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POLYMERIC NANOCOMPOSITES FOR DEHYDRATION OF ISOPROPYL ALCOHOL–WATER MIXTURES BY PERVAPORATION

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Abstract. The present work focuses on poly(vinyl alcohol)/ZnO polymer nanocomposite membranes. The nanocomposite membranes are characterized using FTIR, UV-Vis spectra, XRD and SEM techniques. The membranes exhibited preferential water sorption and permeation. Results manifest that the fabricated films can be efficiently utilized to break the azeotropic point of isopropyl alcohol–water mixture.

Keywords: pervaporation, polymer nanocomposite membrane, isopropyl alcohol–water mixture.

1. Introduction

The present work focuses on the development of high performance polymer nanocomposites materials (PNCs). The nanoparticles or nanofillers of dimension less than 100 nm are dispersed in the polymer matrix in order to obtain high-performance material in a more economic way. Different methods of addition of the inorganic materials into organic polymers have been investigated in the various research studies [1-3]. The addition of nanofillers to polymers provides enhanced structural, optical, mechanical, and thermal resistance and membrane properties of polymers. The increase in demand for the energy requirements in the current energy crisis necessitates the development of efficient separation processes. In comparison with the conventional phase separation processes such as distillation, solvent extraction and adsorption, the membrane separation techniques are energy efficient for azeotropic mixtures, isomers, or heat-sensitive mixtures with an easy operation and low cost [4-6].

Membrane based separation techniques find wide applications in the food, medical, energy, industrial, and environmental fields [7]. Pervaporation (PV) is energy efficient separation technique utilized for the dehydration of organic solvents by evaporation of volatile components through a non-porous selective membrane. The process, which is a cost-effective method, can be carried out at low temperature and pressure. Isopropanol commonly known as isopropyl alcohol (IPA), is one of the most widely used solvents in many industries. IPA is extensively utilized as a cleaning agent in circuit board manufacturing, as well as in making Printed Circuit Board's holes conductive. Isopropanol is also used in printing, pharmaceutical and cosmetic industries. IPA forms a homogeneous azeotrope with water, which has the boiling point of 353.3–353.4 K and 87.7 wt % alcohol. Hydrophilic membranes are primarily utilized for the dehydration of water from organic solvents, specifically the azeotropic mixtures. Since poly(vinyl alcohol) (PVA), a water-soluble polymer, is thermally stable and possess excellent film forming property and transparency, it can be very well used for the dehydration of mixtures. Hydrophilicity of PVA is mainly due to the presence of polar –OH groups. However, because of high hydrophilicity, PVA exhibits high degree of swelling, which usually affects the pervaporation separation leading to poor results.

Hence, in this proposed research work, the polymer is incorporated with the hydrophobic nanometal oxide ZnO as a filler to form composites. Nano ZnO is an inorganic material which can enhance mechanical and optical properties due to its incorporation into organic polymer matrix [8-11] and due to a strong interfacial attraction between polymer and nanomaterial. The composite membranes with different amounts of ZnO nanofiller were prepared. The physical and spectroscopic analyses of the membranes were carried out and the membranes were utilized for pervaporation separation of

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IPA–water mixtures at room temperature. Further, the membrane performance was assessed by evaluating permeation flux and selectivity.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) with molecular weight of 1,25,000 (98–100 mol % hydrolyzed) was purchased from Himedia, India. The nano ZnO particles of the size < 90 nm was purchased from Sigma Aldrich, USA.

2.2. Composite Membrane Fabrication

Solution casting method was used for composite films preparation. PVA solution was prepared by dissolving PVA powder in hot deionized water under agitated conditions. 0.5, 1.0, 2.0 and 4.0 wt % of ZnO nanoparticle dispersed solutions were prepared and sonicated for 1 h. The solutions thus obtained were casted separately on clean glass plates. The casted membranes were then dried at room temperature for 48 h to remove the solvent and then the films were peeled off. The pristine PVA polymer film was also prepared in the same manner. The neat PVA film and other PNC membranes were labeled as pristine PVA; PVA/0.5 wt % ZnO; PVA/1 wt % ZnO; PVA/2 wt % ZnO and PVA/4 wt % ZnO, respectively.

