlg-crosslinked				NHC-10			
5	96.79	573	0.106	5	99.41	3201	0.172
7.5	96.77	370	0.108	7.5	99.41	2078	0.176
10	96.75	268	0.112	10	99.41	1516	0.183
15	95.16	111	0.116	15	98.98	550	0.189

increased from 0.106 to 0.116 kg/m².h in case of water + 1,4-dioxane mixtures with increasing amount of water from 5 to 15 mass% in the feed mixture. However, the selectivity decreased from 573 to 111. On the other hand, for water + THF mixture, the flux has increased from 0.172 to 0.189 kg/m².h, but selectivity decreased from 3201 to 550 for the feed mixtures ranging from 5 to 15 weight% of water. The observed differences in flux and selectivity between these mixtures could be attributed to the differences in their thermodynamic properties in addition to the interactions of the mixtures with the membrane polymer.

The PV results are compared with the vapor liquid equilibrium (VLE) data for both the mixtures with the membranes of this study (see Fig. 14). In case of both the mixtures, the PV curves are higher than the VLE curves, suggesting that the mixtures are broken down at their azeotropic compositions in the presence of membranes acting as the third phase. In order to assess the reliability of the present data, we have compared in Table 4, the flux and selectivity results with those of the previously published data (Aminabhavi et al., 2004; Kurkuri & Aminabhavi, 2003; Kurkuri, Kumbar, & Aminabhavi, 2003; Oikawa, Tamura, Arai, & Aoki, 1995). The present PV results are much superior to those of the previously published results for both the mixtures.

4. Conclusions

Binary blend films comprising two carbohydrate polymers viz., sodium alginate and hydroxyethylcellulose were prepared by solution casting method. Blend compatibility in solution state was studied by density and viscosity data, while the DSC, SEM and DMTA judged the solid-state film compatibility. Judging from the observations of composition dependent T_g and a systematic depression in melting

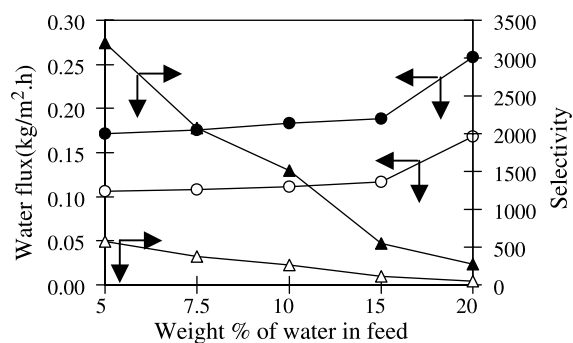


Fig. 13. Plots of water flux and selectivity vs. weight% of water in feed. Open symbols for water + 1,4-dioxane and closed symbols for water + THF mixtures.

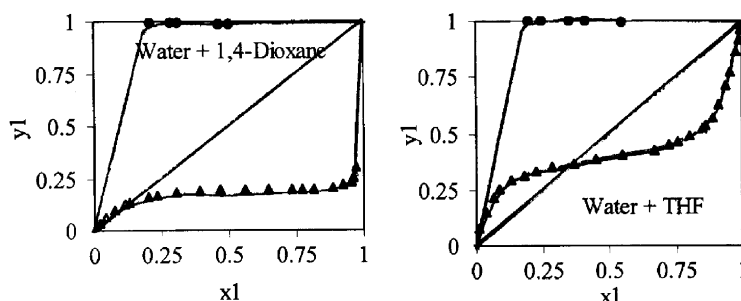


Fig. 14. Comparison of vapor liquid equilibrium curve (▲), with PV data (●) data.

Table 4

Comparison of PV performance of the present membranes with the literature

Membrane	Temperature (°C)	Weight% of water in feed	Total flux (kg/m ² h)	Selectivity	Reference
Water + 1,4-dioxane					
NaAlg (GA + UFS crosslinked)	30	10	0.115	268	Present work
NaAlg (GA crosslinked)	30	10	0.211	111	Aminabhavi et al. (2004)
NaAlg + 10 mass% of PEG + 5 mass% of PVA	30	10	0.058	351	Kurkuri and Aminabhavi (2003)
Water + THF					
NaAlg-HEC-10 (GA + UFS crosslinked)	30	10	0.191	1516	Present work
NaAlg (GA + UFS crosslinked)	30	10			
NaAlg (GA crosslinked)	30	10	0.209	291	Aminabhavi et al. (2004)
NaAlg + 10 mass% of PEG + 15 mass% of PVA	30	10	0.091	591	Kurkuri et al. (2003)
PMCP	30	6.7	0.125	1518	Oikawa et al. (1995)

NaAlg, sodium alginate; HEC, hydroxyethylcellulose; PAAm, poly(acryl amide); PVA, poly(vinyl alcohol); PEG, poly(ethylene glycol); PMCP, pyridine moieties containing poly(vinyl pyrrolidone); GA, glutaraldehyde; UFS, urea–formaldehyde–sulfuric acid.

temperature, it is reasonable to conclude that the blend of sodium alginate and hydroxyethylcellulose would form a thermodynamically miscible phase. Furthermore, the cross-linked membranes are found to be useful in the pervaporation separation of water + 1, 4-dioxane as well as water + THF mixtures.

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