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Preparation, Characterization and Gas Permeation of Polyimide Mixed Matrix Membranes

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Abstract

Some mixed matrix membranes (MMMs) were fabricated using polyimides in order to improve performance of CO_2/CH_4 separation. Polyimides of Matrimid 5218 and P84 were used as the polymer backbones and different inorganic particles including aerosil silica 200, zeolites of 4A and ZSM-5, homemade carbon nanotube (CNT), and carbon molecular sieve (CMS) were used as fillers. Effects of polymers type, type and content of different fillers up to 15%, and fabrication procedure on MMMs separation performance were investigated. Scanning electron microscopy (SEM) images showed acceptable connections between the two phases of polymers and fillers and the MMMs showed better separation performance compared with the pristine polymeric membranes. Although glassy polyimides are hard to connect with the fillers, thermal treatment at temperatures around glass transition temperatures (T_g) of the employed polyimides, repaired probable defects and there were no voids around the fillers as SEM images and gas permeation tests revealed. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) also confirmed good contact between the two phases as MMMs exhibited higher thermal stabilities.

Keywords: Mixed Matrix Membranes; Gas separation; Polyimides; Thermal treatment

Introduction

Green membrane separation technology is a fast growing branch of science and engineering. This technology has emerged in many fields of separations tasks including gas separation. Many worldwide researches are carrying out to improve current membrane processes and materials and/or introduce new membrane processes and materials for the processes [1-4].

Membrane materials are ranged from polymeric to minerals (ceramics, metals and glasses) in different modular forms and membranes processes are employed from suspension clarification (in macro level) to gas separation (in micro or molecular level). Different selected membrane materials can be "tailored-made" in order to adjust their properties for specific separation tasks in this wide range of applications [5]. Membrane material development is an important research area to synthesize higher performance and more durable membranes to meet economical separation requirements.

Membrane gas separation processes have undergone a major evolution since the introduction of the first membrane-based industrial hydrogen separation process about two decades ago [6]. Polymeric membranes, as of the most important class of membranes specially in gas separations, possess many desired properties including low capital investment, low energy consumption, high specific surface area per module and easy processing. At the time, these membranes suffer from low operating temperature and tradeoff between their permeabilities and selectivities and cannot be served in harsh conditions. The tradeoff is one of the biggest problems faced by pure polymeric membranes which greatly limits their economical applications in the chemical and petrochemical industries [7]. Many research activities have been performed to tailor polymeric membranes in order to adjust their separation properties via crosslinking, grafting, blending, curing and etc.

Chemical, thermal and/or photochemical cross-linking modifications are effective methods to reduce interstitial chain space and chain mobility and consequently membrane swelling and/or plasticization and as a result improve membrane selectivity and/ or stability, while permeation rate in most cases reduces [8-10]. Crosslinking is strongly affected by experimental conditions [9].

In grafting, the grafted materials possess both properties of the base materials and the chemically grafted components. The method has benefits of controllable introduction of graft chains and applicability with various polymer films [11, 12]. In grafting both surface and structural properties of the membrane can be tailor-made to improve its separation performance [12]. However, there is a trade off; grafting usually enhances membrane selectivity, while reduces permeation rates [13].

Blending, as another modification technique, is physical mixing of two (or more) polymers to obtain their requisite properties [12]. The objective is to use advantages of all the polymers and/or omit their disadvantages. However, this may increase degree of swelling or plasticization due to higher flexibility of polymer chains and then reduce the membrane selectivity [14].

Although, using these methods exhibited some success in achieving research aims, the tradeoff between permeability and selectivity of polymeric membranes has yet remained [10, 15-18].

On the other hand, inorganic ceramic membranes offer high mechanical, chemical and thermal strengths, and nearly uniform pore size distribution [7, 19]. Size and shape selective nature of zeolites and molecular sieves allows molecular discrimination by permitting smaller gas molecules to diffuse at much higher rates than larger gas

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molecules. Major disadvantages of these types of membranes are their hard and expensive construction for large membrane surface areas, inherent brittleness, and low specific surface area per module. It must be noted that although construction of large membrane surface area of these types of molecular sieves is hard and expensive, their fine particles preparation is much easier and cheaper.