2.3. Membrane Characterizations

The IR spectra of pristine PVA and PVA/ZnO were studied with Nicolet, Impact- 410, USA spectrometer. The spectra were recorded in the range of 4000–400 cm^{-1} under transmittance mode with the resolution of 4 cm^{-1}. UV-Vis absorbance spectroscopic measurements were recorded on a Jasco Spectrophotometer model V-670. The spectral range was 200–800 nm. Morphology of the composite membranes was studied with Rigaku Miniflex 600 advanced wide-angle X-ray diffractometer. The diffraction tracings were recorded at the angle $2q$ in the range of 0–80° at the scanning speed of 8°/min. The surface images were recorded at 5 kV with JSM-5910-JEOL (JAPAN) scanning electron microscopy.

The same polymer nanocomposites were also used to study the electrical properties [11].

2.4. Swelling Measurements

The degree of PVA/ZnO polymer nanocomposite membranes swelling was determined by equilibrating the membranes with different IPA–water compositions for 24 h using an electronically controlled oven (WTB Binder, Germany). The dry membranes were weighed first and later soaked in IPA–water mixtures of varying compositions in a sealed vessel at room temperature for 24 h. The swollen membranes were weighed immediately after careful blotting. The percent degree of swelling (*DS*) was calculated as:

$$DS\ (\%) = \frac{(W_s - W_d)}{W_d} \cdot 100 \qquad (1)$$

where W_s and W_d are the weights of the swollen and dry membranes, respectively.

2.5. Pervaporation Experiments

The setup used for conducting the PV experiments is described elsewhere [12]. The effective membrane area is 34.23 cm^2 and the feed tank capacity is 0.25 l. The permeate pressure of the apparatus was maintained at 133 Pa using a two-stage vacuum pump (Toshniwal, Chennai, India). The composition of water in the IPA-water feed mixture was varied from 10 to 50 wt %. The test membranes were allowed to reach equilibrium for 1 h by keeping them in contact with a known volume of feed mixture. After the reaching equilibrium the permeate was collected on the downstream side in traps immersed in the liquid nitrogen jar at regular time intervals. The permeation flux and separation factor were evaluated by weighing the permeate. The permeate composition was measured using Abbe's Refractometer (Atago-3T, Japan). From the PV data obtained, membrane performance was assessed in terms of total flux (J_P), separation selectivity (a_{sep}) and pervaporation separation index (PSI).

Permeation flux was evaluating the mass of permeate at a predetermined period of time and calculated by Eq. (2):

$$J_P = \frac{W_P}{A \cdot t} \qquad (2)$$

where W_P is the mass of permeate, kg; A is the effective membrane area in contact with the feed mixture, m^2; t is the operating time, h.

The separation factor a_{sep} is defined by Eq. (3):

$$a_{sep} = \frac{P_w / P_{IPA}}{F_w / F_{IPA}} \qquad (3)$$

where P_w and P_{IPA} are the mass fractions of water and IPA in the permeate, respectively; F_w and F_{IPA} are the mass fractions of water and IPA in the feed, respectively.

Pervaporation separation index (PSI) defines the separation capability of a membrane and is evaluated by Eq. (4):

