

Miscibility Studies of Sodium Carboxymethylcellulose/Poly(Vinyl Alcohol) Blend Membranes for Pervaporation Dehydration of Isopropyl Alcohol

C. Venkata Prasad,¹ H. Sudhakar,¹ B. Yerri Swamy,² G. Venkata Reddy,³ C. L. N. Reddy,² C. Suryanarayana,⁴ M. N. Prabhakar,¹ M. C. S. Subha,² K. Chowdoji Rao¹

¹Department of Polymer Science and Technology, S. K. University, Anantapur 515003, Andhra Pradesh, India

²Department of Chemistry S. K. University, Anantapur 515003, Andhra Pradesh, India

³Department of Chemistry, S. R. Institute of Engineering and Technology, Anantapur 515003, Andhra Pradesh, India

⁴Naval Material Research Laboratory, Ambarnath, Mumbai, Maharashtra, India

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ABSTRACT: Miscibility studies of sodium carboxymethylcellulose/poly(vinyl alcohol) (NaCMC/PVA) blends of different compositions (100/0, 80 : 20, 60 : 40, 50 : 50, 40 : 60, 20 : 80, and 0 : 100) were investigated using viscometric method. NaCMC, PVA, and their blend membranes were prepared by solution-casting technique and were then crosslinked with glutaraldehyde (GA). The effect of blend composition on mechanical, swelling, and pervaporation results (flux and selectivity) was also investigated in this study. Attenuated total reflectance–Fourier transform infrared spectroscopy (ATR–FTIR) results showed that the blends are miscible over the entire studied composition range and further confirmed the crosslinking reaction with GA. FTIR studies reveal that the blends containing 50 : 50 (NaCMC/PVA) are an optimum miscible blend. Thermogravimetric analysis confirms that the thermal stability increased with increase in NaCMC

content in NaCMC/PVA blend membrane. XRD and DSC showed a corresponding decrease in crystallinity and increase in melting point with increase in NaCMC content, respectively. NaCMC/PVA blends of all the composition under study were used for dehydration of isopropyl alcohol at different compositions of IPA/water mixture (90 : 10, 87.5 : 12.5, 85 : 15, and 82.5 : 17.5) at 35°C. Swelling studies and PV results reveal that increase in NaCMC content in the blend leads to an increase in flux of water, whereas selectivity decreases. The optimum flux and selectivity were observed for the blend containing 50 : 50 NaCMC/PVA content at a feed ratio of 87.5 : 12.5 IPA/water. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2271–2281, 2011

Key words: miscibility; sodium carboxymethylcellulose; ATR–FTIR; swelling studies; pervaporation

INTRODUCTION

Polymer blends represent class of materials with better mechanical properties and biocompatibility than those of single components.^{1,2} The basis of polymer–polymer miscibility may arise from any specific interaction such as hydrogen bonding, dipole–dipole forces, and charge transfer complexes for homo-polymer mixtures.^{3–5} The importance of polymer blending has been increased in the recent years because of the preparation of polymeric materials with desired properties, low-basic cost, and improved process ability. Polymer blends are physical mixtures of structurally different polymers or copolymers, which interact through secondary forces with no covalent bonding⁶ that are miscible at molecular level.

Sodium carboxymethylcellulose (NaCMC) is carboxymethyl ether of cellulose, a well-known natural polysaccharide comprising the fibrous tissue of plants. Because of its nontoxic, biocompatible, biodegradable, and abundantly available material,^{7–10} it is widely used in different fields ranging from technological industries to the biological, pharmaceutical, petroleum, and medical fields.^{11–14} It has also been used in membrane preparation for pervaporation (PV) dehydration of several-organic compounds from their aqueous feed solutions. NaCMC has also been used as a matrix material in drug-delivery applications.^{15,16} However, because of intrinsically poor mechanical properties of carbohydrate polymers, attempts have been made to develop their blends with the other well-known man-made polymers.

Polyvinyl alcohol (PVA) has received a great deal of attention due to its considerable applications^{17–23} either pure or composite with other materials. It is a semicrystalline, water-soluble, and water-swelling commodity polymer of major industrial importance. Because of its compatible nature with a wide range

Correspondence to: K. C. Rao (chowdojirao@gmail.com).

of water-soluble polymers, it has also been widely used in adhesives, textile fibers, paper products, and PV membranes.²⁴ This versatile material has been more recently used as drug release media²⁵ and is being applied in other biomedical applications.^{26,27} Congming and Kong¹⁶ used NaCMC/PVA blend hydrogel for controlled release of ketorolac tromethamine. Shehap²⁸ studied the compatibility studies of NaCMC/PVA and reported that this blend is compatible in all compositions.

Isopropanol is an important base chemical for a number of applications ranking among the top 20 intermediates. It is also used as a solvent in paint industries and in resin production. Water and isopropyl alcohol (IPA) form azeotropes, and their separation by simple distillation is not very easy due to their close boiling point. As a viable alternative, PV dehydration membranes have been widely used for dehydration of IPA.^{29,30}

In continuing efforts to tackle IPA separation problem using membranes and to search for new environmentally polymeric materials, we thought of combining the properties of NaCMC and PVA to develop the type of novel membranes for the PV dehydration of IPA. Blending of cellulose (in the present case, NaCMC) with PVA is expected to be a useful method to improve the mechanical properties of NaCMC. By systematic variation of the composition, specific characteristics can be obtained for desired applications. In the present work, based on the above considerations, NaCMC/PVA membrane is expected to develop to be used in PV separation of water/IPA mixture. The authors made an attempt to prepare the blend membranes comprising varying compositions of NaCMC and PVA in blend membranes for PV dehydration of IPA.

PV performance of NaCMC/PVA blend membranes, when compared with the pristine NaCMC and PVA membrane, revealed an improved performance. Particularly, the developed membranes were found to be much better than those blend membranes studied earlier. To the best of our knowledge, this type of blend combination is used first time for the PV dehydration of IPA from its feed aqueous solution.

MATERIALS AND METHODS

NaCMC [viscosity (1 w/v %), 1100–1900 cps] was purchased from Merck, Mumbai, India, PVA (mol. wt., 70,000) was purchased from Hi-media (India), glutaraldehyde (GA), hydrochloric acid (HCl), IPA, and acetone are all of analaR grade purchased from Qualigens (Mumbai, India). Doubled-distilled water collected in the laboratory was used through out this research work. All the chemicals were used as received without further purification.

Preparation of membranes

NaCMC, PVA, and their blend membranes of different compositions were prepared by solution-casting method. Following is the procedure adopted for membrane preparation:

Required amount of NaCMC and PVA (1 g each) was dissolved separately in 100-mL distilled water (PVA in hot water) under constant stirring (Remi Motor) for overnight. These solutions were filtered to remove foreign matter and air bubbles and poured onto a cleaned glass plates separately and were kept in a dust-free atmosphere and allowed to dry in oven at 40°C. The dried membranes were crosslinked by dipping in a glass tray containing acetone/water mixture (85 : 10) to which 2.5 mL GA (crosslinker) and 2.5 mL HCl (activator) was added. Dipping was continued for 2 h, then the membranes were removed from the tray and rinsed with distilled water to remove the surface adhered cross-linking agent and then dried in vacuum at 40°C to constant weight, and membranes thus obtained were designed as NaCMC and PVA, respectively.

