

Preparation and Characterization of 4A Zeolite-Filled Mixed Matrix Membranes for Pervaporation Dehydration of Isopropyl Alcohol

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ABSTRACT: Sodium carboxymethylcellulose/poly (vinyl alcohol) mixed matrix membranes filled with different amounts 4A zeolite (0, 5, 10, 15, and 20 wt %) were prepared by solution casting method. Prepared membranes were crosslinked with GA and used for pervaporation dehydration of isopropyl alcohol of different feed mixtures at 35°C. On increment in zeolite content in the membrane it was found the improvement in the performance of the membrane, due to its hydrophilic nature and molecular sieving effect in addition to its favorable interaction with hydrophilic sodium carboxymethylcellulose and polyvinyl alcohol. The structure and chemical constituents of the MMM's were investigated by attenuated total reflectance Fourier transform infrared spectroscopy. Thermal stability of the membranes was assessed by DSC and TGA techniques. Crystallinity of the membranes was assessed using X-ray diffraction, and the morphological properties were

assessed by scanning electron microscopy. Mechanical properties were also carried out to determine the tensile strength and % of elongation at break using universal testing machine. It was found that the mechanical strength increases with increase in the zeolite content upto 15 wt % of zeolite with an optimum tensile strength of 113.31 N/mm². Pervaporation was carried out to assess the membrane performance, the highest flux and selectivity obtained is 0.584 kg/m²/h and 6945 for NaCMCA20 and NaCMCA15, respectively, for a feed composition containing 17.5 and 10 wt % of water in the feed and further swelling studies also supporting the pervaporation results. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 1521–1529, 2011

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

INTRODUCTION

In recent years, there has been increased interest in the use of pervaporation membranes for dehydration water/organic liquid mixtures. A major advantage of this process is the ability to separate azeotropic mixtures such as water/alcohol system. According to the solution diffusion theory, many hydrophilic membranes have been investigated for the dehydration of water/alcohol azeotropic mixtures.^{1,2} Great efforts have been made to develop new effective membranes because it is the key to commercialize the pervaporation process. Mixed matrix membranes

(MMM's) usually shows good mechanical strength, high flux, and separation factor

Purification of organic solvents, such as isopropanol (IPA), containing small amounts of water is of vital significance in the area of organic synthesis. IPA is one of the important solvents used on a large scale in chemical industry and in pharmaceutical laboratories. Further, it has also been used in semiconductor and liquid crystal display industries as a water-removing agent.^{3,4} IPA and water form an azeotropic mixtures at 85.3 mass % of IPA concentration⁵ and hence, the separation of these mixtures by conventional methods such as solvent extraction and rotavapor or by distillation could prove uneconomical. Several membrane materials have been modified recently for the selective separation of water from aqueous mixtures of IPA.^{3–6} However, the membranes used in such separation studies often yield compromised values of flux and selectivity due to trade-off phenomenon existing between the flux and separation factor in PV process.

Polyvinyl alcohol (PVA) has received a great deal of attention in PV membranes because of its

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considerable applications^{7–13} either pure or composite with other materials. The optical uses of PVA are concerned with the retardation polarization and filtration of light and with photography.¹³

Carboxymethylcellulose (CMC), a natural biodegradable anionic polymer with good biocompatibility, has been widely used in various fields ranging from technological industries to the biological, pharmaceutical, petroleum and medical fields, biomedical membrane.^{14–19} Moreover, CMC can interact strongly with PVA. Consequently, CMC/PVA composite membrane with good mechanical property prepared using glutaraldehyde as crosslinking reagent was widely investigated in the fields of pervaporation separation in water–ethanol mixture, separator in electro-generation, antiadhesion after operation.^{20–22} However, usage of NaCMC/PVA membranes in pervaporation is not found in the literature.

On the basis of the above consideration, NaCMC/PVA membranes are expected to develop to be used as pervaporation membrane. In this study, an effort has been made to enhance the flux and separation selectivity simultaneously by judiciously choosing 4A zeolite and incorporating it into sodium carboxymethylcellulose (NaCMC)/poly(vinyl alcohol) (PVA) matrix. The zeolite content with respect to NaCMC and PVA was varied in the range of 5–20% with the aim of improving membrane performance. The physicochemical changes in the resulting membranes were investigated, and the resulting membranes were used for the PV separation of water/IPA mixtures at different concentrations of water (10–17.5%) in water/IPA. The results of permeation flux, separation selectivity, and diffusion coefficients were evaluated. The results were discussed in terms of swelling properties of the membranes.