$$PSI = J_p (a_{sep} - 1) \qquad (4)$$

3. Results and Discussion

3.1. Fourier Transform Infrared Spectroscopy

The interaction between PVA matrix and nano ZnO particles is confirmed by FTIR analysis. It monitors the vibrational energy levels in the region of different molecules. Fig. 1 depicts the FTIR spectra for pristine PVA, nano ZnO and ZnO filled PNCs under transmittance mode. A characteristic band at 3000–3600 cm^{-1} corresponds to O–H stretching vibration of hydroxyl group of PVA [11]. Absorption bands at 2900–2950, 1711–1736, 1420–1463, 1300–1332, and 851–853 cm^{-1} correspond to C–H asymmetric stretching vibration, C=O stretching vibration (of vinyl acetate group of PVA), C–H bending, $–CH_2$ wagging and $–CH_2$ in stretching vibrations, respectively. It is seen that filling with ZnO caused some noticeable changes in the spectral characteristics of the PVA/ZnO composites at around 4000–800 cm^{-1}. No noticeable changes appear in the composite just by loading 0.5–1 wt % of filler. But as the filler content in polymer matrix increases from 2 to 4 wt %, the bands in the region of 1700–800 cm^{-1} are almost disappeared. This change in the composite membranes is due to defects caused by ZnO, which induce the charge transfer reactions between polymer chain and the nanofiller. This indicates the development of conjugated polymer series which are responsible for the formation of polaron and bipolaron [13]. The observed changes such as a new appearance, shifting and splitting of some bands in the IR spectra of PVA due to ZnO filler provide a clear indication of specific interactions in the polymer matrix [14].

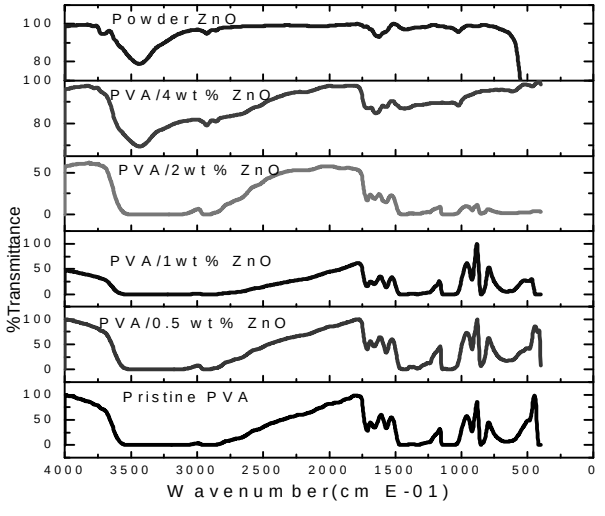

Fig. 1. FTIR spectrum of PVA and PVA/ ZnO composite membranes

3.2. Effect of ZnO Loading on Optical Transmittance Characteristics of PVA

The absorption spectra for pristine PVA and PVA/ZnO PNC membranes are shown in Fig. 2 in the region of 200–800 nm. As the wavelength increased, the absorption spectra for all membranes decreased. With the increase in the weight % of the ZnO nanofiller in the composites, the absorption increases. It is in agreement with the Beer-Lambert's law, which states that absorbance increases with the increase in solution concentration. Appearance of new peaks in the composite films and broadening of the peaks with the increase in the nanofiller content indicates a good interaction between the polymer matrix and nanometal oxide filler.

