

Synthesis of inorganic doped polyvinyl alcohol/hydroxypropyl methyl cellulose mixed matrix membrane for pervaporative separation of dimethyl carbonate/methanol mixtures

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Abstract—Inorganic loaded Polyvinyl Alcohol/Hydroxypropyl Methyl Cellulose (PVA/HPMC) mixed matrix composite membranes were synthesized by filling phosphomolybdic acid (PMA) into PVA/HPMC matrix. The obtained results indicate that the swelling degree of the PMA loaded PVA/HPMC blend membranes enhances with excess PMA amount or high feed methanol (MeOH) concentration. The effects of HPMC ratio in blend membranes, PMA content, feed methanol concentration and operation temperature on separation success of pervaporation (PV) were also examined. The consequences demonstrate that the separation factor decreased with PMA amount and led to the ultimate value at 4 wt% PMA amount. Then the increase of PMA content resulted in the decline of the separation factor. Under all conditions, PMA doped mixed matrix composite membrane had a higher separation factor and flux values according to the pristine PVA membrane. Of all the membranes studied, while the flux increased by the high temperature or feed methanol concentration, the separation factor of MeOH decreased. While the operation temperature was 50 °C, the feed methanol concentration was 10 wt%; 4 wt% PMA doped mixed matrix composite membrane has significant separation performance with a flux of 1.31 kg/m²h and separation factor of 121.04.

Keywords: Dimethyl Carbonate, Methanol, Pervaporation, Phosphomolybdic Acid

INTRODUCTION

Dimethyl carbonate (DMC) is a green chemical material due to its low toxicity and biodegradability. It is known to be an eco-friendly building block [1]. DMC molecule contains CH₃-, CH₃O-, and -CO- chemical structures which act as carbonylation, methylating and methoxylating agent. Due to the environmentally benign features, it can substitute for hazardous, toxic chemicals such as phosgene, dimethyl sulfate, chloromethane, methyl halide and methyl chloroformate [2]. DMC has wide application areas such as medicine, chemistry, material, food, and electronic industry. In addition, it can be used as a fuel additive for internal combustion engines. DMC is a gasoline-miscible fuel additive without modification. DMC possesses high oxygen amount (53 wt%) with respect to methyl t-butyl ether (MTBE) [3]. The usage of MTBE in gasoline has been banned due to environmental concerns. Therefore, dimethyl carbonate is an alternative oxygenate substitute for replacing MTBE [4].

DMC is mainly produced by three different methods: (a) oxidative carbonylation of methanol, (b) phosgenation of methanol, and (c) reaction of ethylene carbonate with methanol [5]. In these production techniques, DMC is produced as a mixture with MeOH due to the usage of excess MeOH feed. Therefore, purification of DMC has gained importance. However, the obtainment of DMC

as pure is difficult, because DMC and methanol constitute an azeotropic mixture [6]. The presence of 30% DMC and 70% methanol in the feed mixture causes the formation of azeotropic mixture [7,8]. Classical separation methods such as azeotropic and extractive distillation could be utilized for separation of DMC/MeOH mixtures. But these classical methods have some undesired properties such as high energy consumption, high cost, low efficiency, complicated operation [5]. To overcome these problems, pervaporation comes as an alternative separation process.

Pervaporation as an alternative to conventional separation processes has received a great deal of attention due to advantages such as environmentally friendly, high separation efficiency, low cost and simple operation [9–13]. There is no vapor-liquid equilibrium limitation in pervaporation process. Pervaporation is an efficient process for the separation of azeotropic and close-boiling mixtures [14–18]. Pervaporation success is mainly related to the physicochemical property of the membrane, so the pervaporation process is based on selective diffusion from the membrane [19,20]. According to the property of the membrane, the selective component is sorbed by the membrane at the feed side in the first step of the solution-diffusion mechanism. At the second step, the selective component permeates through the membrane. Finally, the selective component desorbs into the vapor phase on the permeate side [21–24].

The determination of appropriate membrane material is the most important factor for the success of PV separation [19,20]. PVA and HPMC were chosen as membrane materials. PVA is the most popular membrane type for pervaporation. Obtaining the film is rather easy by using PVA. Hydrophilic properties and resistances of chemi-

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cal and mechanical are quite good [25,26]. HPMC is also hydrophilic cellulose derivative polymer. It is compatible with PVA. In addition, HPMC has some advantageous features such as excellent film forming, biodegradability, and biocompatibility [27]. In this study, the aim was to prepare blend membranes of PVA/HPMC and incorporated with PMA to obtain high separation yield with high selectivity simultaneously for pervaporation separation of DMC-methanol mixtures. The addition of PMA in the polymeric membrane is used to modification of some of the membrane properties such as swelling, permeability, and selectivity. PMA is a kind of heteropolyacid which is widely used as a solid catalyst in catalytic reactions. However, it can be used as filler in the membrane matrix due to its solubility in water. The addition of PMA in PVA/HPMC blend membrane results in H bond formation between -OH in PMA and -OH in blend membrane. The hydrophilicity properties of the membrane may be increased with the addition of PMA, and the performance of the membranes has been enhanced in this manner [28,29]. PMA loaded PVA/HPMC membrane has been called as a mixed matrix PVA/HPMC membrane.