EXPERIMENTAL

Methods

Sodium carboxymethylcellulose (NaCMC, viscosity: 1 wt/vol % 1100–1900 cps) Merck, Mumbai, India. Poly (vinyl alcohol) (PVA, mol wt: 70,000) was procured from Hi-media, India. Glutaraldehyde (GA), hydrochloric acid (HCl), isopropyl alcohol (IPA), and acetone all are of analytical grade were purchased from Qualigens (Mumbai, India), 4A zeolites (particle size: 2.8 Å) was supplied from IICT Hyderabad. Double distilled water collected in the laboratory was used through out the work.

Membrane preparation

NaCMC and PVA (1 g each) was dissolved in 100 mL distilled water separately under constant stir-

ring. The 5, 10, 15, and 20 wt % of 4A zeolite particles was dispersed in 10 mL DI water by sonication for 30 min; this was added to the previously prepared NaCMC/PVA (50 : 50) blend solution and then the whole mixture was kept under stirring for another 24 h. The blend solution was poured onto to a preleveled glass plate in dust-free atmosphere to cast the membranes with uniform thickness. Membranes thus formed were allowed to dry at ambient temperature and then peeled-off from the glass plate and then crosslinked with glutaraldehyde (2.5 mL) containing 85 : 10 acetone/water mixture in which 2.5 mL HCl was added as activator and allowed for crosslinking reaction for 2 h. Acetone being a non-solvent prevents the initial dissolution of the membrane and water present in the feed leading to swell the membrane there by facilitating an easy penetration of GA into the membrane matrix for an effective crosslinking. Crosslinking reaction takes place between the –OH groups of NaCMC, PVA, and –CHO groups of GA because of formation of ether linkages by eliminating water molecules.

The crosslinked membranes were removed from crosslinking bath and washed repeatedly with distilled water to remove the adhered GA and unreacted molecules and then dried in hot air oven at 400°C to constant weight and the membrane. The membranes containing different amounts of 4A zeolite i.e., 5, 10, 15, and 20 wt % were designated as NaCMCA5, NaCMCA10, NaCMCA15, and NaCMCA20, respectively. Plain NaCMC/PVA (50 : 50) blend membrane (without zeolite) was prepared in the same process as described earlier, and it was designed as NaCMC50. Membrane thickness was measured using micrometer screw gauge, and the thickness for the membranes was found to be around $30 \pm 2.0 \mu\text{m}$. MMM's thus prepared were used for further characterization and for dehydration of IPA/water mixture (90 : 10, 87.5 : 12.5, 85 : 15, and 82.5 : 17.5). Zeolite loading was limited to 20 wt % because beyond this concentration membrane becomes brittle.

ATR Fourier transform infrared spectroscopy

FTIR spectra of NaCMC/PVA blend membrane and its MMM's were taken using (Bomem, Model: MB-3000, Canada) FTIR spectrometer, equipped with attenuated total reflectance (ATR). Membranes were characterized at room temperature from 4000 to 600 cm^{-1} under a N_2 atmosphere at a scan rate of 21 cm^{-1} .

Morphological properties

The surface morphology of the blend membrane and its MMM's was scanned at a magnification of 100 μm at an accelerated voltage of 20 kV.

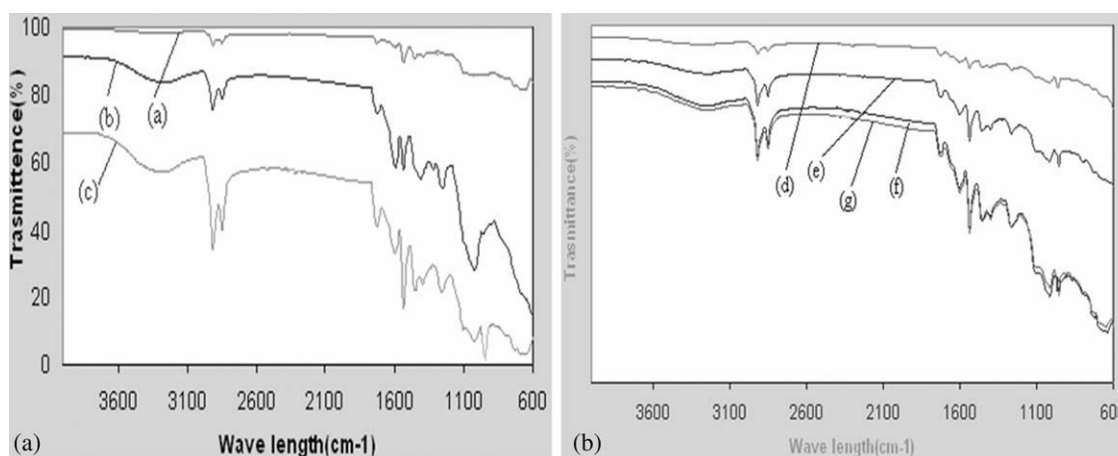


Figure 1 (A) FTIR spectra of un-crosslinked NaCMC50 (a), crosslinked NaCMC50 (b), NaCMCA10 (c). (B) FTIR spectra NaCMCA5 (d), NaCMCA10 (e), NaCMCA15 (f) and NaCMCA20, (g) membranes.