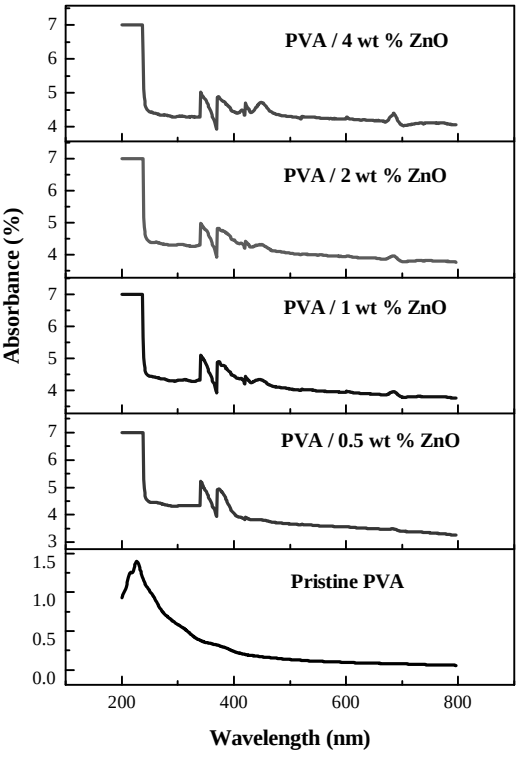

Fig. 2. UV-Vis spectra of PVA loaded and PVA/ ZnO composite membranes

3.3. XRD Analysis of ZnO Nanofiller and Composite Films

The X-ray diffraction profiles of pure ZnO and PVA/ZnO PNCs are given in Figs. 3 and 4, respectively. The crystallinity of nano ZnO was well observed by different sharp peaks as depicted in XRD pattern (Fig. 3). Peaks at 2θ values of 31.44, 34.1, 35.94, 47.24, 56.32, 62.6, 67.68, and 68.84 degree are attributed to nanosized ZnO. All the peaks are indexed to hexagonal wurtzite structure of ZnO (a = 3.2498 Å, c = 5.2066 Å, JCPDS card no. 36-1451) [15-16].

The crystallinity of PVA and the effect of nano ZnO loading into PVA are well explained by the XRD of pristine PVA and PVA/ZnO nanocomposites having 0.5, 1, 2 and 4 wt % of ZnO, respectively (Fig. 4). The maximum intensity diffraction peak at the scattering angle of $2\theta = 22°$ corresponds to d spacing of 4.557 Å. This was due to the 101 crystal plane reflection for pristine PVA, which is in consistence with the earlier studies [17]. All the membranes confirm peak at $2\theta = 22°$, which indicates the semi-crystalline structure of PVA. In addition to this, different peaks were observed at 31.44, 34.1, 35.94, 47.24, 56.32, 62.6, 67.68 and 68.84 degree for all PVA/ZnO composites which correspond to the reflection planes of nano ZnO and consistent with those in the previous report [18].

As PVA possess a plenty of hydroxyl groups, it can reduce the aggregation of nano ZnO particles and facilitate the scattering of nanoparticles in the aqueous PVA solution. The uniformly dispersed nanoparticles increase the surface area of nanocomposites, which, in turn, increases the crystallinity of the polymer nanocomposites [19-20]. It also reveals that strong intermolecular interaction between PVA chains through intermolecular H-bonding results in the crystalline nature of PVA.

