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Hydrophilic Nanocomposite Membranes for the Pervaporation Separation of Water - Ethanol Azeotropic Mixtures

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Abstract: Bentonite nanoclay reinforced Poly (vinyl alcohol) (PVA) nanocomposite membranes were used for the separation of azeotropic composition of water – ethanol mixtures by pervaporation process. Fourier – transform infrared (FTIR) spectroscopic studies revealed the interaction of bentonite nanoclay and the PVA matrix. The dispersion and distribution of nanoclay in the polymer matrix was demonstrated by transmission electron microscopic analysis (TEM). The intrinsic membrane properties with filler loading were also investigated. The results indicate that the hydrophilic nature of the nanoclay influenced the pervaporation to a greater extent. The hydrophilic nature and surface roughness of the nanocomposite membranes was analyzed by atomic force microscopic (AFM) analysis. The pervaporation process illustrates that the permeation flux increases and the separation factor decreases with nanoclay loading. The instrinsic selectivity, which reflects the membrane performance was maximum for 1 wt% clay loaded membranes. PVA with 1 wt% nanoclay loading showed better pervaporation performance. The separation factor of the 1 wt% nanoclay membranes increased to 13, *i.e.* nearly 4 times more than that of neat PVA membranes. Membrane selectivity also increased to 254% than that of pristine PVA membranes. Thus at lower filler loading, maximum separation was achieved. The increase in nanoclay loading is favorable to improve intrinsic permeance at the cost of decrease in selectivity.

Keywords: Poly(vinyl alcohol), Membranes, Pervaporation, Intrinsic Selectivity, Permeance.

INTRODUCTION

The dehydration of organic solvents finds large number of application in industrial process. Membrane based separation processes are widely used due to its and economical environmental advantages. Pervaporation (PV) is one of the unique membrane separation process employed dehydration of organic solvents due to its ease of operation, economical, and ecofriendly nature, and better separation efficiency compared to conventional process [1]. The PV separation of water - ethanol mixture has received widespread attraction because of the availability of organic and inorganic nanocomposite membranes [2-4].

Poly (vinyl alcohol) (PVA) which is used as the base material is a water-soluble synthetic polymer that shows excellent film forming, emulsifying, and adhesive properties. It is a widely used polymer in membrane process on which several studies have been done. The Young's modulus of the PVA membranes showed seven times increment with 10 wt% exfoliated graphene oxide loading, and it depends on the

In this work PVA nanocomposite membrane was prepared via solution casting method with varying concentration of Bentonite nanoclay. The interaction

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environmental humidity [5]. The mechanical behaviour of the PVA/graphene oxide membrane is similar to rubber at 60% relative humidity. Yeom et al. studied the effect of permeant-permeant and permeantmembrane interaction on the pervaporation separation of alcohol/water mixtures [6]. The permeant membrane interaction plays a significant role in the separation performance. The hydrophilic nature and chemical resistivity of PVA make it suitable for membrane based applications but its excess solubility in aqueous solutions limits its applicability. Several organic and inorganic fillers were used to incorporate to PVA matrix in order to enhance its properties. On considering the economic and environmental factors, for the fabrication of nanocomposite membranes, filler with such an attractive property is to be considered and in this study bentonite clay is chosen as an attractive option to be embedded in polymeric matrices. It has good mechanical properties and chemical resistance which make it useful as a reinforcing content for polymeric materials [7]. Polymeric nanocomposites with bentonite nanoclay showed remarkable mechanical, thermal, and sorption properties and hence it is utilized as the filler material [8-10].

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and dispersion of nanoclay in the PVA matrix was studied using Fourier transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM), morphology of respectively. The surface nanocomposite membranes was analyzed by atomic force microscopy (AFM). The effect of Bentonite concentration on the pervaporation performance of azeotropic composition of waterethanol mixtures was analyzed. The intrinsic properties were also studied extensively to find the actual behaviour of the membrane with filler loading.