Blend membranes of NaCMC and PVA were prepared by varying NaCMC and PVA (80/20, 60/40, 50/50, 40/60, and 20/80) contents in the blend, and the membranes were crosslinked as described earlier. Membranes thus formed were designed as NaCMC80, NaCMC60, NaCMC50, NaCMC40, and NaCMC20. The completely dried crosslinked membranes were used for further analysis. Blending of the membrane was assessed by Fourier transform infrared spectroscopy (FTIR) and DSC analysis.

Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectra of NaCMC, PVA, and their blend membranes (crosslinked and uncrosslinked) were taken using Bomem MB-3000 (Make: Canada) FTIR spectrometer, equipped with attenuated total reflectance (ATR). Membranes were characterized at room temperature from 4000 to 400 cm^{-1} under a N_2 atmosphere at a scan rate of 21 cm^{-1} .

Thermal properties

DSC and TGA curves of NaCMC, PVA, and their blend membranes of different compositions were recorded using TA instruments differential scanning calorimeter (Model-SDT Q600, USA). The analysis of the samples was performed at heating rate of 10°C/min under N_2 atmosphere at a purge speed of 100 mL/min.

X-ray diffraction

The X-ray diffraction (XRD) patterns of the membrane samples were obtained with an Inel

diffractometer (Paris, France) with monochromatized Cu K α radiation (wavelength 0.154 nm at 40 kV, 50 mA, and scan speed of 1°/min in a 2 θ range of 5°–40°) at room temperature.

Swelling studies

Equilibrium-swelling experiments were performed in various water/IPA mixtures containing 0–17.5% water at 35°C \pm 0.5°C in an electronically controlled incubator (WTB Binder, Model BD-53, Tuttlingen, Germany). Circularly cut (diameter = 2.5 cm) disc-shaped membranes were stored in a desiccator over anhydrous calcium chloride maintained at 30°C for about 24 before performing the swelling experiments. Mass of the soaked samples was measured using a digital Adam Mettler digital balance (Model AAA 160L, Greifensee, Switzerland) with an accuracy of \pm 0.01 mg. The degree of swelling was calculated using the following equation 1

$$\text{Degree of swelling (\%)} = W_{\infty} - W_0 / W_0 \times 100 \quad (1)$$

Mechanical properties

The equipment used for carrying out the test was UTM (Instron, UK) at an operating head load of 5 kN. Cross-sectional area of the sample of known width and thickness was calculated. The membranes were then placed between the grips of the testing machine. The grip length was 4 cm at a cross-head speed of 12.5 mm/min. Tensile strength was calculated using the equation:

$$\begin{aligned} \text{Tensile strength} \\ = \text{Max.load/Cross-sectional area(N/mm}^2) \quad (2) \end{aligned}$$

$$\begin{aligned} \% \text{ Elongation} \\ = \text{Strain at break - initial strain/Initial strain} \quad (3) \end{aligned}$$

Miscibility studies of NaCMC/PVA blend solution

Miscibility studies of NaCMC/PVA blend solutions of different compositions ranging from 0 to 100% NaCMC in the blend were determined by viscometric measurements at 35°C. The total weight of the two polymers was always maintained at 1 g/dL. The relative viscosities of the blend solutions were determined at 35°C using an Ubbelohde suspended level viscometer.

PV experiments

Pervaporation (PV) experiments were carried out with a laboratory test cell. The feed is kept at a con-

stant temperature (35°C) by a temperature control unit, and a centrifugal pump circulates the feed. The membrane module contains a circular flat sheet membrane with a diameter of 6 in. The permeate is collected in a glass container and cooled in a Dewar flask with liquid nitrogen. The vacuum is maintained by a two-stage vacuum pump. The experimental procedure remained the same as reported elsewhere.³¹

Flux was measured for water at different compositions of water/IPA mixture. The equation for flux J per unit surface area of the membrane ($\text{m}^3 \text{m}^{-2} \text{s}^{-1}$) was calculated using the following equation:

$$J = D_i \times S_i \quad (4)$$

where D_i is the diffusion coefficient of the component in the membrane and S_i is the solubility coefficient of the component in the membrane. For the evaluation of the separation achieved with a given membrane, the separation of IPA from the feed solution was evaluated. The concentration of IPA in the feed and permeate fractions was measured using refractometer (Abbe's).

RESULTS AND DISCUSSION

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is of importance to study the molecular structure. Intermolecular interactions occur when different polymers are compatible. Therefore, the FTIR spectra of the blends are different from those of pure polymers, which is useful to study the compatibility between two polymers. Figure 1(a) shows the infrared spectra of NaCMC (a), PVA (b), and their blend of 50/50 composition in the range of 4000–500 cm^{-1} . The IR spectra of NaCMC/PVA (c) showed absorption bands at 3418 cm^{-1} due to $-\text{OH}$ stretching vibrations of NaCMC and PVA³² and additional bands at 1022–953 cm^{-1} ($=\text{C}-\text{H}$ stretch) and 1435–1409 cm^{-1} (CH_2 stretch) that belong to spectra of PVA. Bands at 1618 cm^{-1} were attributed to the characteristic absorptions of asymmetrical stretching vibration of COO^- of NaCMC.³³ The strong absorption band at 1616 cm^{-1} of NaCMC membrane shifted to 1607 cm^{-1} in NaCMC50. Based upon these results, it seems that the COO^- and OH groups of NaCMC should participate in intermolecular hydrogen bonds with the OH groups of PVA, respectively. In case of crosslinked membrane, all the characteristic bands of both PVA and NaCMC can be observed in addition to a new band at 1021 cm^{-1} due to the formation of an acetyl ring³⁴ formed between hydroxyl groups of NaCMC and PVA due to the reaction with GA. These data confirm the successful crosslinking of NaCMC/PVA with GA. From Figure