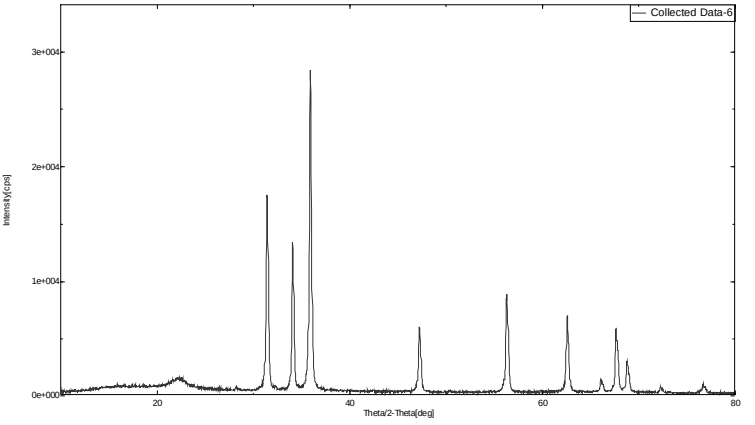

Fig. 3. XRD pattern of ZnO nanoparticles

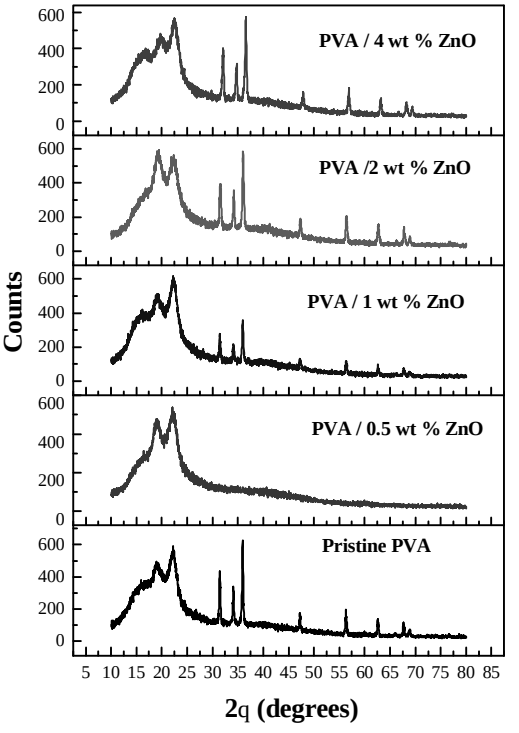

Fig. 4. XRD profiles of PVA and PVA/ ZnO composite membranes

3.4. Scanning Electron Microscopy

SEM analysis of the films was made to examine the morphology and distribution of ZnO nanoparticles on the surface of PVA films. Nano ZnO exhibits flaky nature [21], which is clear from Fig. 5. SEM images of pristine PVA and PVA/ZnO films with 0.5, 1, 2 and 4 wt % of nano ZnO are shown in Fig. 6. Fig. 6a shows nearly smooth and homogenous surface. From the PNC images, it is observed that the nano ZnO particles are smoothly dispersed in the entire PVA polymer matrices and no cracks are observed in the films. As the nano particle content increases, the surface energy of the composites increases and hence the particles show the tendency to agglomerate.

