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Mixed matrix membranes for pervaporative separation of isopropanol/water mixtures

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ABSTRACT

Flat mixed matrix membranes (MMMs) were fabricated. Polyimides of Matrimid 5218 and P84 s backbone and different fillers including silica aerosil 200, zeolite 4A, and carbon molecular sieves were used. Effects of different polymer types and concentrations, and different filler types and contents up to 15 wt.% were studied. Scanning electron microscopy analysis showed acceptable connections between the two phases in addition to a confirmation may be concluded by higher MMMs pervaporation (PV) performances compared to those of neat polymeric membranes. Effective thermal treatment method was used to remove probable MMMs defects. Performed PV experiments showed better separation performances of MMMs with respect to those of neat polymeric membranes. The best results were obtained for hydrophile zeolite 4A filler where its incorporation improved both the filled matrices separation performance especially for Matrimid 5218 (10-wt.%)-zeolite 4A (10 wt.%) up to eight times while its permeation rate nearly increased by ∼35%.

Keywords: Pervaporation; Mixed matrix membranes; Isopropanol/water separation

1. Introduction

Membrane separation technology, as a green technology, is a fast-growing branch of science and engineering. Many research activities are being carried out worldwide to improve current membrane processes and materials and/or to introduce new membrane processes and materials.

In pervaporation (PV) processes, the evaporated penetrate(s) is absorbed and solved in the membrane and diffuses through the membrane based on its vapor pressure difference across the membrane. This vapor pressure difference can be maintained in several ways, e.g. using a vacuum pump to evacuate permeate side in laboratory scale or economically employing a sweeping gas or coolant to carry away the condensed permeated vapor and maintain the vapor pressure difference in industrial scale [1,2].

Pervaporative separation is widely used for a variety of azeotropic (like dehydration of different alcohols such as 12.6 wt.% isopropanol (IPA) aqueous solution [3,4]), close-boiling points, volatile removal from fermentation broth, and/or heat-sensitive mixtures [5–7]. IPA dehydration by the PV technique has been widely studied using different membranes of neat synthetic polymers, blends of polymers, natural

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polymers like sodium alginate (NaAlg), and microporous silica [2,6,8,9].

PV can be potentially employed instead of conventional separation processes since it is very energy effective (pervaporative dehydration of IPA requires 423 kJ/kg IPA, while distillation and azeotropic distillation energy demand is 10,376 and 3,305 kJ/kg IPA, respectively), environmentally cleaner and friendly, low cost, simple for design and scale-up, flexible, and also no need for a third component of entrainer to be added [2,4,5,10]. PV is now commercially available for two main applications of water removal from concentrated alcohol solutions (main application) and small amounts of volatile organic compounds (VOCs) removal from contaminated waters/wastewaters [1,11].

Polymeric membranes are widely used in PV due to their flexibility and low cost. However, instability and swelling of polymeric membranes make them not suitable for harsh chemical and high temperature environments which are often encountered in industrial applications [12,13]. On the other hand, inorganic membranes have advantages of high separation performance due to their unique molecular sieving property and selective adsorption [5]. Also, inorganic membranes exhibit much better structural stability to serve at higher operating temperatures and superior chemical resistance properties [12]. However, their hard and expensive construction for large membrane area surfaces, inherent brittleness, and low specific surface area in modular form restrict their industrial applications, while their fine granular particle preparation is much easier and cheaper [14].

Attractiveness of PV process can be increased via improvement in employed membrane separation performance where it is tried using different approaches such as polymer modifications via cross-linking, blending, grafting, incorporating of fillers and nanoparticles within polymer matrices, and so on [2,9,11,13–17,18–22] while their other properties such as stability, durability, and mechanical strength to withstand the cyclic modes of PV operating conditions should be considered as well [11]. However, from a separation point of view, a tradeoff between permeation rate and selectivity of most modified polymeric membranes remained in many cases, while incorporation of fine and cheap filler particles potentially can increase permeation rates and separation factors of the resultant membranes (called mixed matrix membranes [MMMs]) simultaneously to overcome the mentioned tradeoffs [2,23–26].