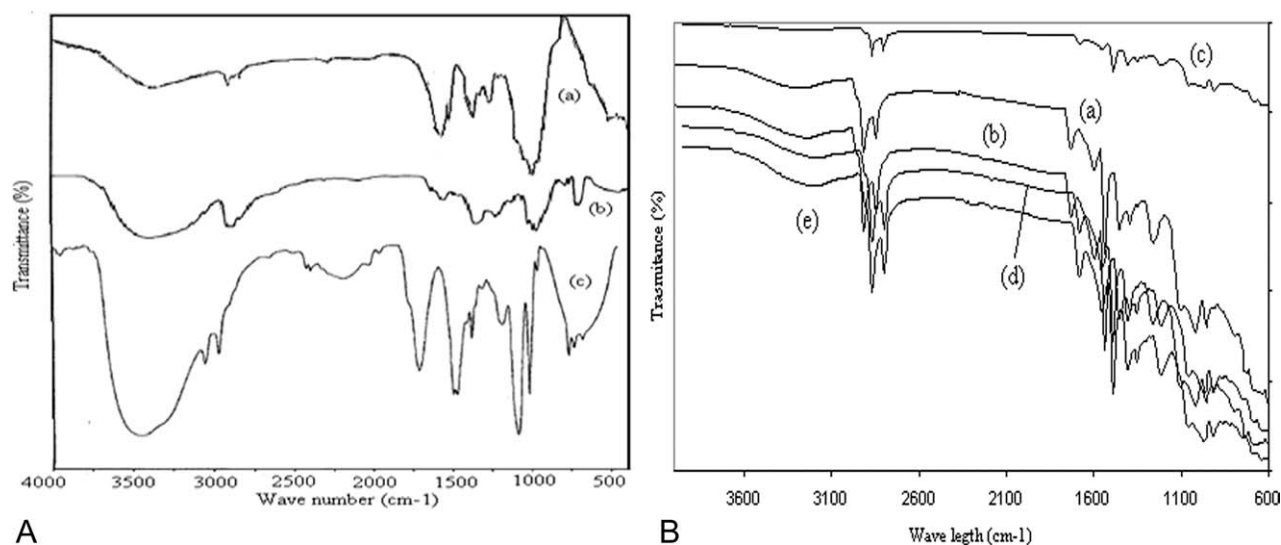


Figure 1 A: FTIR spectra of NaCMC (a), PVA (b), and NaCMC50 (c) membranes. B: FTIR spectra of NaCMC20 (a), NaCMC40 (b), NaCMC50 (c), NaCMC60 (d), and NaCMC80 (e) membranes.

1(b), it is also observed that the peak at 1618 cm^{-1} shifted to lower wave length and the bands at around 3418 broaden and shifted to higher wave-length with increase in the NaCMC composition. This may be due to the participation of intermolecular hydrogen bonding between OH and COO—groups of NaCMC and PVA with GA,³⁵ indicating that the blends are compatible in all compositions.

Scanning electron microscope

Figure 2 shows the SEM images of NaCMC (a), PVA (b), and their blends of different compositions (20/80, 40/60, 50/50, 60/40, and 80/20). From Figure 2, the surface morphology of NaCMC (a) and PVA (b) membranes having smooth surface. Figure 2 also gives the surface morphology of NaCMC/PVA blend membranes with different blending compositions. It is noticed from SEM studies that the morphology of the blends shows homogeneous in nature as observed in case of NaCMC and PVA. Hence, we conclude that the blends of different formulations are miscible in nature; this was also confirmed from viscometric studies.

Differential scanning calorimetry

DSC thermograms of NaCMC, PVA, and their blend membrane (NaCMC50) are displayed in Figure 3. DSC analysis shows that the melting points of NaCMC and PVA membranes decrease on blending NaCMC with PVA, and the melting peak is widen (Fig. 3). The melting points of PVA, NaCMC, and NaCMC-50 membranes are 212.1°C , 213.1°C , and 192.7°C , respectively. Evidently, the interaction between NaCMC and PVA weakens the interaction between PVA chains and hinders the crystallization.

DSC thermograms show that the T_g increases with increase on blending NaCMC with PVA. Blending of NaCMC with PVA will enhance the interaction between NaCMC and PVA, and this renders PVA chains more rigid and increases the glass-transition temperature of the membranes. Xiao and Gao¹⁶ were also reported similar observations in case of NaCMC/PVA hydrogels.

Thermogravimetric analysis

The results of thermogravimetric analysis of pure NaCMC, PVA, and their blend membranes are shown in Figure 4(a,b). The three active weight-loss steps of the blend membranes were found at about $100\text{--}120$, $250\text{--}400$, and $400\text{--}500^{\circ}\text{C}$. The first step was due to the loss of moisture. The second step was attributed to the disassociation of intermolecular side chains.³⁶ The third weight loss was believed to be caused due to chemical reaction, such as main-chain disassociation or rearrangement.³⁶ The starting temperature of the greatest decomposition for the blend membranes is in the order of NaCMC20 (290°C), NaCMC40 (281°C), NaCMC50 (260°C), and NaCMC60 (255°C). NaCMC80 (250°C), NaCMC (248°C), and PVA (262°C). According to Figure 4(a,b), it is understood that the thermal stability of the blend films was improved by blending NaCMC with PVA due to hydrogen-bonding interactions between NaCMC and PVA molecules.

X-ray diffraction

X-ray diffraction (XRD) was performed to investigate whether the crystalline portion of PVA might be influenced or altered by mixing it with NaCMC. The scanning of the samples was carried with an X-ray