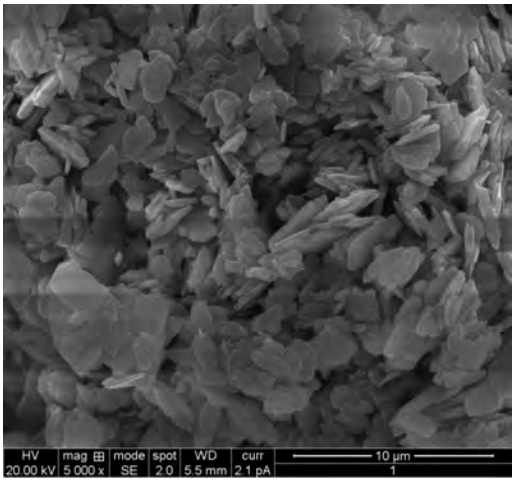

Fig. 5. SEM image of ZnO nano particles

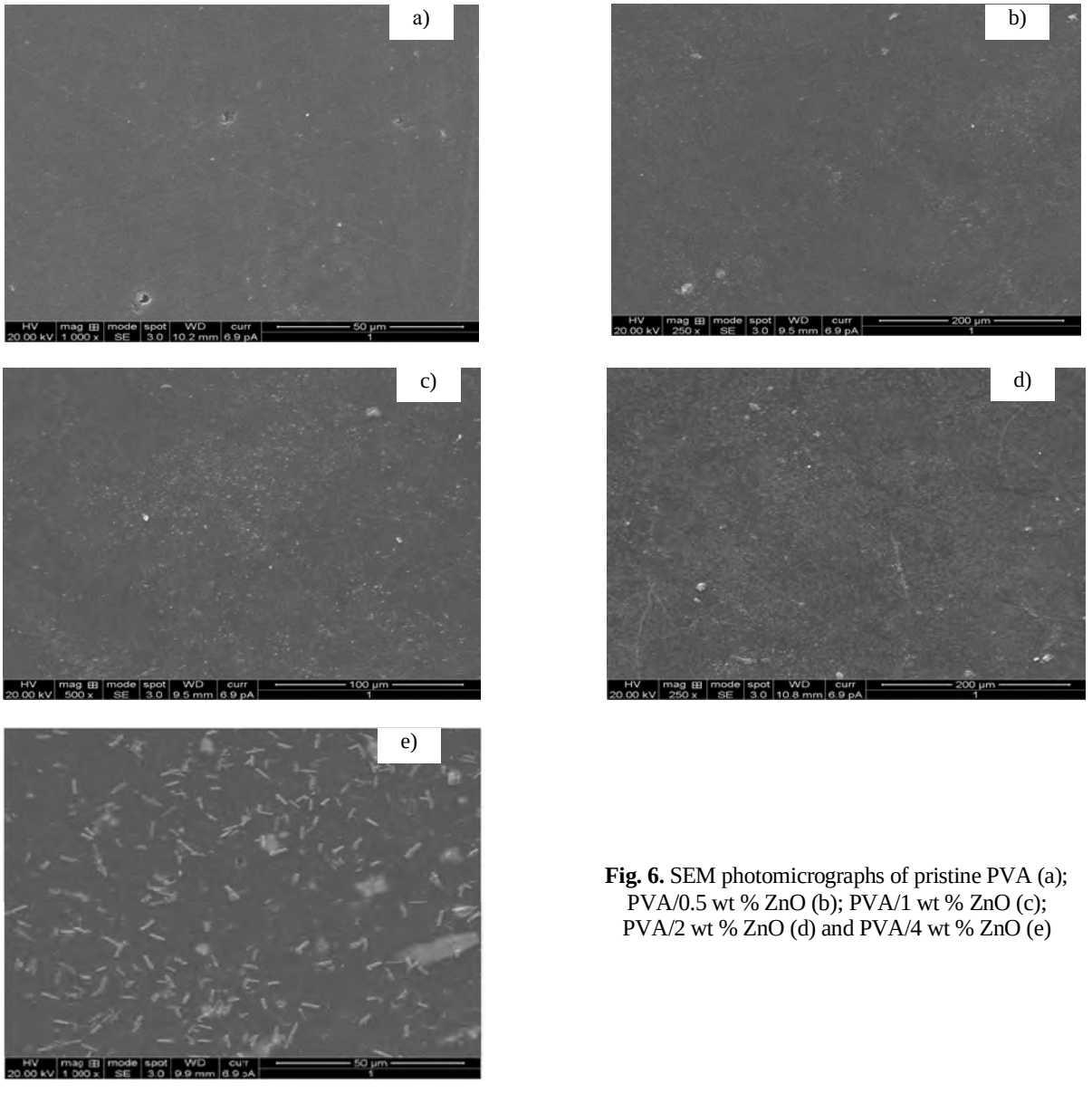

Fig. 6. SEM photomicrographs of pristine PVA (a); PVA/0.5 wt % ZnO (b); PVA/1 wt % ZnO (c); PVA/2 wt % ZnO (d) and PVA/4 wt % ZnO (e)

3.5. Effect of Feed Composition and Nano ZnO Loading on Membrane Swelling

Swelling (sorption) is a thermodynamic phenomenon which controls the movement of permeate molecules under the gradient of chemical potential. Swelling mechanism depends on the morphology and the free volume available within the polymer matrix. Fig. 7 shows the swelling behavior of the PNC films with different content of IPA–water mixture at room temperature. It is clear from the graph that the degree of swelling increases with the increase in the feed water concentration.

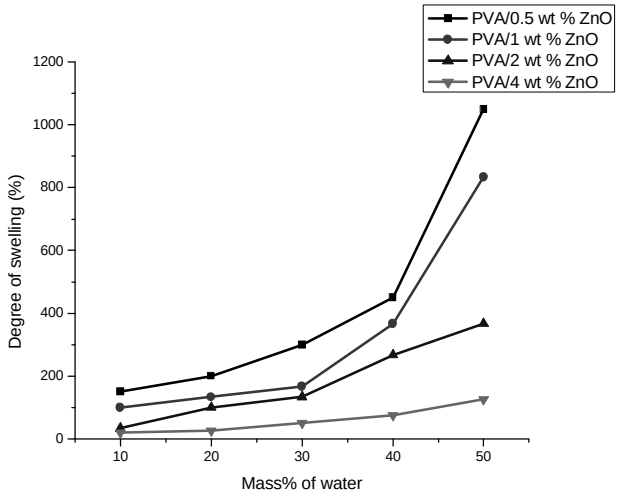

Fig. 7. Effect of feed composition on degree of swelling of PNC membranes

It happens mainly owing to the strong intermolecular interactions occurring between PVA chains, through H-bonding and the water molecules and reactive –OH groups present in the composite matrices. On the other hand, the degree of swelling decreases for the composite membranes as the ZnO loading increases from 0.5 to 4 wt %. The increase in ZnO loading increases the hydrophobicity of the composite membranes and reduces the free volume available for sorption. Hence, as water content increases up to 40 wt %, there is a moderate swelling among the membranes and swelling steeply increases beyond 40 wt %.