MATERIALS

Poly (vinyl alcohol) (PVA) (M_W =1, 25, 00 and degree of hydroxylation= 86-89%) used as the matrix material was obtained from S.D Fine chemicals, Mumbai, India. Bentonite nanoclay of particle size 15nm is used as the filler and it was procured from Sigma-Aldrich, U.S.A. All other chemicals used were of reagent grade and used without further purification.

Preparation of PVA/Bentonite Clay Nanocomposite Membranes

Solution casting is the simplest method for preparing thin PVA nanocomposite membranes through a procedure described in our recent publication [11]. PVA membranes with 0, 1, 3, 5 wt% nanoclay loading were prepared and are denoted as PVA0, PVA1, PVA3 and PVA5, respectively. The thickness of the membranes was around 100 – 150 µm.

Characterization of Nanocomposite Membranes

The nanocomposite membranes were characterized by Fourier transforms infrared spectroscopy (FTIR), Transmission Electron Microscopy (TEM) and Atomic Force Microscopic Techniques (AFM). The FTIR spectrum of the nanocomposite membranes was obtained from PerkinElmer analyzer at the spectrum range of 400 – 4000 cm⁻¹. Jeol JEM 2100, Japan was used to obtain the TEM images of the samples. AFM analysis was done using Digital Instrument's Multimode Scanning Probe Microscope with Nanoscope controller.

Pervaporation Performance of PVA/Nanoclay Nanocomposite Membranes

In the present study, PVA nanocomposite membranes were used for the pervaporation separation of azeotropic composition of water (4.37 wt %) – ethanol (95.63 wt %) mixtures. PV analysis was performed with a dense membrane in a homemade

PV pervaporation apparatus. The details of experiments were described in our earlier works [11]. Azeotropic composition of water and ethanol was taken as feed solution and all analysis were carried out at room temperature. The initial experiment was allowed to run for 1 h to reach a steady state. The experiments repeated for three times under pervaporation conditions. The pervaporation performance of the PVA membranes were evaluated by considering the characteristic properties of PV such as the separation factor (α) , and the separation flux (J)[12, 13]. The flux and separation factor were determined by measuring the weight and composition of the permeate using the following equation.

$$\alpha = \begin{pmatrix} X_B / Y_B \\ \hline X_A / Y_A \end{pmatrix} \tag{1}$$

 X_A and X_B are the composition of water and Y_A and Y_B are the composition of ethanol in the feed and permeate respectively.

$$J = \frac{Q}{A t} \tag{2}$$

J is the molar flux of the membrane in kg m $^{-2}$ hr $^{-1}$, Q is the quantity of permeate in grams, A is the effective area of the membrane in m 2 used for separation, t is time in hours

Component flux for the separation of azeotropic composition of ethanol and water mixture was calculated by using the equation.

$$J_{H_2O} = J X_{H_2O}$$
 and $J_{Ethanol} = J Y_{Ethanol}$ (3)

 J_{H_2O} and $J_{\it Ethanol}$ are the component fluxes, J is the flux, X_{H_2O} and $Y_{\it Ethanol}$ are the permeate composition of the mixtures.

Enrichment Factor (β) is obtained from the eqn. (4)

$$\beta = \frac{X_B}{X_A} \tag{4}$$

 X_{A} and X_{B} are the composition of water in the feed and permeate respectively.

The overall PV performance was calculated by finding the pervaporation separation index (PSI). PSI was calculated using the eqn. (5)

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

The partial pressure difference between either side of the membrane is the real driving force for the transport of components through the membranes [14, 15]. The real intrinsic properties of the membranes were obtained from membrane permeance, permeability and selectivity and were calculated using the eqs 6, 7 and 8 respectively. Most common ways to express the permeance as gas permeation unit (gpu) $(1\text{gpu} = 3.349 \times 10^{-10} \text{mol/m}^2.\text{s.Pa})$

$$Permeabilty(P_i^G) = J_i \frac{l}{P_{i0} - Pil}$$
 (6)

$$Permeance (P_i^G/l) = \frac{J_i}{P_{i0} - P_{il}}$$
 (7)

The membrane intrinsic selectivity is the ratio of pemeabilities or permeance of the components i and j through the membrane and can be obtained from the expression

$$\alpha_{ij} = \frac{P_i^G}{P_j^G} \tag{8}$$

where J_i is the molar flux, P_{i0} and P_{il} are the partial pressure difference of component i (water) in the feed and permeate side, I is the thickness of the membranes. P_i^G and P_j^G are the permeability of component i (water) and j (ethanol) respectively.