Thermal analysis

DSC thermograms and TGA curves of NaCMC/PVA and their MMM's were recorded using TA instruments sequential thermal analyzer (Model-SDT Q600, USA). Analysis of the samples was performed at heating rate of 10°C/min under N₂ atmosphere at a purging rate of 100 mL/min.

X-ray diffraction

A Siemens D 5000 powder X-ray diffractometer was used to assess the crystallinity of different membranes. X-rays with a wavelength of 1.5406 Å was generated by a CuK α source. The angle of diffraction was varied from 0 to 500 to identify the change in the crystal structure.

Swelling studies

Weighed samples of crosslinked NaCMC/PVA and its MMM's (3 cm diameter) were soaked in IPA/water mixture of different compositions for 48 h. Membranes were removed from the crosslinking reaction solution and were wiped with tissue paper to remove the adhered liquid and weighed immediately to determine the amount of liquid sorbed by the membranes. The degree of swelling was calculated using the following equation:

$$\text{Degree of swelling} = (M_s/M_d) \times 100 \quad (1)$$

where M_s is the mass of the swollen polymer in grams and M_d is the mass of the dry polymer in grams.

Mechanical properties

Tensile strength and elongation at break of NaCMC50 and it's MMM's was measured using Universal Testing Machine (Instron, UK). Test specimens were prepared in the form of dumbbell shapes

as per ASTM D-638 standards. Membranes of gauge length of 50 mm and width of 10 mm were stretched at the crosshead speed of 10 mm/min at 200°C containing 65% relative humidity.

RESULTS AND DISCUSSION

ATR-Fourier transform infrared spectroscopy

Figure 1(a,b) shows the FTIR spectra of pure NaCMC/PVA and its MMM's of various formulations containing different amounts of 4A zeolite (5, 10, 15, and 20 wt/wt %). A characteristic strong and broad band exhibited at around 3440 cm⁻¹ in NaCMC50 membrane (curve a and b), corresponds to O—H stretching vibrations of NaCMC and PVA. Bands at 2937 and 2907 cm⁻¹ indicates aliphatic C—H stretching vibrations, peaks at 1604 and 1425 cm⁻¹ are due to asymmetric and symmetric stretching of carboxylate groups of NaCMC, whereas peaks observed at 1120 and 1028 cm⁻¹ represents C—O—C stretching vibrations.²³ In case of crosslinked NaCMC50 membrane, in addition to the peaks observed in un-crosslinked membrane (curve a), a new peak at 1248 cm⁻¹ (curve b) was observed due to the formation of ether linkage on crosslinking NaCMC/PVA membrane with GA [Fig. 1(a)]. In zeolite-filled membranes, in addition to the peaks observed in NaCMC50, a new peak was observed at 956 cm⁻¹ due to Si—O—Si group of 4A zeolite (curve c). From Figure 1(b), it is observed that as the zeolite content increases the intensity of the peaks did not alter, instead the peaks shifted to lower wavelength for membranes containing 5–20 wt % zeolite (curves d–g). This is due to the increase of Si—O—Si groups of 4A zeolite,²⁴ which appear almost at the same frequency of C—O stretching. All these evidences ascertain the increase of zeolite incorporation in the membrane matrix.