These facts lead the researchers to incorporate proper filler particles into polymeric matrices in order to employ desired properties of both materials simultaneously. Mechanical, optical, and thermal properties of the resulted MMMs are also improved in addition to their separation characteristics by proper filler particles, incorporation into polymer matrices [11,13,14,27].

Different MMMs prepared using proper polymers and filler particles like zeolites or carbon molecular sieves (CMS) or other appropriate organic/inorganic fillers have been widely studied for pervaporative dehydration of organics and gas separations [5,12,13,28]. The most important point in MMMs fabrication is appropriate selection of both polymer matrix and filler particles to preferentially pass the desired component(s) [13,20,29]. Polyvinyl Alcohol (PVC), NaAlg, and polyimides of Matrimid 5218 and P84 are hydrophile and pass water rather than inorganic couple of the feed mixture [5,11,12,30]. As it can be seen, incorporated hydrophile fillers could facilitate water transport through the resulted MMMs and simultaneously improve their separation factor since they can act as crosslinkers to avoid excessive membrane plasticization by water [20,30,31]. Other factors such as size and crystal shape of fillers, homogeneity of filler particles' dispersion, good connection between polymers and fillers, and appropriate membrane preparation procedure to avoid defects in the MMM structure should also be considered for successful MMMs preparation [11,13,29,30].

Generally speaking, MMMs, as new promising membrane generation, have made many hopes to commercialize potential membrane processes or economically improve current working processes and many research activities are being carried out to achieve these goals (Table 1).

In this study, some flat MMMs were prepared using polyimides of Matrimid 5218 and P84 as polymer matrices and aerosil silica 200, zeolite 4A, and CMS as filler particles in order to enhance pervaporative dehydration performance of IPA.

2. Experimental

2.1. Materials

Different single-layer MMMs were prepared using Matrimid 5218 (Huntsman Chemical Corporation, USA), P84 (dedicated by HP Polymer Co., Australia), nanosized aerosil silica 200 (dedicated by Evonika Ltd., 12 nm), nanosized zeolite 4A (dedicated by Iranian Research Institute of Petroleum Industry), and CMS (dedicated by Activated Carbon Business Divisions, Japan EnviroChemicals Ltd.). Normal methyl pyrrolidone (NMP, >99.5%) was purchased from Merck Chemicals Co. as solvent and used as received. IPA was purchased from Sepidar Chemicals (>99%).

2.2. Membranes preparation

Polymers and fillers were activated at 120°C under vacuum overnight to remove any adsorbed adsorbates like water and/or VOCs. After that, fillers were suspended in the solvent (up to 15 wt.% Fill./wt. Poly.) and stirred for 24 h at room temperature, then polymers were added (up to 10 wt.% Poly./Vol. Sol.) and stirred at room temperature for another 24 h. After degassing under vacuum (−0.02 MPa, 120°C) for 4 h, solutions were spread over some glass sheets that were bounded by paper tapes (11 by 16 cm). Certain volumes of solutions were selected in a such manner that after solvent evaporation, thin films of 40–80 μm (Mitutoyo digital micrometer, 1 μm accuracy) remained on the glass surfaces. In order to avoid films' rupture during peeling, films were peeled at high temperature (around 170°C). After peeling of the nascent membranes, they were placed between two stainless steel meshes on oven trays to treat as mentioned by Ying Jiang et al. [13], without N_2 purging. The neat polymeric membranes were also prepared in this manner.

2.3. Membranes characterization

Membrane samples were immersed and fractured in liquid N_2, coated with Au/Ag, and their morphologies were studied using scanning electron microscopy (SEM) images taken from VEGA II TESCAN Company.