In the literature, there are studies in which pervaporative separation of mixtures was carried out using hybrid membrane. Magalad et al. [29] studied the pervaporative dehydration of ethanol. Hybrid poly(vinyl alcohol)-poly(vinyl pyrrolidone) membranes loaded with phosphomolybdic acid were used. The membranes were characterized by FTIR, XRD, SEM, DSC, dynamic mechanical testing analysis (DMTA) and contact angle measurements. 4, 8 and 12 wt% of phosphomolybdic acid were added to the blend membrane. The effect of PMA content on swelling and PV performance was investigated. The authors found that 4 wt% PMA loaded PVA-PVP blend membrane enhanced the pervaporation performance according to the pristine PVA-PVP blend membrane during ethanol dehydration. However, higher PMA loading ratios (8 and 12 wt%) did not affect considerably pervaporation performance [29]. Teli et al. [30] presented pervaporation separation of water-isopropanol mixtures by using poly(vinyl alcohol) membrane loaded with phosphomolybdic. The change of flux and separation factor values was investigated at the different phosphomolybdic content and feed water concentration. While the 7 wt% HPA loaded PVA membrane exhibited a water selectivity to of 89,991 for 10 wt% water in the feed, the pristine crosslinked PVA membrane showed a water selectivity of 77 under the same operation conditions. At the end of the experiment, the presence of HPA in membrane increased the hydrophilicity of the membranes and separation of water molecules from aqueous isopropanol mixture [30]. Chen et al. [31] used silicotungstic acid hydrate loaded chitosan membranes for separation of MeOH/DMC mixtures by pervaporation. The membranes were characterized by Fourier transform infrared, X-ray diffraction, scanning electron microscopy and contact angle meter. Operation parameters such as silicotungstic acid hydrate content, feed methanol concentration and feed temperature were examined on the flux and separation factor. The best separation performance was obtained by using 8 wt% silicotungstic acid hydrate loaded membrane. The silicotungstic acid hydrate (8 wt%) loaded chitosan hybrid membrane exhibited superior performance with a flux of 1,163 g/m²h and separation factor of 67.3 at 50 °C when the feed methanol concentration was 10 wt% [31].

The structural analysis of membrane was realized by using SEM, FTIR, TGA, XRD, contact angle and DSC. The influence of the feed concentration and PMA amount on the swelling degree of the membrane was investigated. Effects of HPMC ratio, PMA amount, feed concentration and temperature on separation properties of PV were also investigated.

EXPERIMENTAL

1. Materials

Hydroxypropyl methyl cellulose (~99% purity) and Polyvinyl alcohol (PVA) (99+% hydrolyzed) were purchased from Kimetsan and Sigma Aldrich. The phosphomolybdic acid, dimethyl carbonate (99% purity), and methanol (≥99.8% purity) were purchased from Sigma Aldrich.

2. Preparation of Mixed Matrix Membrane

PVA membrane solution was prepared with dissolution in water for 6 h at 90 °C to form a solution of 5.0 wt% PVA. 5 wt% of hydroxypropyl methyl cellulose solution was prepared and stirred at room temperature. These two polymeric membrane solutions were mixed for 2 h to form a homogeneous mixture. Different weight ratios of PVA/HPMC (60/40 to 90/10) blend membranes were prepared. The 4, 8, 12 and 16 wt% of phosphomolybdic acid particles (in accordance with the total polymer weight) were dispersed in water separately by sonication for 30 min; these mixtures were added to the pre-prepared blend polymeric membrane solution. Inorganic filler PMA additive blend membrane solution was mixed for 24 h. The mixed matrix membrane solution was poured on a glass petri dish for drying. Membrane thickness was determined by using a micrometer and thickness was around 35–40 μm.

3. Membrane Characterization

3-1. SEM

SEM images of the PVA/HPMC blend membrane and mixed matrix PVA/HPMC blend membrane were obtained by JEOL/JSM-6510-LV, Scanning electron microscope (SEM). SEM images were taken at Tubitak Marmara Research Center. The fracturing of membranes was done by using liquid nitrogen; after that the broken membranes were covered with gold.

3-2. FTIR

FTIR analysis was performed in the region of 4,000–650 cm⁻¹ under at 4 cm⁻¹ resolutions and 4 scans per sample using Thermo Nicolet 5700 spectrometer.

3-3. TGA

TGA curves of PVA/HPMC blend membrane and mixed matrix PVA/HPMC blend membrane were determined using Mettler Toledo thermal analyzer. The measurements were performed at the heating rate of 10 °C/min with the temperature increasing from 25 °C to 600 °C.

3-4. XRD

XRD patterns of membranes were recorded on Shimadzu XRD-6000 equipment. Analysis was performed by using CuKα radiation at rate of 0.02° over the 2 θ range of 5–60°.

3-5. Contact Angle

The determination of hydrophilicity/hydrophobicity of the membrane was carried out by contact angle measurements. Attension KVS Instrument was used for analysis. Measurements were per-

formed with methanol. Measurements were taken in different locations for each membrane sample and the average contact angle values were determined. The measurements were performed with an accuracy of $\pm 1^\circ$.

3-6. DSC

The DSC spectra of membranes were reported on a Mettler Toledo instrument. Measurements were performed over the temperature range of 25–250 °C at a heating rate of 10 °C/min in a nitrogen atmosphere.

4. Swelling Experiments

The membrane pieces were left in DMC/MeOH binary mixtures for the determination of swelling degree at 25 °C for 24 h, and then were taken away from the mixtures at appropriate intervals. The surface solvent was cleaned by filter paper, and then the mass of the membranes was determined.

The degree of swelling (DS) of the membranes was calculated by using Eq. (1):

$$DS (\%) = \frac{m_s - m_d}{m_d} * 100 \quad (1)$$

where m_d and m_s indicate the dry membrane mass and the swollen membrane mass (g), respectively [32].

5. Pervaporation Experiments

The scheme of the pervaporation unit, which was used in experiments, is shown in Fig. 1.