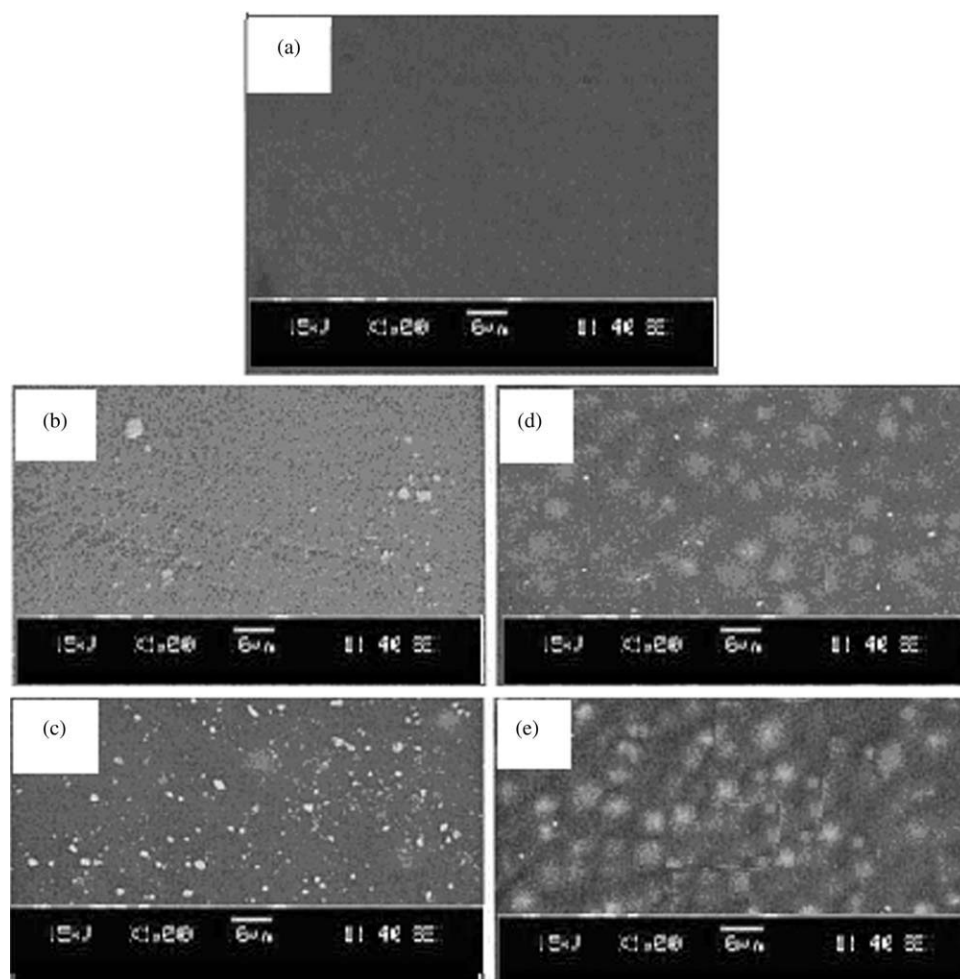


Figure 2 SEM micrograms of surface NaCMC50 (a), NaCMCA5 (b), NaCMCA10 (c), NaCMCA15 (d), and NaCMCA20 (e). Membranes at $\times 100$ magnification.

Scanning electron microscope

Figure 2 represents the SEM micrograms of surface morphology of NaCMC50 and its MMM's. The micrograms indicate that the zeolite distribution increased from membrane NaCMCA5 to NaCMCA20 with increasing zeolite loading. The zeolite was distributed evenly throughout the membrane, which would enhance the transport of water molecules through the membranes,²⁵ but when the zeolite content reaches 20 wt %, part of the zeolites aggregate at the interface of the membrane that could be disadvantageous for pervaporation performance. Furthermore, the micrograms clearly show that the zeolite particles are embedded in the membrane with no voids around them (upto 15% zeolite content in the membrane). This ensured that the possible defects upto 15% zeolite.

Differential scanning calorimetry

DSC thermograms of NaCMC/PVA and its MMM's are illustrated in Figure 3. In comparison with

NaCMC/PVA membrane, MMM's exhibited higher T_g values due to the presence of Si—O—Si groups of 4A zeolite. In case of MMM's, containing 20 wt % of zeolite (NaCMCA20) showed higher T_g than the membranes with lower amount of zeolite (5, 10, and 15). This indicates that addition of zeolite to NaCMC/PVA membranes increases the overall thermal stability of the membrane.

Thermogravimetric analysis

Figure 4 gives TGA curves of NaCMC50, NaCMCA5, NaCMCA10, and NaCMCA15, respectively. It can be seen from Figure 4 that there are two weight loss stages for zeolite-filled membranes at around 40–245°C and 245–700°C. The weight loss takes place in the first stage for different membranes is about 4.5 wt %, and the lost components are mainly small molecules such as physically absorbed water.²⁶ Weight loss in the second stage for all membranes began due to chain cleavage, which is followed by further oxidation of the residue char.