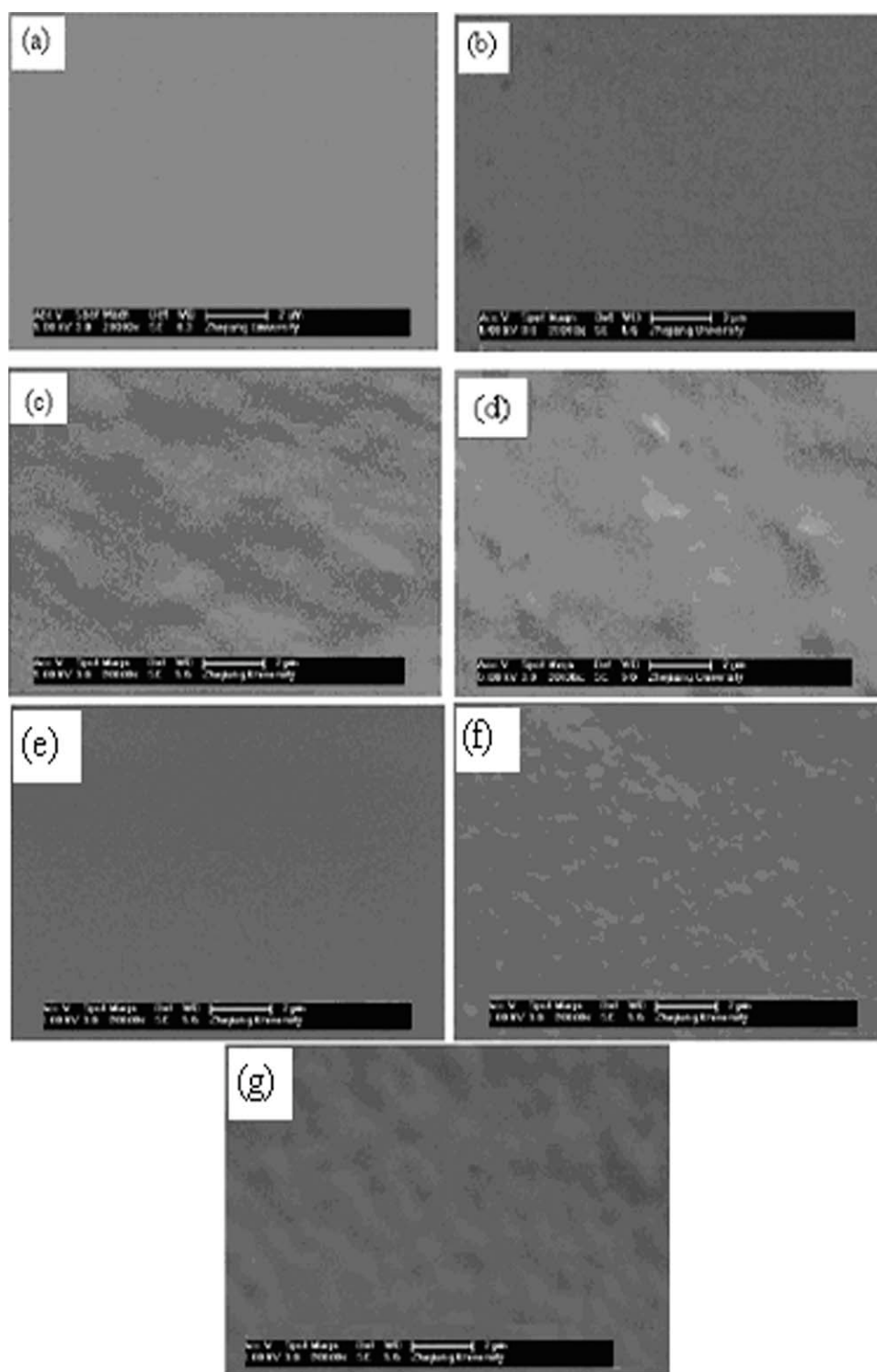


Figure 2 SEM images of surface morphology of NaCMC (a), PVA (b), NaCM20 (c), NaCMC40 (d), NaCMC50 (e), NaCMC60 (f), and NaCMC80 (g).

diffractometer at room temperature. The typical XRD patterns of PVA, NaCMC and their blend of 50 : 50 compositions are shown in Figure 5. It is clear that the samples under investigation are not completely amorphous, but have a relatively higher degree of crystallinity. The observed crystalline

peaks in both PVA and NaCMC are in good agreement with that reported previously.^{37–39} The diffractogram of the blend is similar to pure NaCMC and PVA, which indicate that this blend is miscible. Perhaps, the miscibility of this blend can result due to hydrogen bonding interaction.

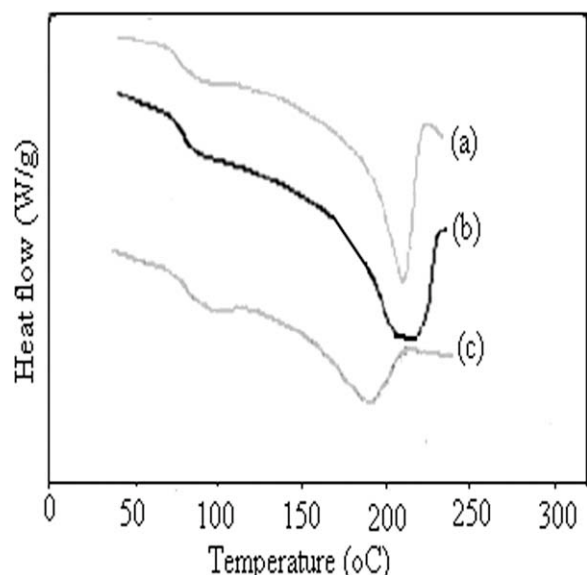


Figure 3 DSC thermograms of PVA (a), NaCMC (b), and NaCMC50 (c) membranes.

Miscibility studies

The measured values of densities (ρ) (not shown) and absolute viscosities (η_{ab}) were used to calculate the values of relative viscosities (η_r) and reduced viscosities (η_{red}) over the wide range concentrations of blend solutions of different compositions [0/100, 20/80, 40/60, 50/50, 60/40, 80/20, and 100/0 of 1% (w/v)] of NaCMC/PVA blends in water at 35°C. The absolute viscosity versus concentration curves for different compositions of the blends are shown in Figure 6(a). It is clearly evident from Figure 6(a) that the curves are linear in nature for all the blend

compositions, which, in turn, indicate that these blends are miscible in all compositions.⁴⁰

From Figure 6(a), it is also observed that, as the concentration of NaCMC increases in the blend, absolute viscosity also increases. This may be attributed that the —OH group of PVA can interact with several chains of —COO⁻ of NaCMC and would form highly crosslinked structure leading to high-viscosity solution due to increase in hydrogen bonding between hydroxyl groups of NaCMC and PVA.

The Huggins plots of reduced viscosity against concentration for different compositions of NaCMC/PVA blend at 35°C are shown in Figure 6(b). On extrapolating to zero concentration, the intrinsic viscosities were determined, and the values of NaCMC, PVA, and NaCMC/PVA blends of different compositions (20/80, 40/60, 50/50, 60/40, and 80/20) are 22.7, 5.12, 7.21, 11.36, 14.87, 16.93, and 19.29 dL/g, respectively. These values indicate that the intrinsic viscosity values of NaCMC/PVA blends for different compositions are in between the individual hom-polymer values. These attractive interactions may lead to decrease the intermolecular excluded volume effect and decrease the hydrodynamic volume. As a consequence, the NaCMC/PVA blend coils expand, which causes an increase in the intrinsic viscosity.

Chee and Sun methods

To quantify the miscibility nature of the present polymer blend system, interaction parameters ΔB and μ suggested by Chee and α suggested by Sun and Wang⁴⁰ were calculated with the help of the following equations for NaCMC-PVA blend systems