RESULT AND DISCUSSION

Fourier Transform Infrared Spectroscopy (FTIR)

The interaction between PVA and bentonite nanoclay was clear from the FTIR spectra and was shown in Figure 1. The presence of methyl group was confirmed by the presence of bands corresponding to its symmetric and asymmetric stretching in the frequency range 2900 - 2800 cm⁻¹. The bending and rocking vibrations of C-H bonds are also seen in the spectra (1450 and 1360 cm⁻¹). The Si - O bond absorption is the characteristic absorption of the nanoclay and the peak at 1028 cm⁻¹ corresponds to this characteristics absorption. The silanol hydroxyl group showed a broad peak at 3640 cm⁻¹ [16]. The interaction of nanoclay and PVA was clearly confirmed by the diminishing peak intensity of Si-O bond and the Si-O stretching is shifted to 1085 from 1028 cm⁻¹ due to the interaction. The interaction of polymer and filler is generally indicated by the shift in their stretching peak intensity [17]. The crystallinity of semi crystalline polymer, PVA, also changed upon filler loading. The absorption band 1142 cm⁻¹ correspond to the crystalline region is altered with the addition of nanoclay loading.

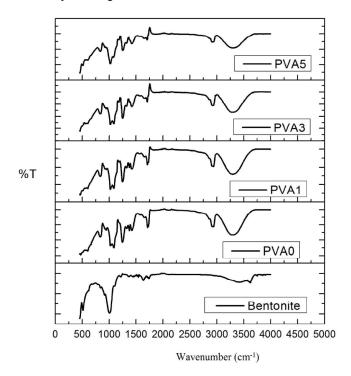


Figure 1: FTIR spectra of the Bentonite nanoclay and PVA/Nanoclay membranes.

Morphological and Surface Analysis of PVA Nanocomposite Membranes

The morphology and surface characteristics of the PVA nanocomposite membranes were analyzed using Transmission Electron Microscopy (TEM) and Atomic force microscopic (AFM) analysis, respectively. The TEM images of PVA1 and PVA5 samples are shown in Figure 2(a). The dispersion of nanoclay without any aggregation is an important aspect for nanocomposites to obtain a membrane system with good performance. On the basis of TEM analysis, one may conclude that the well dispersion and allocation of the nanoclay in the PVA matrix. From TEM images, any aggregation or phase separation of nanoclay has not been observed. This shows that the nanoclay is well dispersed into the polymer matrix and gives uniform and homogeneous dispersion in the PVA matrix. According to the TEM images, the 1 wt% clay loaded membranes showed an intercalative structure and the nanoclay exfoliates at higher filler loading, i.e., at 5 wt% nanoclay loading.

The surface roughness is one of the important characteristic of a good pervaporation membrane material. From AFM images shown in Figure 2(b),

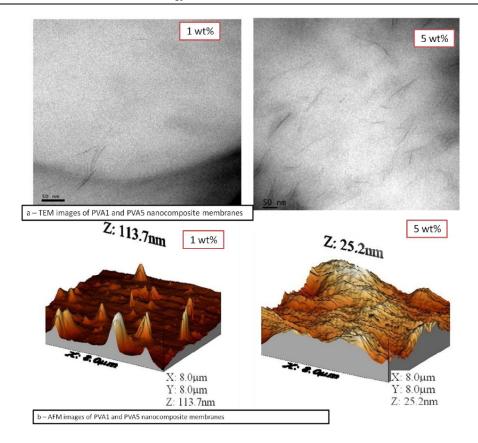


Figure 2: (a) TEM images of 1 and 5 wt% nanoclay loaded PVA membranes. (b) AFM images of 1 and 5 wt% nanoclay loaded PVA membranes

surface roughness was calculated in terms of average roughness. The surface roughness of 1 and 5 wt% clay loaded membranes are 9.78 and 3.76 nm, respectively. Higher surface roughness value is showed by PVA1 membrane, reflecting increased hydrophilicity and effective transport area of the membrane [18, 19]. Thus the well dispersed nanoclay induces hydrophilicity to the PVA nanocomposite membranes and it increases the interaction of the membrane and the permeant components when the membrane is used for pervaporation. So the present hydrophilic PVA membrane is more suited for the selective transport of permeant components, especially water through it.