2.4. Permeation tests

Performances of MMMs in PV separation of an aqueous solution of IPA in distilled water were evaluated using a setup as shown schematically in Fig. 1. Temperature was set at 30°C (mercury bubble thermometer) and vacuum pressure controlled at 6 torr (Lutron vacuum sensors, accuracy of 1 torr). The permeate water concentration was measured using a manual refractometer (2 W AJ).

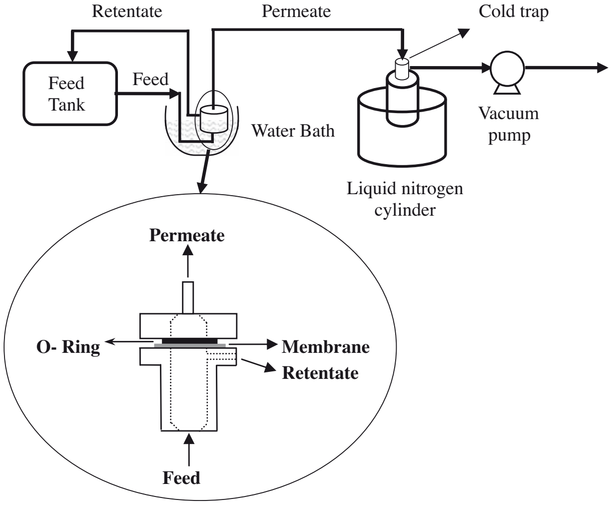

Fig. 1. Schematic diagram of the set-up used for PV experiments.

Steady-state conditions were achieved in any case of PV experiment. After that and at the end of experiments with run times of around 2 h, collected frozen permeates inside the cold trap were weighed (Precisa 310 M, accuracy of 1 mgr) and their concentrations were evaluated using the 2 W AJ refractometer. The permeation rate was calculated as per the following formula [10]:

$$J = \frac{m}{A_{\mathrm{Mem}} \cdot t} \tag{1}$$

where J is the permeation rate in kg/m^2 h, m is condensed permeated vapor mass in kg, A_{Mem} is membrane effective surface area in m^2, and t is permeation time in h. Membrane effective surface area inside the module was 11.95 cm^2. Separation factor, α, was defined as [10]:

$$\alpha = \frac{y/(1-y)}{x(1-x)} \tag{2}$$

where x and y are water mass fractions in feed and permeate streams, respectively.

3. Results and discussion

3.1. Dispersion of fillers inside the MMMs

Morphology of MMMs was investigated using SEM images. As mentioned above, the main defect in MMMs structures is void formation around incorporated fillers. As SEM images in different magnifications (1–100 μm) indicate (Figs. 2–4), there are no formed voids (at least connected) around incorporated fillers inside the polymer matrices, and nearly uniform distribution of fillers without serious agglomeration within polymer matrices is observed while a simple method of stirring is used and relatively large particles employed. The proper polymers–fillers connections were confirmed by PV experiments, also. This can be attributed to the MMM preparation at higher temperatures and relatively viscous suspensions [13]. As the polymer concentration in suspension increases from 10 (Fig. 3a) to 15% P84 (Fig. 4a) and then suspension becomes more viscous, more uniform distribution of fillers is obtained due to lower filler sedimentation and/or their convective migration to the surface of forming MMM [13,29].