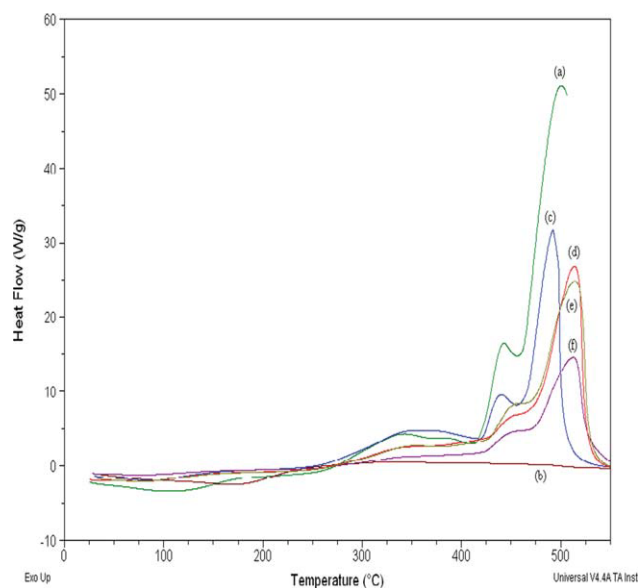


Figure 3 DSC thermograms of NaCMC50 (a), plain 4A zeolite (b), NACMCA5 (c), NACMCA10 (d), NACMCA15 (e), NACMCA20, (f) membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.].

X-ray diffraction

The XRD patterns of plain 4A zeolite, plain NaCMC50, and its MMM's are presented in Figure 5. NaCMC50 exhibits crystalline peaks at 11.2° , 15.0° , 18.0° , 20.9° , and 23.8° , the 4A zeolite shows a crystalline form as reported earlier.²⁷ On incorporation of 4A zeolite into NaCMC50 matrix, membrane patterns show the characteristic peaks of both the 4A zeolite

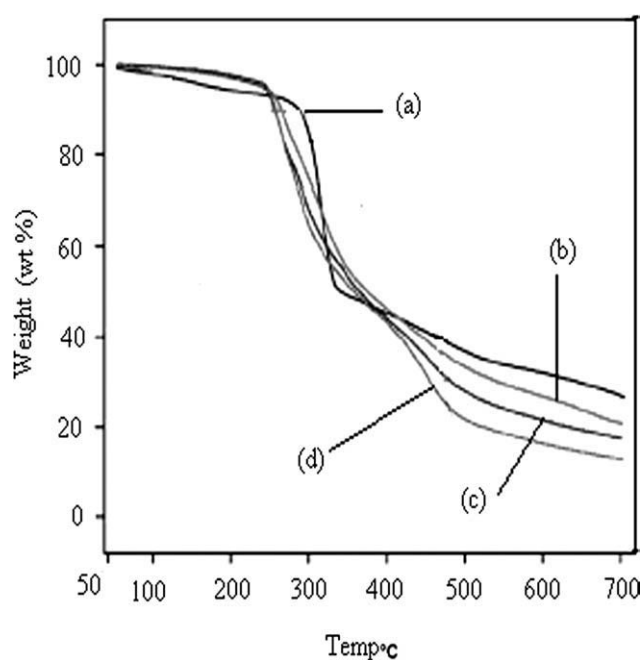


Figure 4 TGA Thermograms of NaCMC50 (a), NACMCA5 (b), NACMCA10 (c), and NACMCA15 (d).

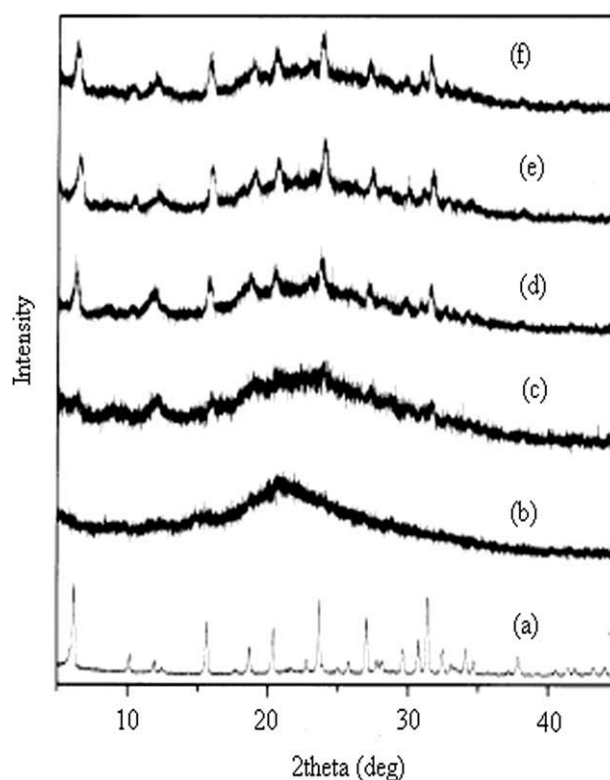


Figure 5 XRD patterns of plain 4A (a), NaCMC50 (b), NACMCA5 (c), NACMCA10 (d), NACMCA15 (e), and NACMCA20 (f).

and NaCMC/PVA. However, on increasing the zeolite content (5–20%) in the membrane matrix, the intensity of the zeolite peaks increased marginally, suggesting the increase in its crystallinity. This is attributed due to the increase of zeolite content in the membrane matrix, morphological studies (in this study) also reveals similar results.