Pervaporation Performance of the PVA Nanocomposite Membranes

PVA nanocomposite membranes were used for the separation of azeotropic composition of water-ethanol mixtures. The separation factor and flux for PVA nanocomposite membranes are displayed in Figure 3 as a function of filler loading. In comparison with the pristine PVA membrane, the separation factor and permeate flux of PVA1 membranes increased from 4 to 13 and 41 to 65 g/m²h, respectively. It was because that bentonite nanoclay is hydrophilic in nature, and it

induced hydrophilicity the nanocomposite to nanoclay membranes. The hydrophilic content increases the selective interaction of water molecule and membrane material rather than its organic counterpart. The PVA1 membrane with a unique surface property has the best separation performance (represented by peak in the curve), which was because of its high surface roughness and hydrophilic nature.

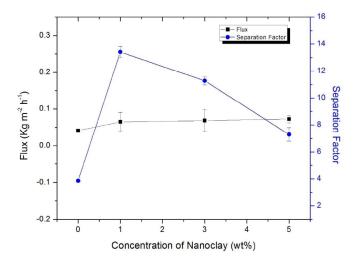


Figure 3: Variation of Flux and Separation Factor of PVA nanocomposite membranes with filler loading.

As shown in Figure 3, the permeate flux was increased whereas separation factor decreased with further increase in nanoclay concentration. This is due to the excess hydrophilicity induced by the nanoclay at higher filler loading and it enhanced the sorption of water molecule. This increased the swelling of nanocomposite membranes at higher filler loading and swollen membranes create a diffusive path for the transport of ethanol molecule through the membranes. This in turn reduce the separation factor with permeate flux at higher filler loading. Moreover, the excessive swelling of PVA nanocomposite membranes in the feed mixture induced sufficient free volume and mobility of polymer chains, which led to a higher flux and lower separation factor at higher filler loading.

The effect of nanoclay concentration on component flux and total flux is given in Figure 4. The total flux increases with filler loading and is due to the increased hydrophilicity of the PVA nanocomposite membranes. The increased hydrophilic nature of the membrane would cause the swelling of membrane in water containing organic mixture. So the diffusive transport of water and organic components through the membranes increases and accordingly, the total flux increased upon filler loading. PVA with 1 wt% nanoclay membrane has average surface roughness of 9.78 nm and is more favorable for the diffusive transport of water components through it. Thus the water flux and correspondingly total flux increased with 1 wt% nanoclay loading. But with further increase in filler loading, the hydrophilic nature of the PVA membranes increased, and the specific selectivity of water components is reduced. So the water flux decreased at higher filler loading. But the hydrophilic nature of the PVA and nanoclay was more favorable for the diffusive transport of water components through the membranes and so excessive swelling of the membranes occurred in the feed composition. These excessive swelling create large free volume in the membrane, and so the

organic counterpart is diffused through the channel. So ethanol component is maximum in the permeate side rather than water at higher filler loading. The presence of large amount of free volume in the swollen membranes decreased the selective interaction of water component and membrane material. This decreased the separation factor and increases the permeation of the components through it.

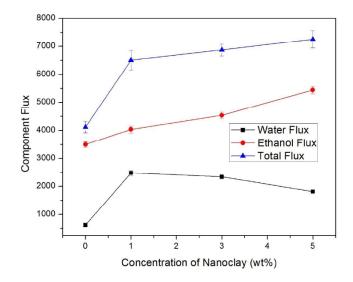


Figure 4: Variation of component flux with filler loading.