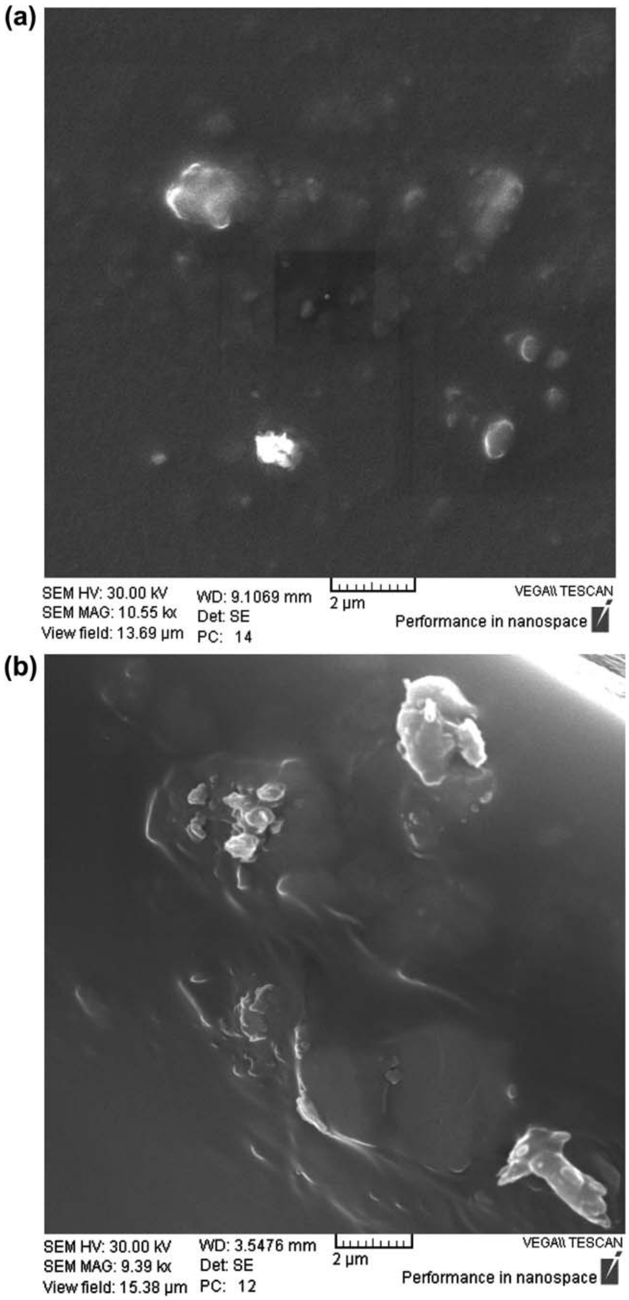

Fig. 2. SEM image of Matrimid 5218 (10 wt.%)-CMS (10 wt.%) MMM, average thickness of 55 μm, (a) top surface and (b) cross section.