3.6. Effect of Feed Composition on Pervaporation Performance

Fig. 8 represents the effect of water composition on the total permeation flux for all the composite films. It is clear that the total permeation flux or the amount of permeate obtained increased linearly with an increase in the composition of water in the feed mixture for all the PNC membranes. When the concentration of the feed mixture decreases, the membranes absorb water molecules resulting in higher swelling. This causes membranes to become more flexible [22-23] but mechanically stable. Hence, the energy required for diffusive transport through the membranes decreases and thereby more amount of permeate is being absorbed.

To study the extent of permeation, the total flux is plotted against the wt % of nano ZnO at 10 wt % of water in the feed mixture (Fig. 9). Reduction in the flux was observed with an increase in the wt % of the nano ZnO. This is due to the decrease of free volume in the composite membranes.

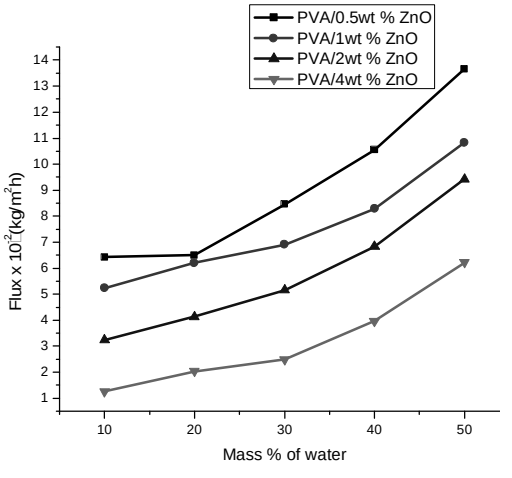

Fig. 8. Effect of feed composition on total pervaporation flux for PNC membranes

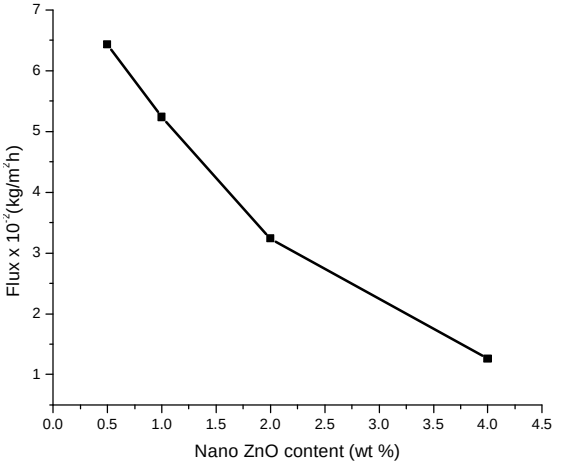

Fig. 9. Effect of nano ZnO loading on total pervaporation flux for 10 wt % of water in the feed