The active surface area of the membrane was 9.62 cm². The membrane was placed in the stainless-steel membrane chamber. DMC/methanol mixture was fed to the membrane chamber. The feed mixture was stirred by a mechanical mixer. The desired temperature was supplied by an oven and measured with a thermocouple. While the feed mixture was under atmospheric pressure, permeate pressure was kept at 20 mbar by using a vacuum pump. The permeate stream was acquired as a vapor phase and liquid nitrogen was used for condensation of vapor into a cold trap and liquid phase was obtained. The mass of collected liquid in the trap was measured and the flux value was calculated. The concentration of components in the permeate stream was specified by gas chromatography to compute separation factor. The results for per-

vaporation experiments were consistent with a mean error around 2%. Separation ability of the membranes was identified by flux and separation factor.

The flux value (J) was calculated with Eq. (2):

$$J = \frac{m}{S \cdot t} \quad (2)$$

where m indicates the weight of the permeate stream in the liquid nitrogen trap. S is the active membrane area and t is the permeation time.

The separation factor of the membrane is defined by Eq. (3):

$$\alpha = \frac{P_a/P_b}{F_a/F_b} \quad (3)$$

where α is the separation factor, F and P show mass fractions of the feed solution and permeate solution, respectively [33].

RESULTS AND DISCUSSION

1. Membrane Characterization

1-1. SEM

The surface SEM images of the PVA/HPMC blend membrane and mixed matrix PVA/HPMC blend membrane are reflected in Fig. 2(a) and 2(c).

Fig. 2(a) shows that the compatibility between PVA and HPMC was quite good. Blend membrane has a smooth surface. There is good interaction between PVA and HPMC polymers in blend membranes (Fig. 2(b)). There is no phase separation. Fig. 2(c) indicates that the phosphomolybdic acid dispersed homogeneously into the PVA/HPMC matrix. Fig. 2(d) indicates that the dispersed phosphomolybdic acid particles have good compatibility with the hydrophilic PVA/HPMC chains, and also the harmony and compatibility of the two different polymers (PVA and HPMC) within the mem-

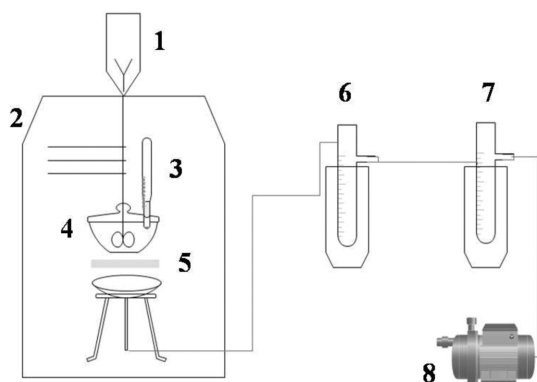


Fig. 1. Schema of PV.

- | | | |
|---------------------|---------------------|------------------|
| 1. Mechanical mixer | 4. Membrane chamber | 6, 7. Cold traps |
| 2. Oven | 5. Membrane | 8. Vacuum pump |
| 3. Thermocouple | | |

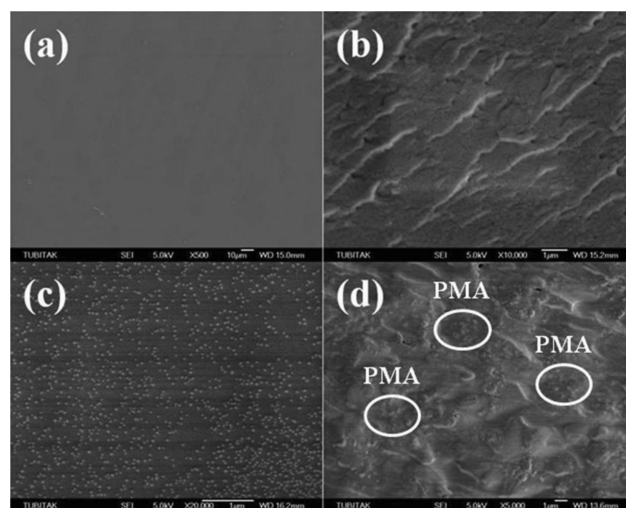


Fig. 2. SEM images of the (a) surface of PVA/HPMC blend membrane without PMA, (b) cross-section of PVA/HPMC blend membrane without PMA, (c) surface of PMA doped mixed matrix PVA/HPMC blend membrane, (d) cross-section of PMA doped mixed matrix PVA/HPMC blend membrane.