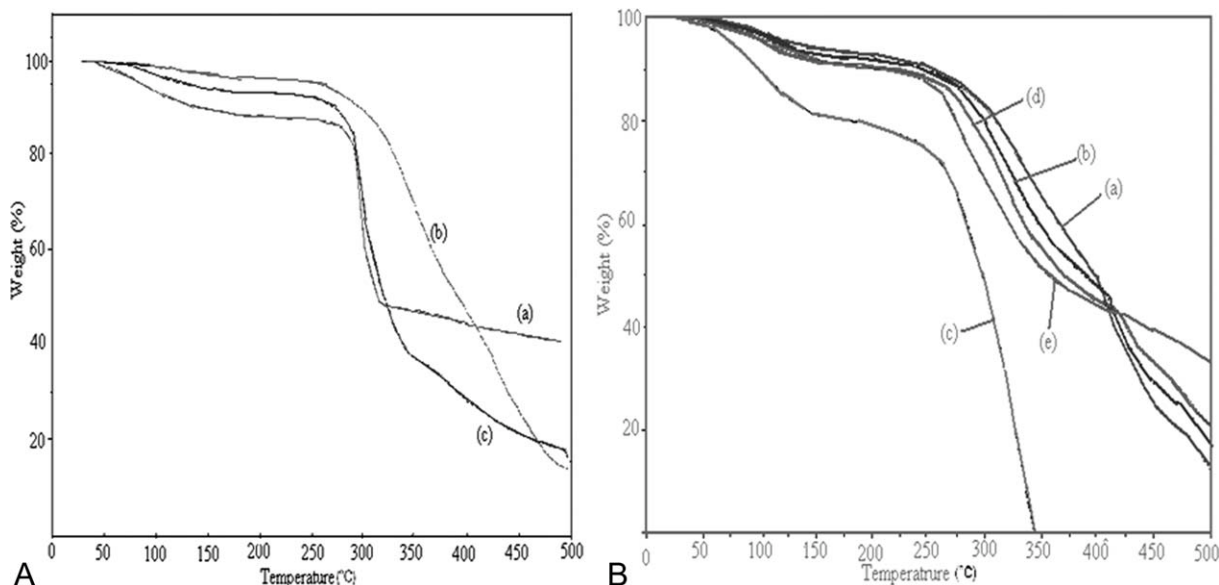


Figure 4 A: TGA curves of PVA (a), NaCMC (b), and NaCMC50 (c) membranes. B: TGA curves of NaCMC20 (a), NaCMC40 (b), NaCMC50 (c), NaCMC60 (d), and NaCMC80 (e) membranes.

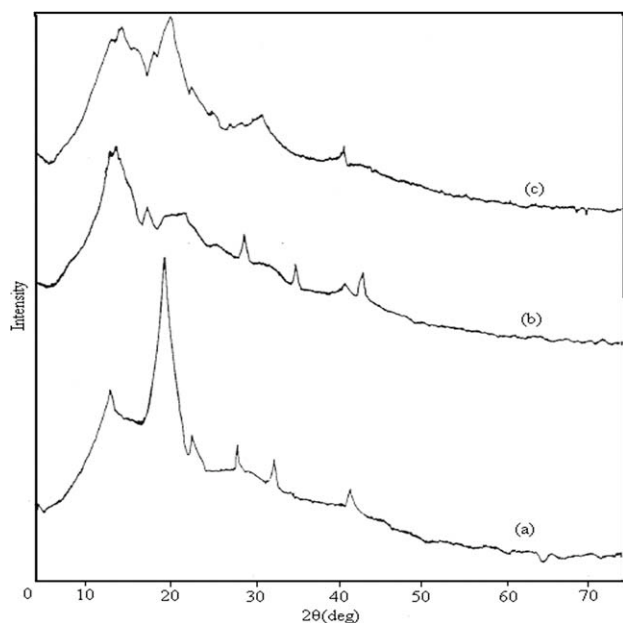


Figure 5 X-ray diffraction patterns of PVA (a), NaCMC (b), and NaCMC50 (c) blend membranes.

in water at 35°C, and the values are presented in Table I.

$$\Delta B = b - \bar{b}/2w_1w_2$$

where

$$\bar{b} = w_1b_{11} + w_2b_{22} \tag{5}$$

where b_{11} and b_{22} are the slopes for the reduced viscosity curves (obtained from Fig. 8.6b) for the pure components, and b is related to Huggins coefficient K_H as

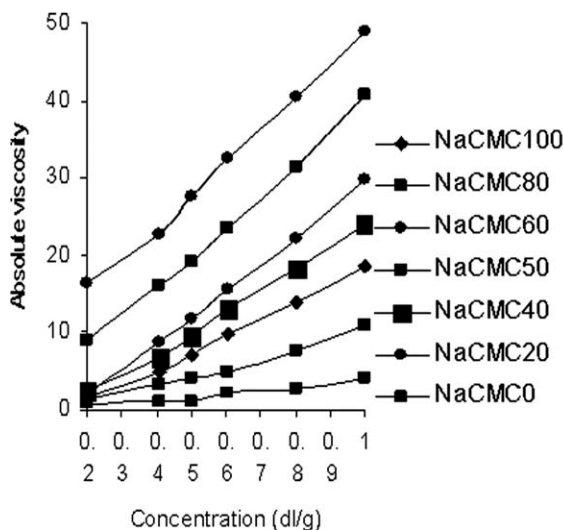


TABLE I
Chee and Sun's Interaction Parameters for Different Compositions of 1% (w/v) NaCMC/PVA Blend in Water at 35°C

Formulation code	Chee's differential interaction parameters		Sun's miscibility parameter ($\alpha \times 10^3$)
	ΔB	μ	
NaCMC20	+2.12	+0.12	+3.16
NaCMC40	+11.24	+0.24	+3.72
NaCMC50	+9.36	+0.13	+3.93
NaCMC60	+6.97	+0.079	+4.19
NaCMC80	+3.14	+0.096	+4.92

$$b = K_H[\eta]^2 \tag{6}$$

where $[\eta]$ is the intrinsic viscosity for binary system, and it is modified and given as

$$b = w_1^2b_{11}^2 + w_2^2b_{22}^2 + 2w_1w_2b_{12} \tag{7}$$

where b_{12} is slope for the blend solution.

However, Chee's theory fails, because experimental data are in conflict with the theoretical predictions. Using these values, Chee defined a more effective parameter:

$$\mu = \Delta B / \{[\eta]_2 - [\eta]_1\}^2 \tag{8}$$

where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure component solutions.

The values of μ are calculated and also included in Table II. The polymer blend is miscible if $\mu \geq 0$ and immiscible when $\mu < 0$.

Recently, Sun and Wang⁴⁰ have also suggested a new formula for the determination of miscibility of polymer blends.

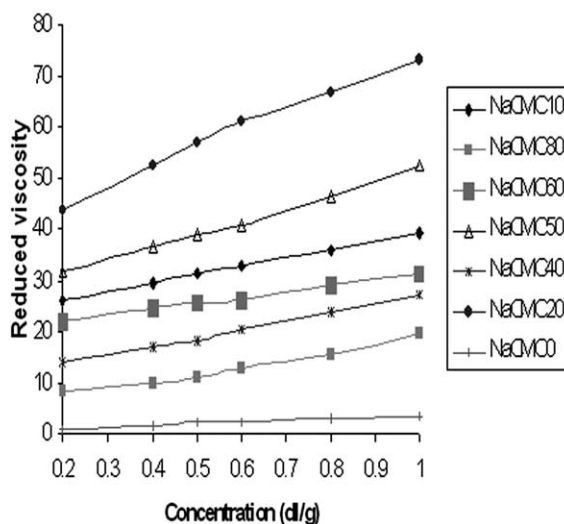


Figure 6 (a) Variation of absolute viscosity with concentration of different compositions of NaCMC/PVA blends in water at 35°C. (b) Variation of reduced viscosity with concentration of different compositions of NaCMC/PVA blend in water at 35°C.