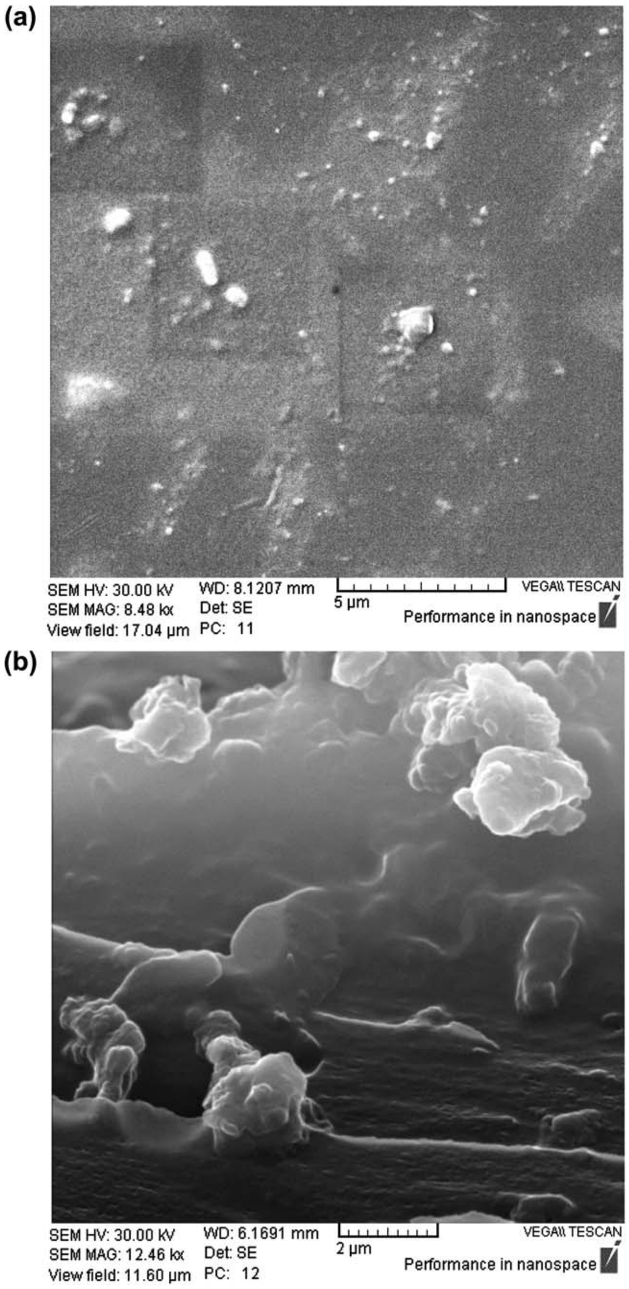

Fig. 3. SEM image of P84 (10 wt.%)-zeolite 4A (10 wt.%) MMM, average thickness of 40 μm, (a) top surface and (b) cross-section.

Another important factor that could considerably affect filler distribution in polymer matrix is the density difference between filler and film solution. In the current study, zeolite 4A (typically of zeolites is in the 2.1–2.5 gr/cm^3 range [32]) and CMS (typically 0.5–1.5 gr/cm^3 [33]) have different densities and resulted in various distribution patterns inside the same polymer solution of P84 due to lower applied gravitational forces on CMS and lower sedimentation of CMS. It also should be mentioned, while the buoyant force was reported to be negligible with respect to surface tension at typical thicknesses of casted films [29], larger buoyant force was applied on bigger CMS fillers. And finally, additional parameter of more viscous solution in the case of CMS (15 wt.% of P84 in solution) incorporated MMM resulted in further uniformity of CMS fillers' distribution (Table 1).