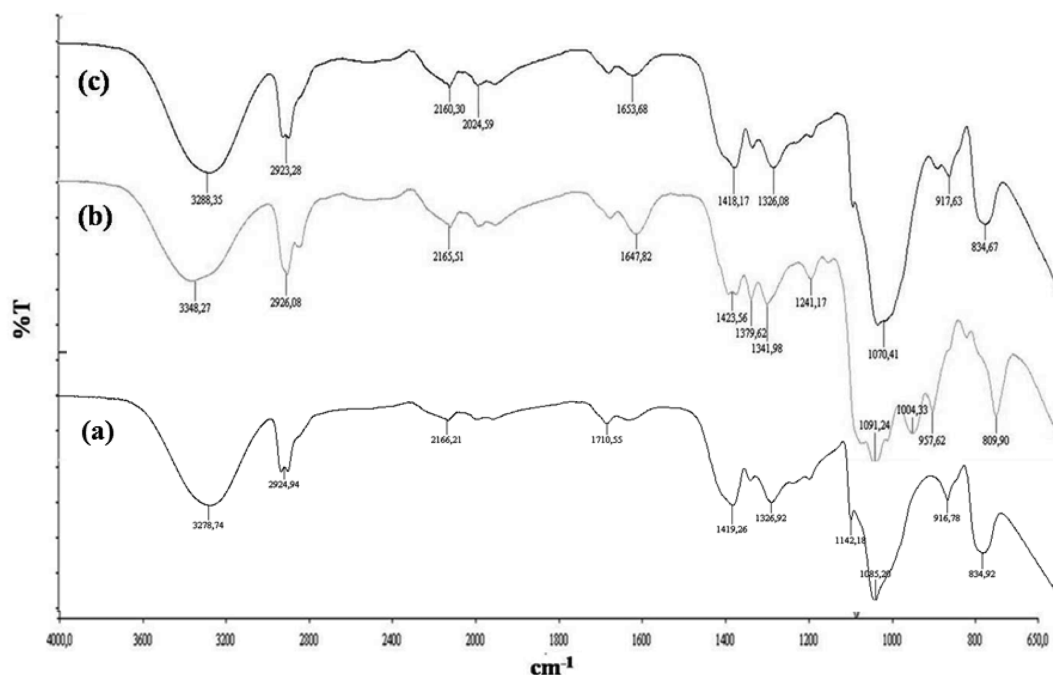


Fig. 3. FTIR spectra of (a) PVA membrane (b) PMA doped mixed matrix PVA/HPMC blend membrane (c) PVA/HPMC blend membrane without PMA.

brane can be seen in that figure. The PVA/HPMC chains can promote good contact with the phosphomolybdic acid particles. The bright or dark particles in Fig. 2(c)-(d) are corresponding to phosphomolybdic acid. Furthermore, there are no voids around the membrane and phosphomolybdic acid. Homogeneous mixture and good dispersion and compatibility were obtained (Fig. 2(d)).

1-2. FTIR

Fig. 3 shows the FTIR spectrum of the membranes.

Fig. 3(a) illustrates the FTIR spectrum of the pristine PVA membrane. The bands at 3,278, 2,924, 1,710, and 1,085 cm^{-1} can be assigned to the characteristic peaks of -OH, C-H, C=O, and C-O bands in PVA, respectively, for the pristine membrane. Fig. 3(c) shows the FTIR spectrum of the PVA/HPMC blend membrane. A band appearing at 3,288 cm^{-1} corresponds to O-H groups of PVA/HPMC blend membrane. Strong hydrogen bonds occur between HPMC and PVA polymers during the blending process. Saccharide bonds in PVA/HPMC blend membrane can be seen between 1,660 cm^{-1} and 1,400 cm^{-1} . Fig. 3(b) exhibits the characteristic peaks of PMA doped mixed matrix PVA/HPMC blend membrane. The peak intensity of -OH groups increases with the presence of PMA particles amount. This state indicates the increase of hydrophilicity of PVA/HPMC blend membranes with the addition of PMA. The presence of PMA in the membrane is proven by the characteristic peak of 1,091, 1,004, 957, 809 cm^{-1} . The bands which are seen in 1,091, 1,004, 957, 809 cm^{-1} are ascribed to the presence of (P-O), (M_e =O_t), (Mo -O_c-Mo) and (Mo -O_c-Mo) bonds [35-37].

1-3. TGA

The degradation of PVA/HPMC blend membranes with temperature was examined by thermogravimetric analysis (TGA). The results are shown in Fig. 4.

The weight loss, which was seen in the temperature range of

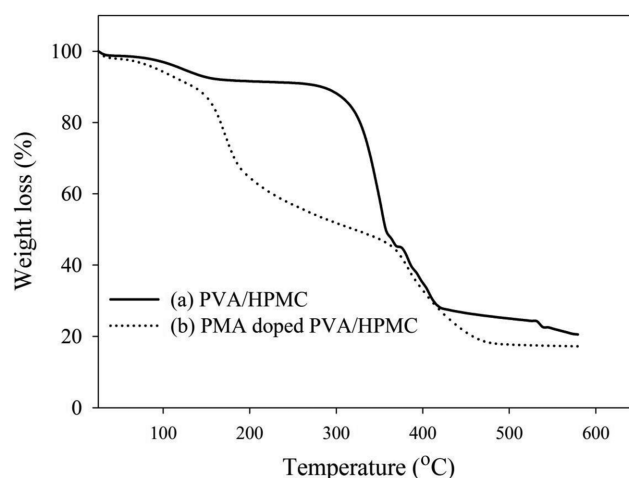


Fig. 4. TGA data of membranes (a) PVA/HPMC blend membrane without PMA, (b) PMA doped mixed matrix PVA/HPMC blend membrane.

50-150 $^{\circ}\text{C}$, is due to the evaporation of water from the structure of membrane samples. The decomposition between temperature values of 270-450 $^{\circ}\text{C}$ can be explained with the chemical degradation process in the polymeric backbone. In addition, the additive PMA chemical degradation reaction $\text{H}_3\text{PMo}_{12}\text{O}_{40} \rightarrow (1/2) \text{P}_2\text{O}_5 + 12\text{MoO}_3 + (3/2)\text{H}_2\text{O}$ ($\text{Mo}=\text{W}$) occurs in this temperature range [35,36].

1-4. XRD

The XRD patterns of the pristine PVA membrane, PVA/HPMC blend membrane and PMA doped PVA/HPMC membrane are shown in Fig. 5.