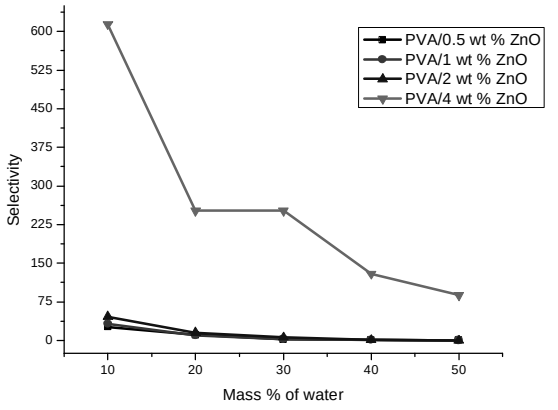

Fig. 10. Effect of feed composition on separation selectivity for PNC membranes

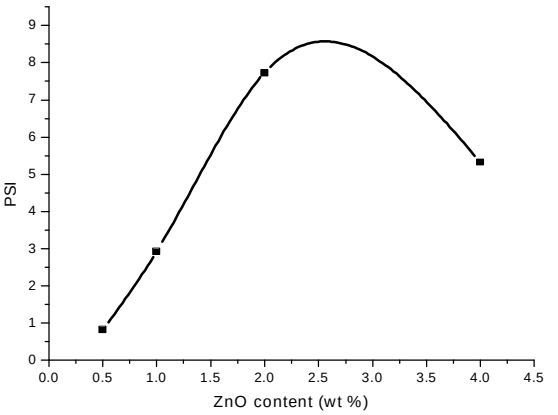

Fig. 11. Effect of nano ZnO loading on PSI at 10 wt % of water in the feed

The overall selectivity of a membrane in pervaporation process depends on the interaction between membrane and the permeating molecules, molecular size of the permeating species and pore diameter of the membrane. The effect of water composition on the selectivity for the membranes is shown in Fig. 10. There is a radical increase in selectivity for 4 wt % ZnO filled PNC membrane when compared to the other composite membranes. This is due to the fact that ZnO particles, when present in the composite matrix, act as a reinforcing agent, thus making the matrix more rigid tighter and decreasing its hydrophilicity. Also, it is observed that the selectivity decreases significantly for all the membranes with the increased water composition in the feed mixture. As a result, the swollen membranes with increased free volume allow some IPA molecules to permeate through the membrane along with water causing the decrease in selectivity.

3.7. Pervaporation Separation Index

The PSI compares and characterizes the performance of pervaporation composite membranes. Fig. 11 shows the variation of PSI as a function of wt % of ZnO in the PNC films. It is observed that the PSI values increase up to 2 wt % of nano ZnO and then decrease for 4 wt % nano ZnO. This is mainly due to hydrophilicity and swelling at higher wt % ZnO loading. Despite this, the PNC films show higher PSI values, indicating that the membranes prepared with nano ZnO filler exhibit an outstanding PV performance.

4. Conclusions

The membranes of PVA/ZnO with different weight percentages of ZnO were prepared. Morphological and optical properties of the membranes were studied by varying the ZnO nano filler content. Pervaporation dehydration of the membranes was tested for isopropyl alcohol–water mixtures at 303 K. Good interaction between PVA matrix and nano ZnO filler was supported by FTIR studies. UV-Vis study confirmed that the inclusion of nano ZnO material does not affect the absorbance or transparency in the visible region. XRD characterization confirms the unaltered crystal structure of nano ZnO in the composite membranes. The SEM images show evenly distributed nano ZnO in PVA matrix. Incorporation of nano ZnO in PVA improved the performance of membranes for the separation of isopropyl alcohol–water mixture. The separation factor of 614.33 was the highest for 4 wt % composite membrane with a flux of $1.26 \cdot 10^{-2}$ kg/m^2·h for 10 wt % of water in the feed. The pervaporation separation index data also support the assumption that membrane with higher amount of ZnO content exhibits an outstanding PV performance. Hence, ZnO filled PVA membranes are novel and suitable for dehydration of isopropyl alcohol.

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ПОЛІМЕРНІ НАНОКОМПОЗИТИ ДЛЯ ДЕГІДРАЦІЇ СУМІШЕЙ ІЗОПРОПІЛОВИЙ СПИРТ–ВОДА ДИФУЗІЙНИМ ВИПАРОВУВАННЯМ

Анотація. *Досліджено полімерні нанокомпозитні мембрани полівініловий спирт/ZnO. З використанням методів ІЧ-Фур'є- і УФ-спектроскопії, рентгено-дифракційного аналізу та скануючої електронної мікроскопії проведено аналіз нанокомпозитних мембран. Встановлено, що мембрани є переважно водосорбційними і водопроникними. Показано що одержані плівки можуть бути ефективно використані для руйнування азеотропної суміші ізопропіловий спирт–вода.*

Ключові слова: *дифузійне випаровування, полімерна нанокомпозитна мембрана, суміш ізопропіловий спирт–вода.*