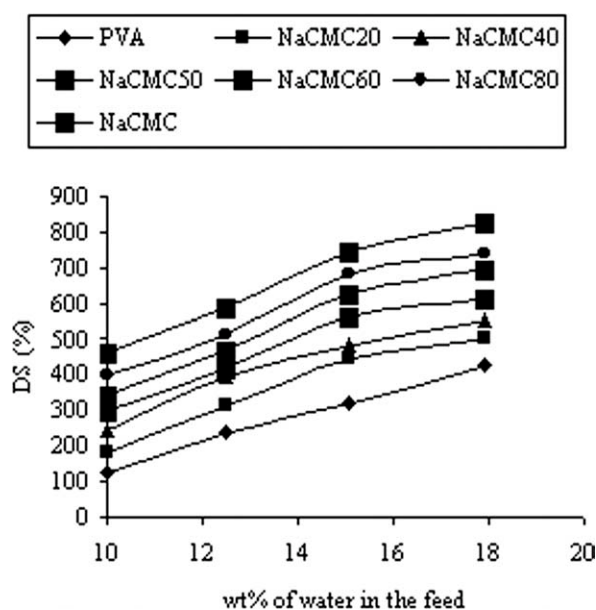


Figure 7 Effect of wt % of water on swelling properties of different formulations at 35°C.

$$\alpha = K_m - \frac{k_1[\eta]_1^2 W_1^2 + k_2[\eta]_2^2 W_2^2 \sqrt{k_1 k_2 [\eta]_1 [\eta]_2 W_1 W_2}}{\{[\eta]_1 W_1 - [\eta]_2 W_2\}^2} \quad (9)$$

where k_1 , k_2 , and K_m are the Huggins constants for individual components 1, 2, and blend, respectively.

It is observed from Table I that the values of ΔB , μ , and α are positive for all the compositions of NaCMC/PVA blend in water at 35°C. In general, if ΔB , μ , and α are positive for any polymer blend system, it is considered as miscible one, whereas, if these values are negative, the polymer blends are immiscible one. Based on this, it was concluded that NaCMC/PVA blend shows miscibility nature in all compositions. Similar observations were also made by Prasad et al.,⁴¹ in case of sodium alginate/poly(acryl amide) blends from their viscosity measurements.

TABLE II
Effect of Feed Composition on Permeate Water Concentration and Water Flux

Formulation code	Chee's differential interaction parameters		Sun's miscibility parameter ($\alpha \times 10^3$)
	ΔB	μ	
NaCMC20	+2.12	+0.12	+3.16
NaCMC40	+11.24	+0.24	+3.72
NaCMC50	+9.36	+0.13	+3.93
NaCMC60	+6.97	+0.079	+4.19
NaCMC80	+3.14	+0.096	+4.92

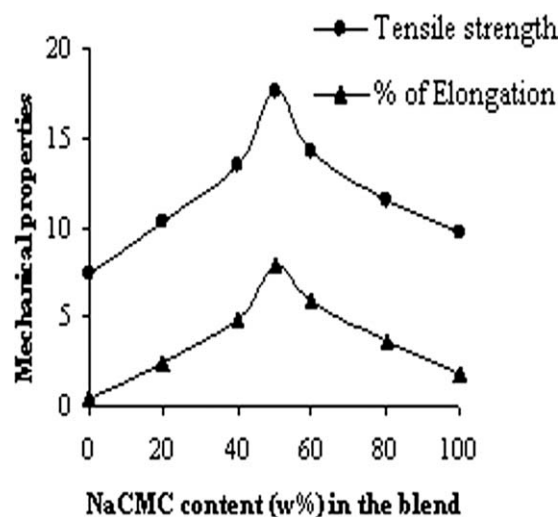


Figure 8 Effect of NaCMC content in NaCMC/PVA blend on tensile strength and % of elongation at break.

Degree of swelling

Percentage of degree of swelling at 35°C for plain NaCMC, PVA, and their blend membranes of different compositions (NaCMC20, NaCMC40, NaCMC50, NaCMC60, and NaCMC80) was measured as a function of wt % of water in water/IPA feed mixtures. The results are displayed in Figure 7. Swelling kinetics is a dynamic process, which depends on the mutual diffusion of solvent molecules in response to polymer-relaxation processes. Formulations containing higher amount of NaCMC showed higher swelling rates than the formulations containing lower amount of NaCMC. This increase in swelling rate is due to more hydrophilic nature of NaCMC, thereby leading to higher water up-take. Swelling rates of NaCMC/PVA blend membranes are much greater than PVA membranes and less than pure NaCMC membrane. For instance, swelling is higher for NaCMC80 than those of NaCMC60, NaCMC50, NaCMC40, and NaCMC20 membranes, degree of swelling for all the blend membranes is lower than pure NaCMC and higher than plain PVA membrane, indicating their hydrophilicity. This means that water molecules are preferentially more sorbed by the blend membranes of NaCMC/PVA than plain PVA, and hence water will diffuse out more easily through blend membranes than the plain PVA membranes.

Swelling behavior in various feed compositions of water/IPA (90 : 10, 87.5 : 12.5, 85 : 15, and 82.5 : 17.5) mixture was also investigated for predicting the PV performance. The degree of swelling increases with increasing water concentration in the feed. This is understandable, because most hydrophilic polymer membrane shows enhanced degree of swelling at higher water concentration. The higher NaCMC in the blend membrane, the lower concentration of IPA