From the patterns, characteristic peaks can be seen for PVA and

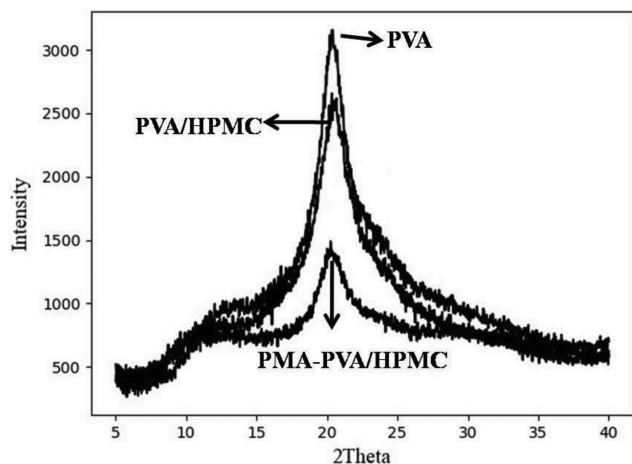


Fig. 5. XRD patterns of PVA, PVA/HPMC and PMA-PVA/HPMC membranes.

PVA/HPMC membrane around $2\theta=20^\circ$ due to the PVA crystalline planes. The peak intensity decreases with the addition of HPMC in PVA/HPMC membrane for PVA/HPMC blend membrane. It indicates that the crystallinity of membrane decreases with HPMC, because HPMC is less crystalline than PVA. There is no additional diffraction peak in the XRD pattern for PMA-PVA/HPMC membrane. The absence of characteristic peaks of PMA in the XRD pattern of PMA-PVA/HPMC suggests that PMA units are uniformly dispersed in the polymeric matrix of the membrane. The addition of PMA in PVA/HPMC blend membrane also resulted in decrement of peak intensity prominently. The amorphous regions of membrane increase, diffusion of water gets easy and flux increases. The obtained results were reported as similarly by Magalad et al. [29].

1-5. Contact Angle

The hydrophilicity of the membrane is important analysis for the PV performance of membrane. The smaller the contact angle means greater hydrophilicity. Fig. 6 shows the change of contact angle

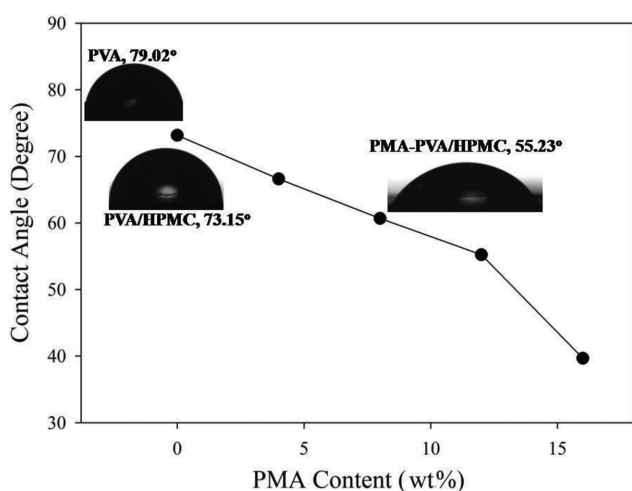


Fig. 6. The contact angle values of PVA, PVA/HPMC and PMA-PVA/HPMC membranes.

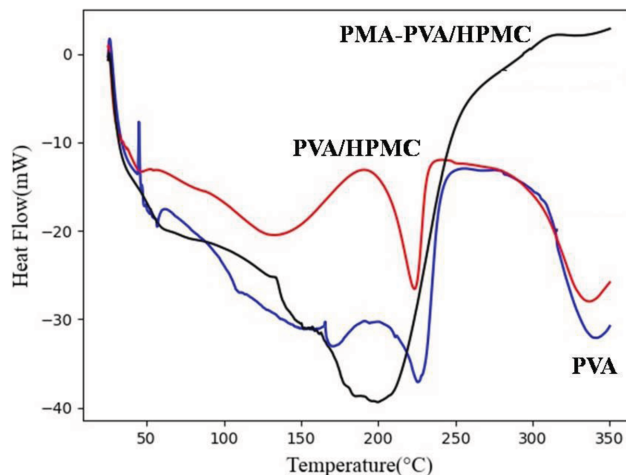


Fig. 7. DSC curve of membranes.

of membranes.

As shown in Fig. 6, the contact angle of the membranes gradually decreases with increasing PMA content. This result is related to addition of more PMA introduced into the PVA/HPMC blend matrix. Also, the contact angle values of PVA, PVA/HPMC and PMA-PVA/HPMC membranes are given in Fig. 6. The contact angle of PVA membrane is higher than PVA/HPMC membrane. It may be attributed to the increase of the hydrophilic groups when the HPMC is blended with PVA. PMA-PVA/HPMC membrane has the lowest contact angle value according to the other membrane types. This is related to the increment of counts of polar groups with PMA addition in membrane. Therefore, a polar component can permeate through the membrane easier than a non-polar component.

1-6. DSC

The DSC curves of the PVA, PVA/HPMC, and PMA-PVA/HPMC membranes are shown in Fig. 7.

From Fig. 7 it is observed that PVA showed a sharp endothermic melting curve at 230°C . The PVA/HPMC had close melting points with pristine PVA membrane. This result showed that micro-phase separation was not observed during the membrane formation process, good compatibility between PVA and HPMC matrix. With addition of PMA, melting temperature of PVA/HPMC membrane shifted to lower temperature. The melting temperature was observed at 195°C for PMA-PVA/HPMC. This decrease in the melting temperature can be explained with the decrement of the ordered packing association of membrane with PMA addition, because PMA was taken a role as reinforcing bridges in polymeric matrix. The similar observation was also reported by Teli et al. [30].

2. Swelling Results

To examine the influences of the feed concentration and PMA amount on the sorption ability of membrane, the swelling degree of membranes was specified and the change of swelling degree was shown in Fig. 8 versus different feed methanol concentration.