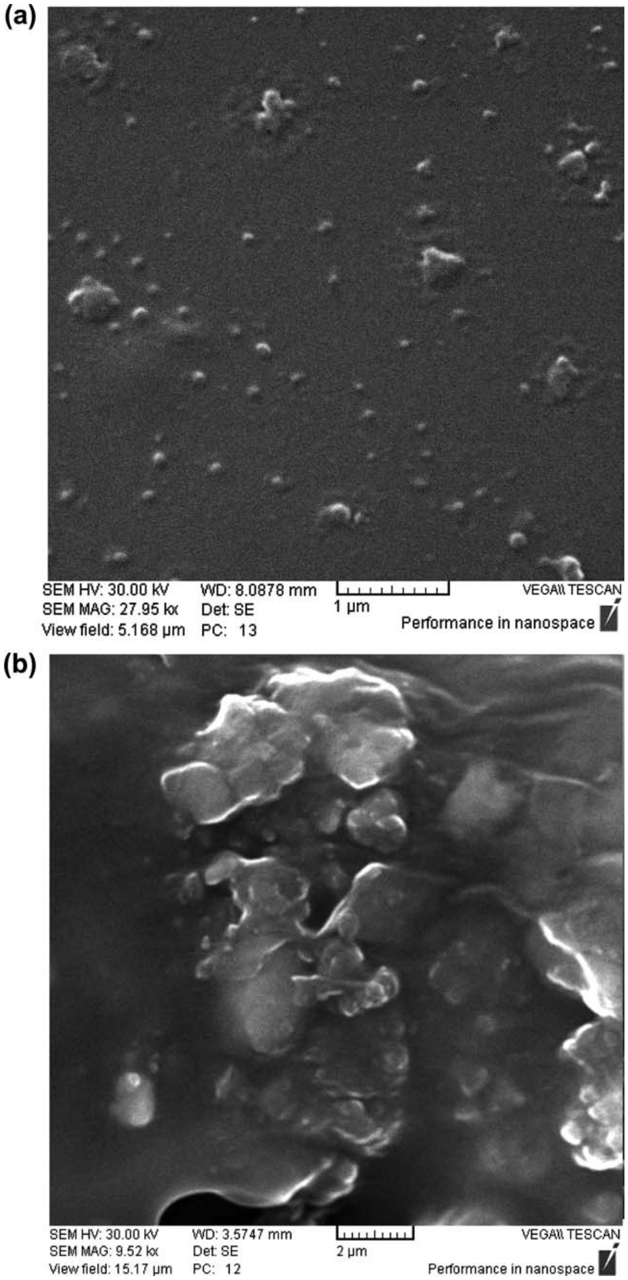

Fig. 4. SEM image of P84 (15 wt.%)-CMS (5 wt.%) MMM, average thickness of 80 μm, (a) top surface and (b) cross section.

Our previous studies [34] on a comparison of the MMM structure before and after thermal treatment at elevated temperatures of around polymer glass transition temperature showed that the proper thermal treatment potentially can anneal the probable defects which may arise during the MMM formation by drying stresses [13].

3.2. PV results

Some PV tests were performed at conditions as reported in Table 2. As it can be seen, both neat polymeric membranes of Matrimid 5218 and P84 originally have the same separation performance in PV process due to their close structure. There are two construction moieties in the repeating units of polyimides namely acid anhydride and diamine where acid anhydrides are the same in both the selected polyimides while their diamines are different [17,35,36]. Water molecules are small enough to pass within both void fractions of selected matrices that are increasing due to swelling.

On the other hand, incorporation of almost all filler particles resulted in better both membranes permeation rates and separation factors, simultaneously. Incorporation of aerosil silica 200 nanoparticles resulted in lower selectivity regarding its hydrophobic nature and then disturbance of polymer tight alignment after its incorporation resulted in higher permeation rates and lower selectivities. Polymer matrix has hydrophilic channels, formed by polyimide chain carboxylic groups and hydrophilic channels formed by free volumes. Incorporation of hydrophobic filler particles such as silica aerosil 200 can support the latter channels to lower the membrane selectivity while it resulted in a more plasticizable and swellable structure to pass water more easily [13].

Zeolite 4A incorporation in both matrices of Matrimid 5218 and P84 resulted in higher flux and at the same time more selectivity up to eight times for Matrimid 5218 (10 wt.%)-zeolite 4A (10 wt.%) MMM. This is due to the high hydrophilic nature of zeolite 4A. The molecular sieving nature of zeolite 4A has also made a significant contribution to the water transport. Zeolite hydrophilicity/hydrophobicity ratio is generally controlled by its Si/Al molar ratio where it is low enough (1) for employed zeolite 4A to make it hydrophile and it can act as polymer chains binder at the same time [2]. P84 (10 wt.%)-zeolite 4A (5 wt.%) MMM showed a better separation factor (up to two times) based on the same phenomena, but the filler content is lower than that of the former resulting in lower separation performance improvement. This considerable improvement is due to zeolite 4A contribution to affinity (hydrophile) and shape selectivity (kinetic diameter of 4.7 Å compared with 3 Å water molecules [12]) of filled polymer matrices. IPA molecules have more tortuous path to pass around the filled particles while water molecules can pass through the "low resistance avenue" inside the zeolite 4A particles.