Swelling studies

Swelling properties of different formulations are presented in Table I. Figure 6 presents the results of % degree of swelling of NaCMC50, and its MMM's filled with 4A zeolite membranes in different mass % of water/IPA mixture at 35°C . The results indicate that the swelling ratio of NaCMC/PVA increases with increase in the zeolite content upto 15%.

Both 4A zeolite and NaCMC, PVA are hydrophilic, so 4A zeolite-filled MMM's can be used effectively for the dehydration of IPA by PV technique, mainly at azeotropic mixtures. Zeolite-filled membranes are maintained by the strong interaction between 4A zeolite and NaCMC/PVA. During the PV processes, when water molecules diffuse into the membranes (beyond 15% zeolite), the membranes become swollen; swelling leads to decrease the interaction between 4A zeolite and NaCMC/PVA; this might result in the formation of some tiny cracks (in the present case beyond 15% zeolite content) developing

TABLE I
Swelling Properties of Various Formulations in Different Water/IPA Feed Mixtures at 35°C

Formulation code	NaCMC/PVA composition (50/50)		4A zeolite content (wt %)	Feed water concentration (w/w%)	% of Degree of swelling
	NaCMC (g)	PVA (g)			
NaCMC50	1	1	0	10	298
				12.5	418
				15.0	513
				17.5	614
NaCMCA5	1	1	5	10	368
				12.5	491
				15.0	580
NaCMCA10	1	1	10	17.5	685
				10	440
				12.5	540
				15.0	697
NaCMCA15	1	1	15	17.5	774
				10	496
				12.5	645
				15.0	765
NaCMCA20	1	1	20	17.5	868
				10	563
				12.5	760
				15.0	856
				17.5	960

at the interface between the zeolite and NaCMC/PVA, which allows IPA molecules to pass through. The reason that the membranes containing 15 wt % of zeolite particles manifest good stability through the PV process, beyond this concentration stability of the membrane decreases due to decrease in the interaction between polymer matrices.

Mechanical properties

Figure 7 shows the mechanical properties of different membranes. In general, high tensile strength and low elongation at break results in poor quality membrane.

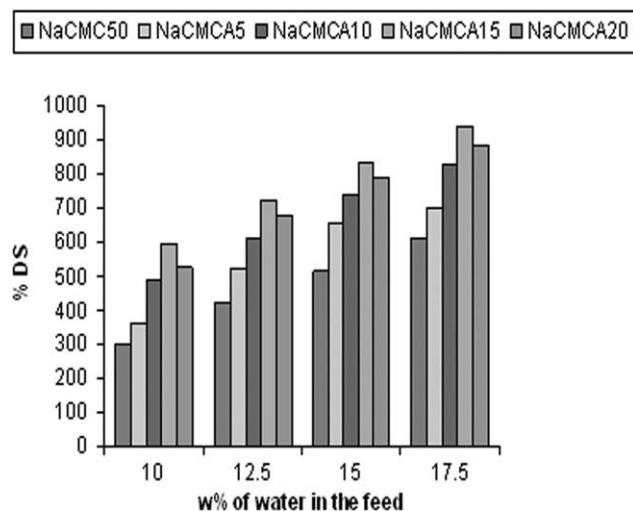


Figure 6 Effect of zeolite content on % DS for different feed compositions of water/IPA mixture.

Tensile strength and elongation at break have a reciprocal relationship. For a good membrane, there should be an optimum balance between tensile strength and elongation at break.²⁸ MMM's prepared in this study were found to have a good balance of tensile strength with elongation at break. It is observed from Figure 7 that the MMM's fall into acceptable range of tensile strength and elongation at break as required for pervaporation applications.²⁹ It is also observed from these values that tensile strength increases with increase in the zeolite content from 0 to 15% while elongation at break decreases; beyond this concentration (15%) decrease in tensile strength and increased % of elongation was observed. On adding 4A zeolite,

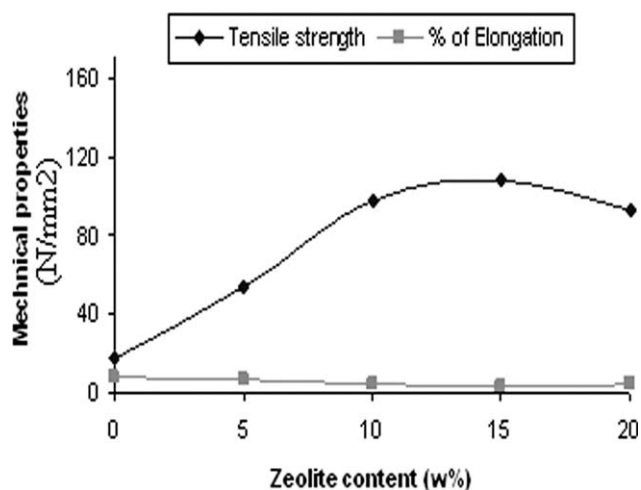


Figure 7 Effect of zeolite content on mechanical properties.