The swelling degrees of the membranes increased with increasing feed methanol concentration for all the PMA loading ratios. The swelling degree had a minimum value for PVA/HPMC membrane. The addition of PMA increased the swelling degree of the membrane for DMC/methanol mixtures. This can be related to the

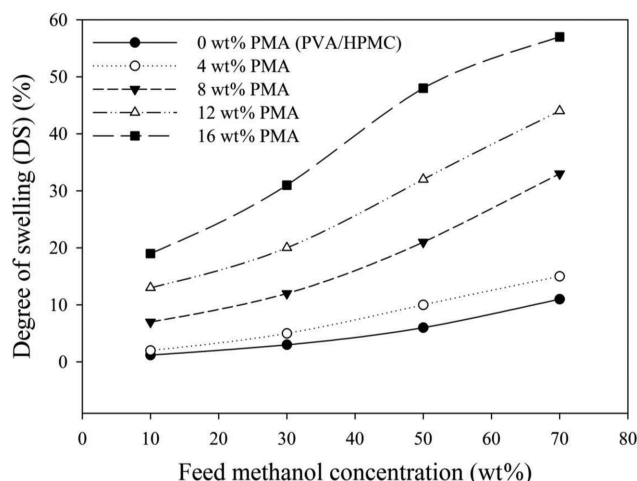


Fig. 8. Effects of feed concentration of methanol and PMA amount in membrane on swelling degree.

hydrophilic nature of PMA particles and the hydrogen bond formation among PMA and PVA/HPMC chains. As hydrophilicity of membrane is enhanced, the affinity of the membrane to methanol increases because methanol and water have close polarity value. The crystallinity of the membrane decreases and free volume increases. Therefore, the swelling degree of membrane is enhanced. The obtained results show that the mixed matrix PVA/HPMC blend membrane is more methanol-selective than DMC.

3. Pervaporation Results

3-1. Effect of HPMC Ratio in Membrane

Polymer blending for the membrane synthesis is one of the membrane modification methods. In this research, blend membranes were manufactured by utilizing PVA and HPMC polymers. Fig. 9 reflects the effect of HPMC content on the permeation flux and separation factor. The methanol concentration was 10 wt% and operation temperature was 50 °C.

With increased HPMC ratio, the flux increased and the separation factor decreased. The addition of HPMC into PVA disarrays the alignment of the PVA chains, causing the decrement of the tight

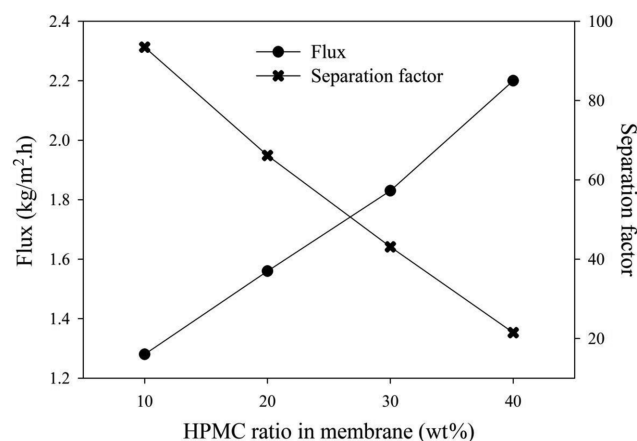


Fig. 9. Effect of HPMC ratio in membrane on flux and separation factor.

structure of the membrane, so that the crystallinity degree of the PVA decreased and the free volume of the membrane increased. As a result, the swelling degree of the membranes increased. In addition, HPMC is a strong hydrophilic membrane material; the addition of HPMC increases the hydrophilicity of the membranes. Hydrogen bonding is formed between the membranes and methanol. Therefore, the affinity between methanol and membrane increased. For all the reasons mentioned above, more methanol was sorbed by the membrane. An increase in the diffusion of methanol contributes significantly to the swelling ratio of the membrane. High swelling degree results in high free volume and, consequently, easy diffusion of components. Therefore, DMC transport through the membrane with MeOH and separation factor decreases. Therefore, the decrease of separation factor and increase of permeation flux were observed with increasing the HPMC ratio.

As the HPMC ratio in blend membranes increases from 10 wt% to 40 wt%, the permeate flux increases from 1.28 kg/m²h to 2.20 kg/m²h, the separation factor decreases from 93.47 to 21.47. When the blend membrane incorporates 90 wt% PVA and 10 wt% HPMC, the membrane has the best separation performance such as separation factor of 93.47 and a permeate flux of 1.28 kg/m²h. Therefore, 90 wt% PVA and 10 wt% HPMC containing membrane was used to detection of other reaction parameters.

3-2. Effect of PMA Amount in Membrane

The usage of PMA as an additive in the blend membrane has an important effect on the separation ability of membrane. Fig. 10 shows the variation of permeation flux and the separation factor as a function of PMA amount in the blend membranes for 10 wt% feed concentration of methanol at 50 °C.

The incorporation of the PMA into the blend membrane matrix alters the membrane's framework, which has a great effect on membrane separation features. The PMA loaded mixed matrix PVA/HPMC blend membranes have higher permeation flux and separation factor values than the pristine PVA/HPMC blend membrane.