CMS surface contains both hydrophobic and hydrophilic sites and can be employed in hydrophilic

Table 1
Some previous works on MMMs performance evaluation in PV

Polymer	Filler (wt.%)	Feed	Temp. (°C)	Membrane selectivity		Membrane flux (kg/m^2 h)		MMM thick. (μm)	Feed water (wt.%)	Permeate pres	Reference
				Neat	MMM	Neat	MMM				
PVA	TiO$_2$ (0.5–1)	Water–IPA	30		∞	1.6	0.312	50–55	10–30	0.05 mm Hg	[11]
NaAlg	MAS (5–15)	Water–IPA	30–50		17,991	0.177	0.174	50	10–50	10 torr	[10]
Matrimid	Beta Cyclodextrin (2–10)	Water–IPA	22.4		–	–		27–30	14	–	[5]
NaAlg,	Silicalite-1 (5–10)	Water–IPA	30–60		17,991	0.067	0.027	50	10–40	0.05 mm Hg	[41]
PVA					2,241	0.095	0.069				
P84	5A,13X (20–40)	Water–IPA						20–30	15		[12]
Matrimid	MgO (8–50)	Water–IPA	100		–	–	–	30–60	10–80	1 kPa	[13]
Polysulfone	4A,13X (15–45)	Water–ethanol	25		–	–	–		10–90		[42]
PVA	Na + MMT (5–10)	Water and IPA_1,4 dioxan	30–60		–	–	–	50	10–40	0.05 mm Hg	[43]
PVA	Polyaniline-III	Water and IPA	30	773	564.2	0.095	0.069		10	10 torr	[2]
NaAlg	MCM-41 (20)	Water and IPA	30	653	29,991	0.067	0.110		10		[23]
NaAlg	Co(III) (5)	Water + acetic acid	30	18	174	0.051	0.123		10	6.667 Pa	[31]
Poly(vinyl alcohol)	Phosphomolybdic heteropolyacid (7)	Water–IPA	10	77	89,991	0.132	0.032		10	10 torr	[28]
	Phosphomolybdic heteropolyacid (3)	Water–IPA	10	77	1,828	0.132	0.059		10	10 torr	[28]

Table 2
PV results of Water/IPA (10/90 wt.%) separation using prepared neat and MM membranes at 30°C and vacuum pressure of 6 torr

Polymer (wt.% in NMP)	Filler (wt.%)	J (kg/m^2 h)	x (wt.%)	α
P84 (10)	–	0.116	0.927	115
P84 (10)	Aerosil silica (10)	0.121	0.90	80
P84 (10)	Zeolite 4A (5)	0.125	0.96	220
P84 (10)	CMS (5)	0.114	0.94	140
Matrimid 5218 (10)	–	0.118	0.93	120
Matrimid 5218 (10)	Zeolite 4A (10)	0.159	0.99	890
Matrimid 5218 (10)	CMS (5)	0.114	0.95	170

and hydrophobic matrices for dehydration or removing organics based on affinity and size discriminations [37–39]. A polar adsorbate will be preferentially adsorbed, initially, on the polar sites [40], and as a result water can be preferentially adsorbed on the incorporated CMS and accelerate solution step in solution–diffusion mechanism model of PV for both CMS-filled matrices of Matrimid 5218 and P84. However its hydrophilicity and size discrimination for water/IPA are lower than those of zeolite 4A.

4. Conclusion

Prepared MMMs, especially those of hydrophile zeolite 4A incorporated, showed better performances with respect to those of neat polymeric membranes. Generally, zeolite 4A has more hydrophilic nature and molecular discrimination ability than other employed fillers and potentially can improve MMM PV separation factor regarding the neat membranes by several times while its permeation rate is also increased. In almost all prepared MMMs, selectivities improved while permeabilities remained nearly constant or slightly increased and results were moderate when comparing to the published reports on pervaporative separation of water/IPA. Although there was no filler modification agent employed and a simple method of stirrer mixing was used, there was good connection between fillers and polymer chains as confirmed by SEM images and PV separation performance of prepared MMMs. Fillers were dispersed inside the polymer matrix with low agglomeration. MMMs made many hopes in order to combine desired properties of polymeric and inorganic membranes and make PV and other membrane process, e.g. gas separation reverse osmosis, and fuel cells more and more attractive.

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