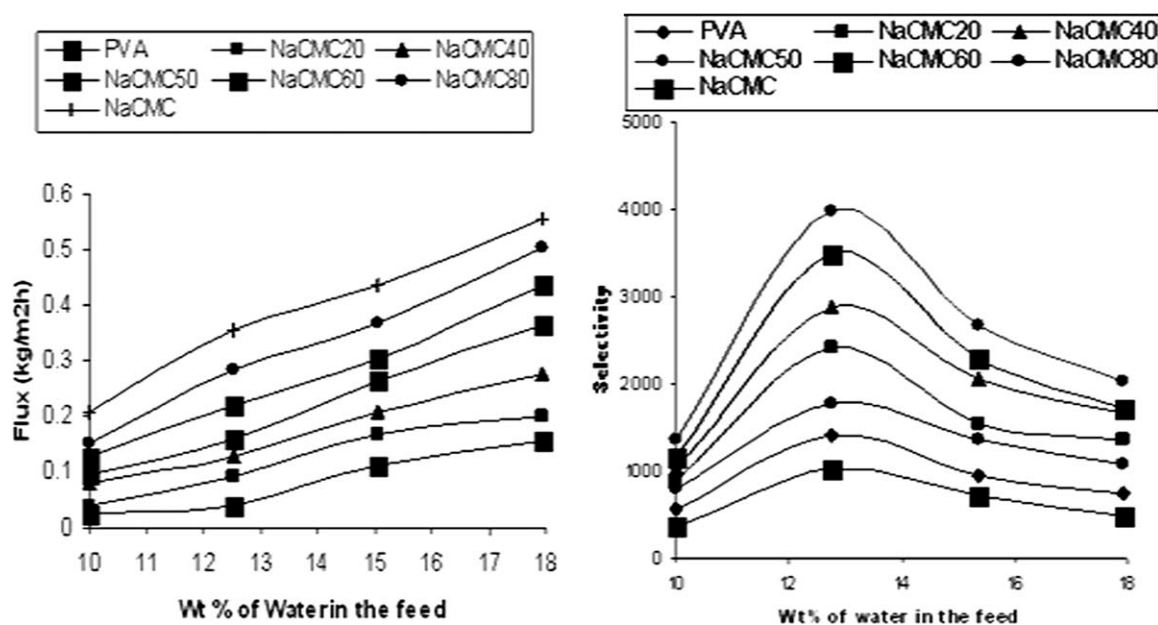


Figure 9 (a) Effect of water content in the feed on selectivity of water. (b) Effect of water content in the feed on flux of water.

on permeates solution; it proves that NaCMC resists the IPA permeability. The existence of NaCMC reduces pores of the membrane, and so IPA is difficult to go through the membrane. The lower IPA permeability makes NaCMC as potential and principal material to be used as membrane for PV on blending it with PVA.

Different from IPA uptake, the water uptake is also affected by the amount of NaCMC in the blend membranes. The higher amount of NaCMC in the membrane, the more water is absorbed. NaCMC will increase the membrane hydrophilicity character and cause strong interaction with water. This interaction is related to hydrogen bond between water and complex NaCMC/PVA H–H interaction. Therefore, NaCMC/PVA membranes can absorb water effectively.

Mechanical properties

With polymer blends exhibiting two behaviors, definite advantages can be derived if mechanical compatibility can be achieved. With miscible polymer mixtures, the mechanical compatibility is assured, and a property compromise between the constituents is therefore achieved. Thus, with a miscible polymer blend, a range of performance characteristics between the component polymers can lead to a large number of potentially useful and different products.⁴²

The effect of NaCMC content in NaCMC/PVA blend on tensile properties is graphically shown in Figure 8. Tensile strength seems to vary in two steps as the amount of NaCMC content varies in the blend membranes. In the first step, the tensile strength increased linearly with the increase in NaCMC content, and a maximum value of 17.51 mPa is achieved

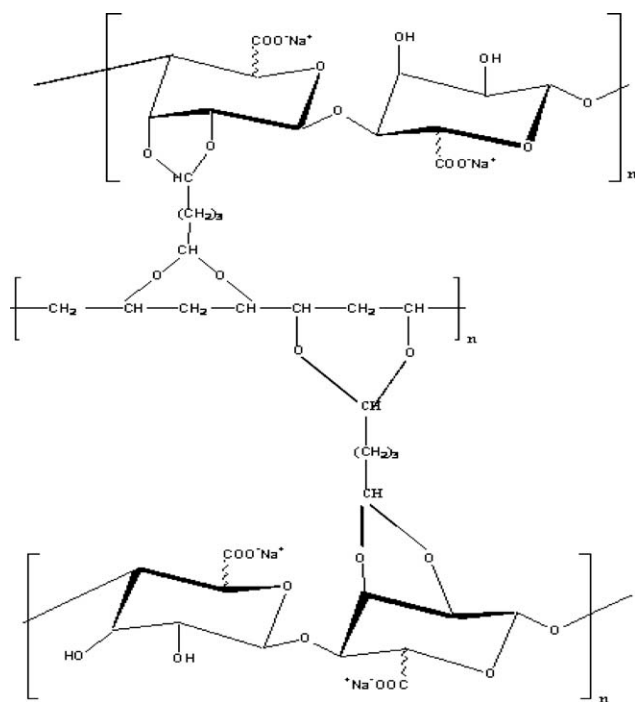
for NaCMC50. In the second step, the tensile strength decreasing trend was observed with increasing the NaCMC content. Figure 8 also shows the dependence of the elongation at break on NaCMC content for the pure and blend membranes, and the curve of % elongation at break expresses a tendency similar to that of tensile strength and reaches to a maximum value when NaCMC content in the blend membrane was 50 wt %. Conclusion can be drawn that blending of NaCMC with PVA is effective in inducing significant changes to the mechanical properties of the membranes.⁴² The improved mechanical properties of the blend membranes were believed to be due the intermolecular interactions through hydrogen-bond formation.

Pervaporation

Dehydration experiments were performed with the GA crosslinked NaCMC, PVA, and their blend membranes of different compositions at different feed mixtures of IPA/water (10, 12.5, 15.0, and 17.5 wt % of water in the feed mixture) at 35°C. As a control, separation results of crosslinked NaCMC, PVA, and their blend membranes were reported. In this study, the effect of feed composition on the membrane performance was also evaluated.

Effect of feed composition

The effect of feed IPA concentration on PV performance of water/IPA mixture through NaCMC/PVA blend membranes is illustrated in Figure 9. It demonstrates that the permeate flux toward water increases and the selectivity decreases with



Scheme 1 Crosslinking reaction mechanism of NaCMC and PVA with glutaraldehyde.

increasing water content in the feed mixture. The tendency for the permeate flux, increased with feed concentration, is similar to swelling behavior of the membranes. Higher swelling of the membrane made permeate easily to penetrate through the membrane. However, extensive swelling of water molecules loosens and plasticizes the polymer chains in the membrane and then assists the penetration of IPA. Swollen water molecules at higher water concentration act as a plasticizing agent in this case. Similar observation was also reported by Yong et al.,⁴³ in case of PV separation of water/IPA through carboxymethylated PVA composite membranes.

Effect of NaCMC/PVA blend composition

Effect of blending on PV performance of water/IPA mixture through NaCMC/PVA membranes is shown in Figure 9. It is observed from Figure 9(a) that NaCMC membrane showed higher flux than those of PVA and NaCMC/PVA blend membranes. The higher permeation flux of NaCMC/PVA membranes than PVA can be explained by similar trends in swelling behavior. Blending of NaCMC with PVA enhanced the affinity to water molecules; this may be due to the presence of carboxymethyl groups in the blend membranes resulting in an increase in sorption of water. In NaCMC/PVA blend membranes with increasing NaCMC content, selectivity of the membrane toward water molecule decreased and the permeate flux increased. Note that the

degree of swelling increases upon blending PVA with NaCMC, causing a reduction of relative crystallinity of NaCMC/PVA blend membranes. In fact, the decrease of relative crystallinity and an increase in the carboxymethyl group content both affected the swelling of the membrane.