In the beginning, the addition of PMA enhanced physical cross-linking and plasticization was restricted. The high separation factor and low permeation flux could be explained by the becoming compact structure of PMA introduced. Initially, the separation fac-

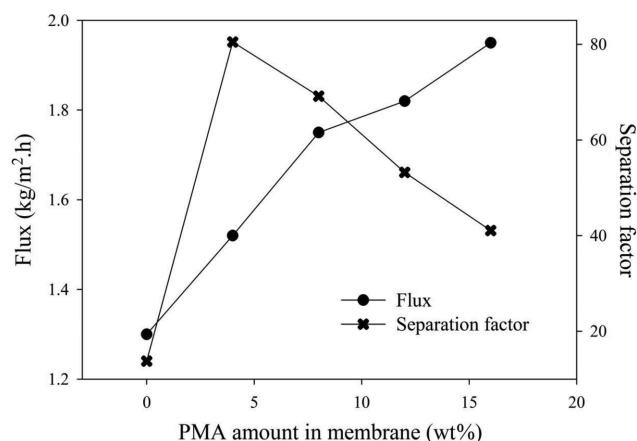


Fig. 10. Effect of PMA ratio in membrane on flux and separation factor.

tor of 4 wt% PMA loading blend membrane is rather higher than the pristine PVA/HPMC membrane. However, at higher loading ratios of PMA, the separation factor values reduced substantially. Despite this, the separation factor values for mixed matrix membrane are still greater than that obtained for pristine PVA/HPMC blend membrane. This quick decline in separation factor is related to the high loading ratio of PMA. Hydrophilic-hydrophilic interactions between PMA particles and the PVA/HPMC blend membrane structure increased. Intermolecular hydrogen-bonding occurs between PVA/HPMC blend membranes and the PMA particles. The usage of PMA of more than 4 wt% could cause interfacial defects. Also, the diffusion channels of the membrane expand, which facilitates the diffusion of the methanol. The components transport through the free volume of the membrane with ease. However, the high amorphous structure and wide diffusion channel facilitate the DMC diffusion through the membrane, thus decreasing the selectivity values for PMA loading blend membranes [27,29-31,39].

From Fig. 10, the permeation flux increased from 1.30 kg/m²h to 1.95 kg/m²h when the PMA amount was increased from 0 to 16 wt%. However, the separation factor increased from 13.75 to 41.07. The highest separation performance was observed in 4 wt% PMA doped mixed matrix membrane. The calculated permeation flux and the separation factor showed that optimum PMA loading ratio was 4 wt%. This value was kept constant for investigation of other reaction parameters.

3-3. Effect of Feed Methanol Concentration

Fig. 11 shows the effect of MeOH concentration on PV performance of the pristine PVA/HPMC and PMA loaded mixed matrix PVA/HPMC blend membranes (4 wt% PMA) hybrid membrane at 50 °C.

The MeOH flux increases with rising MeOH concentration from 10 wt% to 70 wt%. This increment is related to the driving force. The change of MeOH driving force is responsible for the MeOH flux, because the driving force has a crucial role in permeation flux. As the MeOH concentration increases, the blend membrane contacts much more MeOH molecules and flux increases. The pervaporation process is also affected by the swelling ratio of the mixed

matrix membrane. Swelling ratio rises with an increment of MeOH concentration in the feed. The pervaporation process is also affected by the swelling ratio of the mixed matrix blend membrane. As the feed MeOH concentration increases, the sorption capacity of the membrane increases [5]. This facilitates the transport of MeOH and DMC molecules through membranes. The molecular magnitude of MeOH is smaller than that of the DMC. Therefore, MeOH can penetrate through the swollen membrane easily. As a result, flux increases and the separation factor decreases [41]. Methanol is the basic component that impacts the sorption features of the membrane, because methanol has high affinity value for the PVA/HPMC polymeric blend. The close solubility parameter leads to the higher affinity between MeOH and PVA/HPMC membrane. This makes the permeation of MeOH higher as shown in Fig. 11. Due to the membrane swelling, the diffusion channels expand, and these wide channels facilitate the diffusion of DMC molecules with methanol through the membrane. Increasing diffusivity causes a low separation factor value [42].

With the feed MeOH concentration increasing from 10 to 70 wt%, the total flux of mixed matrix membrane increased from 1.31 kg/m²h to 1.98 kg/m²h, while the separation factor of mixed matrix membrane decreased from 121.04 to 34.06. When the pristine PVA/HPMC membrane was used, the total flux increased from 1.275 kg/m²h to 1.79 kg/m²h, while the separation factor decreased from 95.39 to 12 with the increasing of MeOH concentration.

3-4. Effect of Temperature

Temperature is a substantial quantity influencing the separation process of pervaporation. Effect of temperature on separation performance was examined at the azeotropic point of the mixture of MeOH/DMC (70 wt% feed MeOH concentration) at 30, 40, 50 and 60 °C for the pristine PVA/HPMC and PMA doped mixed matrix PVA/HPMC blend membranes (PMA 4 wt%).

Fig. 12 shows that increasing temperature increases the permeation flux and decreases the separation factor of methanol. This fact is related to the increment of the driving force and the expanding of diffusion channel at the higher temperature.

The driving force in the pervaporation process is the partial pressure difference between retentate and permeate stream. The

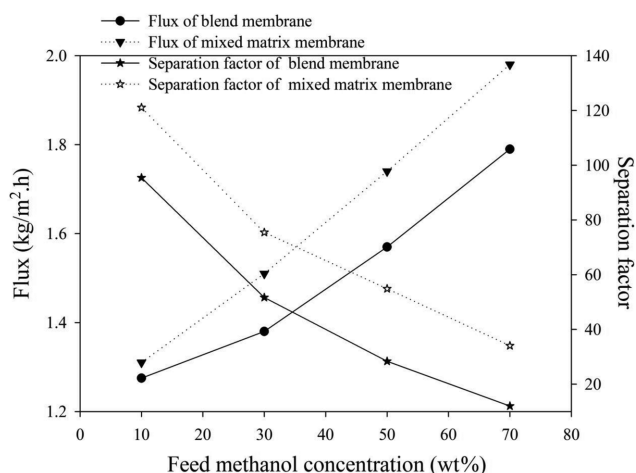


Fig. 11. Effect of feed methanol concentration on flux and separation factor.