The pervaporation separation index (PSI) was used to analyze the overall membrane performance in PV process. PSI value of pristine PVA and PVA/nanoclay membranes is given in Table 1.

The PSI values of pristine PVA membrane is 117 and is increased to 807 for 1 wt% nanoclay loading. An average of around 6.9 times increase in PSI value was observed. The water enrichment factor is also showed the same trend. i.e, PVA with 1 wt% clay loaded membranes showed the maximum separation efficiency. This tremendous enhancement minimum filler loading is due to the presence of hydrophilic filler in the polymeric matrix.

Table 1: The PV Performance Date of the PVA Nanocomposite Membranes for the Separation of Azeotropic Composition of Water - Ethanol Mixtures

Sample	PSI	Enrichment Factor	Water Permeance (gpu)	Ethanol Permeance (gpu)
PVA0	117	3.43	1058	4659
PVA1	807	8.69	1339	1698
PVA3	705	7.78	1435	2165
PVA5	456	5.72	1600	3732

The intrinsic membrane properties such as water and ethanol permeance are also calculated and are shown in Table 1. The permeance of water and ethanol increases with increase in filler loading. But due to the good dispersability and interaction of nanoclay and polymer matrix, the ethanol permeance of 1 wt% clay is lesser than that of other membranes. Thus the selectivity of PVA1 is very close to unity, so it is good membrane system for alcohol dehydration. The variation of intrinsic selectivity with filler loading is given in Figure 5. The hydrophilicity of PVA and nanoclay was more favorable to water components for their transport through the membrane material. But at higher filler loading, the excess swelling of the membrane is occurred due to the excess hydrophilicity. So comparatively larger molecules such as ethanol easily diffused through the swelled membranes, and thus, the component flux and permeance increased on filler loading.

The intrinsic selectivity of PVA1 is higher compared to other membranes. The bentonite nanoclay dispersed uniformly in the PVA matrix and so the organic are retained on the feed side, and water component selectively diffuse through the membranes. Thus the intrinsic selectivity increases with minimum filler loading (Figure 5). When the concentration of nanoclay increases, then the membranes become more hydrophilic and it permits the transport of ethanol components through it. So the permeance of the membranes increases and consequently intrinsic selectivity decreases.

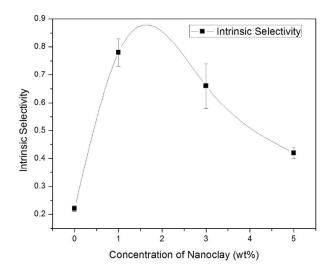


Figure 5: Variation of intrinsic selectivity with filler loading.

The water molecules are small in size as compared to ethanol components, and so it can easily diffuse

through the membranes. Thus the separation factor and selectivity initially ascends and then it decreases due to the breakdown of the hydrogen- bonds between permeant constituents and the polymer because of excessive swelling of the membranes [20]. In the present work, one can observe a similar changing trend for both permeance and flux with filler loading. It is rational because nanoclay affects the intrinsic properties of the membranes. The selectivity reflects the selectivity of the membrane with particular system and separation factor is for pervaporation process. Thus the PVA1 is as good membrane system in both aspects, while considering its membrane and pervaporation performance.

CONCLUSION

Bentonite nanoclay reinforced PVA nanocomposite membranes were used to investigate the pervaporation separation of water – organic azeotropic mixtures. The interaction of nanoclay and PVA matrix was investigated by FTIR analysis. The dispersion and interaction of nanoclay was revealed using TEM analysis. The nanoclay has significant effect on the PV separation of azeotropic water-organic mixtures.

The nanoclay induced hydrophilicity to the PVA hydrophilic membranes. The nanocomposite membranes were effectively used for the separation of water-ethanol mixtures. The separation factor is increased 6.9 times than that of pristine PVA membranes. The 1 wt% clay loaded membranes showed better performance. The intrinsic selectivity of the 1 wt% clay loaded membranes is very close to unity, so it reflects the better separation efficiency of the membranes. Thus PVA with 1 wt% clay loaded membrane is good membranes system for the selective removal of water from azeotropic water - organic mixtures.

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