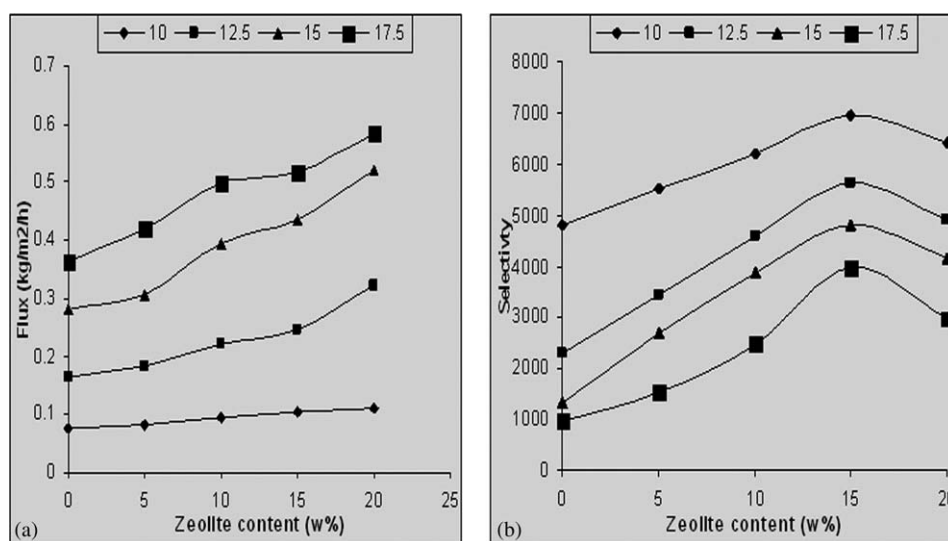


Figure 8 (a) Effect of zeolite content on Flux for different wt % of water in the feed. (b) Effect of zeolite content on selectivity for different wt % of water in the feed.

hydrogen bond formation may happen between polymer molecules and zeolite particles. The hydrogen bond formation of polymer chains prevents high elongation, which in turn leads to decrease in elongation at break and increase in tensile strength.

Pervaporation

The efficacy of the membranes in PV process is generally assessed based on the permeation of individual components. Therefore, the extent of permeation was determined by plotting the flux of water as a function of zeolite content in the membrane for 10–17.5 mass % of water in the feed.

Effect of zeolite content on pervaporation performance

The amount of zeolite added into the polymer matrix is an important parameter in the preparation of MMM's.^{30–32} Zeolites that are having molecular sieving properties^{33,34} enhance the selectivity's of polymeric membranes either because of their intrinsic properties or by modifying the membrane morphology.^{31,35}

The effect of zeolite loading on membrane performance (0–20 wt %) was tested, since the addition of zeolite results in varying flux and selectivity for the MMM's. The MMM's showed improved performance than that of pristine NaCMC/PVA membrane, and this may be due to the filler–polymer and membrane–solvent interactions. The effect of zeolite content on membrane performance was investigated for feed containing different amount of water with increasing loadings of 4A zeolite. Both flux and selectivity were increased upon increasing zeolite content up to 15% in the membrane; the reason would be the

hydrophilic nature and pore size (pore size of 4A zeolites pore size is smaller than IPA molecules and larger than water molecules) of 4A zeolite, which absorbs large amount of water through the pores, thereby creating free channels for transportation of water molecules through the membranes. Hydrophilic–hydrophilic interactions would reject the organic (in the present case IPA) component of the feed, but allows water molecules. This leads to an increase in the flux with increasing the zeolite loadings up to 15% in the membrane for all the studied range concentrations of water in the feed as shown in Figure 8(a). A strong interaction between 4A zeolite (hydrophilic) and water molecules would allow water to transport through the membrane at 15 wt % zeolite loading. Hence, higher water flux of 0.517 kg/m²h obtained at a feed concentration of 17.5 wt % in the water/IPA mixture. Beyond 15 wt % zeolite, increase in flux and decreasing selectivity [Fig. 8(b)] was observed over the investigated range of water concentration in the feed, this might be due to the increase in the zeolite content that further leads to increase in the hydrophilic nature of the membrane matrix leading to plasticization which further leads to allow IPA molecules to pass through, this leads to reduction in selectivity. The good contact between zeolite particles and polymer matrix are upto 15 wt %. Zeolite content play a key role in increasing the membrane separation factor (15 wt %), beyond this concentration interaction between zeolite particles and polymer matrices decreases due to increase in the zeolite density.