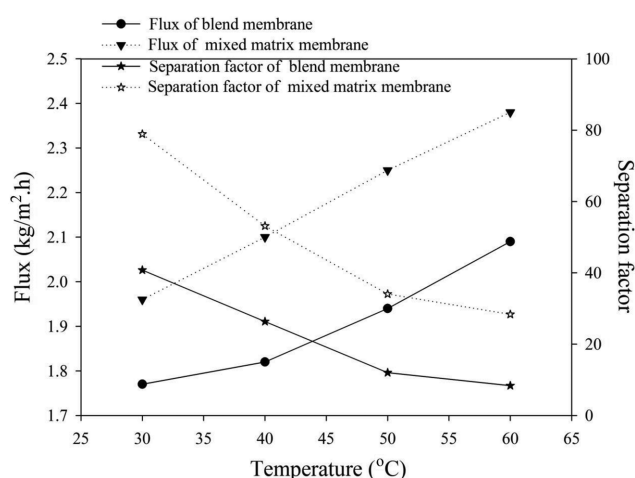


Fig. 12. Effect of temperature on flux and separation factor.

Table 1. Comparison of pervaporative separation performance of DMC/methanol mixtures with literature

Membrane	Feed methanol concentration (wt%)	Operation temperature (°C)	Flux (kg/m ² h)	Separation factor of methanol	Reference
PVA-PVP/PAN	70	55	0.243	16	[41]
Chitosan	10	50	0.13	3.2	[4]
Chitosan	70	50	1.37	6.76	[44]
PAA/PVA	10	60	0.6	1	[5]
PAA/PVA	70	60	0.55	13	[5]
ZSM-5 Filled Chitosan	10	25	0.165	24.2	[39]
ZSM-5 Filled Chitosan	70	25	0.692	2.4	[39]
STA/ Chitosan	10	50	1.15	65	[31]
STA/ Chitosan	70	50	1.5	33	[31]
PMA doped PVA/HPMC	10	50	1.31	121.04	This study
PMA doped PVA/HPMC	70	50	1.98	34.06	This study

downside of the membrane is always under the vacuum pressure, and temperature change in the membrane cell does not affect the vapor pressure at the permeate side. As the operation temperature increases, the vapor pressure of components in the feed mixture increases. Increment of vapor pressure creates a driving force for the easy diffusion. As a result, the transport of all molecules in the feed mixture increased, high flux and low separation factor are observed. Furthermore, high temperature enhances the mobility of the polymer chains. The diffusion pathway of the membrane expands, methanol and DMC molecules diffuse through the membrane easily [31,39,41-43].

While the mixed matrix membrane showed the highest separation factor of 78.91 and a permeate flux of 1.96 kg/m²h at 30 °C for separating DMC/MeOH azeotrope, the blend membrane exhibited the ultimate separation factor of 40.77 and a permeate flux of 1.77 kg/m²h under the same operation conditions.

4. Comparison of Pervaporation Performance with Literature Data

The permeation flux and separation factor for pervaporative separation of DMC/MeOH azeotrope mixture were compared with other blend membranes studied in literature, and Table 1 presents the comparison results.

There is no study that pristine PVA/HPMC and also PMA loaded PVA/HPMC as the membrane is used for separation of DMC/methanol mixture. Therefore, this paper is rather original due to these properties. There are some studies for pervaporation of DMC/methanol mixtures in the literature, but the membrane is made from a different material. The listed results show that this paper has a higher permeation flux value and better separation factor value.

CONCLUSION

PVA/HPMC blend membrane was successfully synthesized to separate methanol from a DMC solution. The blend membrane filled with PMA heteropolyacid showed an increment in the separation performance of the membrane. Higher feed composition and PMA loading resulted in higher membrane swelling. Therefore, flux increased and the selectivity decreased with the increase of

PMA amount in the PVA/HPMC blend membrane. This situation was related to the increase of the free volume of the membrane as evidenced by the swelling study. As a result of the increase of temperature, high flux and low selectivity were observed due to the high chain mobility and flexibility. The effect of different HPMC content in the blend membrane was examined; 10 wt% of HPMC displayed the maximum separation factor of 93.47 and a permeate flux of 1.28 kg/m²h at 50 °C for DMC/MeOH azeotrope. The mixed matrix membrane had a separation factor of 121.04 and a total flux of 1.31 kg/m²h in the pervaporation of 10 wt% MeOH containing DMC-methanol mixture at 50 °C. Furthermore, the membrane exhibited high separation performance according to the literature. Therefore, the developed mixed matrix PVA/HPMC membrane is an important alternative membrane for obtaining DMC as pure from the mixture by pervaporation.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

NOMENCLATURE

α	: separation factor
DMC	: dimethyl carbonate
DS	: degree of swelling
F_a, F_b	: mass fraction of a and b constituents in the feed
J	: flux [kg/m ² ·h]
m	: permeate weight [g]
m_s	: weights of swollen membranes [g]
m_d	: weights of dried membranes [g]
P_a, P_b	: mass fraction of a and b constituents in the permeate
S	: active membrane area [m ²]
t	: time [h]
HPMC	: hydroxypropyl methyl cellulose
MeOH	: methanol
MTBE	: methyl t-butyl ether
PMA	: phosphomolybdic acid
PVA	: poly (vinyl alcohol)
PV	: pervaporation

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