CONCLUSIONS

Blend solutions of NaCMC/PVA were prepared in different compositions (0/100, 20/80, 40/60, 50/50, 60/40, 80/20, and 100/0), and miscibility of the blend was determined by viscometric method and found that the blends are miscible in all compositions. Membranes prepared by blending NaCMC and PVA in different compositions followed by chemical crosslinking with GA were used to study the PV performance. The excellent hydrophilicity of both membrane constituents was exploited to develop water selective PV membranes. The membranes were subjected to PV for water–IPA separation and to sorption studies over a wide range of feed compositions. The membrane permselectivity was primarily derived from its sorption selectivity, and there existed a strong coupling effect for the permeation and sorption of permeating species in the membranes. For comparison purposes, membranes were also fabricated from NaCMC and PVA alone, and the permeation and sorption behavior of these membranes were evaluated as well to elucidate the characteristics of the blend membranes in view of permeant-membrane interactions and the interactions between NaCMC and PVA in the blend membranes.

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References

1. Gedde, U. W. *Polymer Physics*, Chapter 4. Chapman & Hall: London, 1995.
2. Devi, C. U.; Sharma, A. K.; Rao, V. V. R. N. *Mater Lett* 2002, 56, 167.
3. Krause, S. In *Polymer-Polymer Compatibility in Polymer Blends*, Vol.1. Academic Press: New York, 1978.
4. Varenell, D. F.; Runt, J. P.; Cdeman, M. M. *Polymer* 1983, 24, 37.
5. Varnell, D. F.; Coleman, M. M. *Polymer* 1981, 22, 1324.
6. Woo, E. M.; Barlow, J. W.; Paw, D. R. *J Appl Polym Sci* 1986, 32, 3889.
7. Charpentier, D.; Mocanu, G.; Carpov, A.; Chapelle, S.; Merle, L.; Muller, G. *Carbohydr Polym* 1997, 33, 177.
8. Ito, H.; Shibata, T.; Miyamoto, T. *J Appl Polym Sci* 1986, 31, 2491.
9. Wach, R. A.; Mitomo, H.; Yoshii, F.; Kume, T. *J Appl Polym Sci* 2001, 81, 3030.

10. Kim, J.; Yun, S.; Ounaies, Z. *Macromolecules* 2006, 39, 4202.
11. Menjivar, J. A. *Adv Chem Ser* 1986, 213, 209.
12. Liu, P.; Zhai, M.; Li, J.; Pengfi, J. *Radiat Phys Chem* 2002, 63, 525.
13. Lin, O. H.; Kumr, R. N.; Rozmann, H. D.; Mnoor, M. A. *Carbohydr Polym* 2005, 59, 57.
14. Cao, Y.; Li, H. *Eur Polym J* 2002, 38, 1457.
15. Ajit, P.; Sunil, A. R.; Agnihotri, A.; Sangamesh, A.; Patil, A.; Nadagouda, N.; Padmakar, V. M.; Kulkarni, B.; Aminabhavi, T. M. *Carbohydr Polym* 2006, 65, 243.
16. Xiao, C.; Gao, Y. *J Appl Polym Sci* 2008, 107, 1568.
17. Kader, F. H. A.; Osman, W. H.; Ragab, H. S.; Shehap, A. M.; Rizk, M. S.; Basha, M. A. *J Polym Matter* 2004, 21, 49.
18. Tawansi, A.; Elkhodary, A.; Abdelnaby, M. M. *Curr Appl Phys* 2005, 5, 572.
19. Lee, J.; Bhattacharrya, D.; Easteal, A. J.; Metson, J. B. *Curr Appl Phys* 2008, 8, 42.
20. Abdel-Kader, F. H.; Shehap, A. M.; Abellil, M. S.; Mahmoud, K. H. *J Appl Polym Sci* 2005, 95, 1342.
21. Kader, F. H. A.; Shehap, A. M.; Abellil, M. S.; Mahmoud, K. H. *J Polym Mater* 2005, 22, 349.
22. Ragab, H. S.; Aboellil, M. S.; Shehap, A. M.; AbdelKader, F. H. *J Appl Polym Sci* 2003, 7, 1748.
23. Kader, K. A. M. A.; AbdelHamid, S. F.; Mansour, A. B.; Ellawindy, A. M. *J Polym Test* 2002, 21, 847.
24. Gref, N.; Nguyen, Q. T.; Schaetzl, P.; Neel, J. *J Appl Polym Sci* 1993, 49, 209.
25. Mallapraga, S. K.; Peppas, N. A.; Colombo, P. *J Biomed Mater Res* 1997, 36, 125.
26. Nuttleman, C. R.; Henry, S. M.; Anseth, K. S. *Biomaterials* 2002, 23, 3617.
27. Darwis, D.; Stasica, P.; Razzak, M. T.; Rosiak, J. M. *Radiat Phys Chem* 2002, 63, 539.
28. Shehap, A. M. *Egypt J Solids* 2008, 31, 1.
29. Kariduragavannar, M. Y.; Kittur, A. A.; Kulkarni, S. S.; Ramesh, K. *J Membr Sci* 2004, 238, 165.
30. Moon, G. Y.; Pal, R.; Huanh, R. Y. M. *J Membr Sci* 1999, 156, 17.
31. Lokesh, B. G.; Rao, K. S. V. K.; Reddy, K. M.; Rao, K. C.; Rao, P. S. *Desalination* 2008, 233, 166.
32. Okieimen, F. F.; Ogbeifun, P. E. *J Appl Polym Sci* 1996, 59, 981.
33. Williams, D. H.; Fleming, I. *Spectroscopic Methods on Organic Chemistry*, 3rd ed.; McGraw-Hill: London, 1980.
34. Xiao, C.; Lu, Y.; Liu, H.; Zhang, L. *J Appl Polym Sci* 2001, 80, 26.
35. Anita, G. S.; Manjeshwar, L. S.; Aminabhavi, T. M. *J Appl Polym Sci* 2010, 116, 1226.
36. Togawa, E.; Kondo, T. *J Polym Sci Part B: Polym Phys* 1999, 37, 451.
37. Fischer, S.; Voigt, W.; Fisher, K. *Cellulose* 1999, 6, 213.
38. Singh, Y. P.; Singh, R. P. *Eur Polym J* 1983, 19, 535.
39. Singh, Y. P.; Singh, R. P. *Eur Polym J* 1984, 20, 201.
40. Sun, Z.; Wang, W.; Feng, Z. *Eur Polym J* 1992, 28, 1259.
41. Prasad, C. V.; Saraswathi, M.; Babu, B. C.; Reddy, K. S.; Sudhakar, H.; Prasad, M.; Rao, K. C.; Subha, M. C. S. *J Pure Appl Ultrason* 2008, 30, 117.
42. Devi, D. A.; Smitha, B.; Sridhar, S.; Aminabhavi, T. M. *J Membr Sci* 2006, 280, 138.
43. Nam, S. Y.; Chun, H. J.; Lee, Y. M. *J Appl Polym Sci* 1999, 72, 241.