Effect of feed composition on pervaporation performance

In PV process, the overall selectivity of a membrane is generally explained based on the interaction

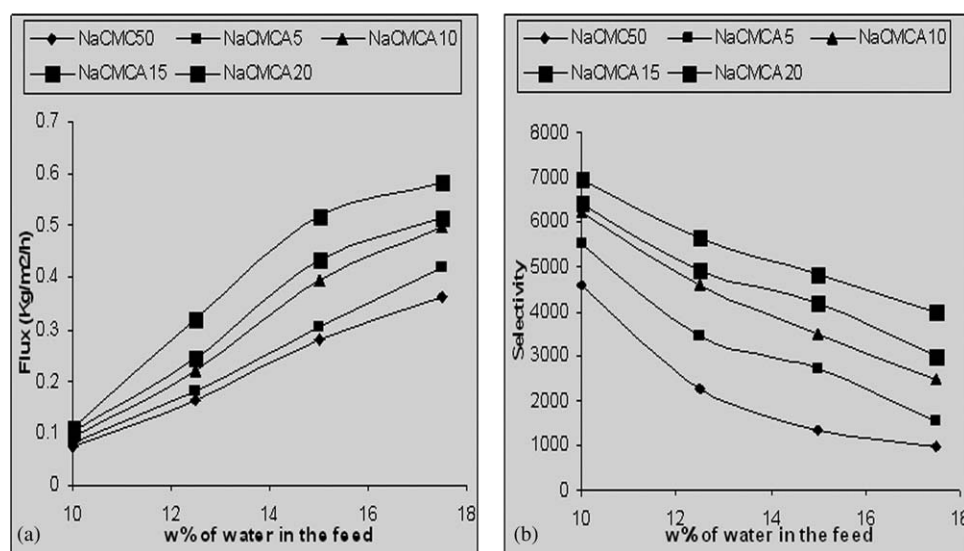


Figure 9 (a) Effect of wt % of water in the feed on flux for different formulations. (b) Effect of wt % of water in the feed on selectivity for different formulations.

among the membrane and permeating molecules, molecular size of the permeating species. Figure 9(a) displays the effect of water compositions on the flux for all the membranes prepared with different amounts of 4A zeolite in NaCMC/PVA matrix. It is observed that the flux of water in the feed increased drastically for all water/IPA compositions under the studied zeolite concentration range (5–20 wt %). At higher concentration of water in the feed, the membranes swell greatly due to the formation of a strong interaction between the membrane and water molecules. This might have led to allow water molecules to pass through the membranes.³⁶ As a result, flux of water increases drastically at higher concentration of water in the feed, irrespective of the amount of zeolite loading in the membrane matrix.

On the contrary, the selectivity decreased significantly from 10 to 17.5 upon increasing the water content in the feed. This can be clearly observed from Figure 9(b) showing the variation of selectivity as a function of wt % of water in the feed in the membrane for different mass % of 4A zeolite (5–20 wt %) in the membrane. In general, with increasing the water content in the feed compositions, the permeation flux increases and selectivity decreases.^{6,37} Similar observations were also observed in the present case with increasing water content in the feed composition. The highest flux observed for NaCMCA20 is 0.584 kg/m²/h at a feed composition of 82.5/17.5 IPA/water mixture, whereas highest selectivity observed is 6945 for NaCMCA15 at 10 wt % of water in the feed.

CONCLUSIONS

The effect of zeolite content significantly influenced the characteristics of NaCMC/PVA membrane. Mem-

branes containing lower amount of 4A zeolite has the weak hydrogen-bonding interactions between NaCMC/PVA and zeolite substantially loosed the blend polymer chains, and the free volume cavity size was increased correspondingly. The transport of IPA in all the membranes was mainly controlled by the diffusivity. Hydrophilic zeolite preferentially adsorbed IPA, leading to increase in water uptake, swelling and decreased IPA permeability.

The IPA permeability was slightly decreased with the zeolite content, indicating that only a small portion of IPA passed through the zeolite filled membrane. The IPA permeability of the MMM's reduced with increase in zeolite content, most probably due to the increase in diffusion resistance. The MMM's membranes displayed desirable thermal and mechanical stabilities within the working temperature range.

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