This fact leads membrane researchers to incorporate these valuable inorganic particles into organic matrices in order to employ desired properties of both inorganic and organic materials simultaneously. Mechanical and thermal properties of the resultant MMMs are also improved (as predicted by Maxwell model) in addition to their separation characteristics. In fact, the idea of making composite materials to improve mechanical and/or electrical properties of the resultant composites, has led to mixing of two phases of organic and inorganic materials to make MMMs [7, 19, 20]. Fabrication of MMMs is an appropriate and promising approach in addition to the other efforts like polymer crosslinking and blending to pass Robeson upper bound limit [9, 10, 21, 22]. The so called Robeson upper bound limit was reported by Lloyd M. Robeson who examined selectivities of polymeric membranes versus their permeabilities and observed their trade off [23]. In other words, increasing polymeric membranes selectivity can be achieved by compensation of their permeation rates and vice versa.

Many researches have been carried out world widely to incorporate different appropriate inorganic (nanoporous molecular sieving materials, such as CMSs, zeolites, and CNTs) and even though organic filler particles (polypyrrole, trimethylsilyl-glucose, and fullerene) to organic matrices in two recent decades [2, 7, 19, 20, 24-30]. Many of these researches resulted in improved performances of prepared MMMs compared to those of pristine polymer membranes and made hope to overcome the Robeson upper bound limit [2, 7, 19, 20, 24-31]. However, some other researchers found worse performances compared to polymeric membranes as reason of different difficulties which might be encountered in preparation of MMMs. Formation of voids in the particle-polymer interface in the case of poor compatibility where results in considerable permeability increment (hydrodynamic permeation through the voids instead of discriminative passage of molecules), blockage of filler particles pores , and rigidification of polymer chains around the filler particles can be mentioned as these difficulties [32-34]. It can be mentioned that it is also possible to reverse membrane selectivity by incorporating special fillers [35, 36]. Finally it can be said that almost all researches resulted in fabrication of MMMs where their separation performance was located in desired economic operation region offered by Robeson [19]. Activated carbon or some other adsorbents have been dispersed inside polymeric matrices for different membrane separation applications and resulted in enhanced filtering capabilities for microscopic and submicron particles, such as enzymes or monosaccharides from polysaccharides [36].

In membrane gas separation area, there are many attractive opportunities including natural gas sweetening, landfill gas recovery, olefin/paraffin separation, air separation, hydrogen recovery, greenhouse gases removal, and etc. [7, 31, 37-41]. Almost all pristine polymeric membranes, with those mentioned good properties, cannot achieve or exceed the Robeson upper bound limit to fully exploit these potential opportunities, while MMMs are moving in a such direction to pass this limit. For instance, some MMMs were prepared for N_2/O_2 separation and achieved this limit [19, 31].

As mentioned above, one of major difficulties encountered in preparation of MMMs is formation of voids around filler particles. Also, some other technical challenges for MMMs preparation, including poor compatibility, chain rigidification and pores blockage can be mentioned resulting in low selectivity [7]. These problems should be overcame to obtain high acceptable separation performance of MMMs. Some attempts including proper selection of compatible polymers (glassy or rubbery) and filler particles, priming of filler particles sizing, usage of more viscous suspensions, controlling evaporation rates of solvents, employing of silane coupling agents, preparation, pretreatment and post-treatment procedures, using low molecular chain polymers capable of hydrogen bonding between polymers and filler particles, and coating upper surface of MMMs with thin appropriate layers, were performed to overcome these defects [7, 31, 36, 42-44].

Based on reported desired properties of MMMs mentioned above, some MMMs were prepared in this study using polyimides of Matrimid 5218 and P84 and some fillers (aerosil silica 200, zeolites of 4A and ZSM-5, homemade CNT [45], and CMS) in order to improve performances of the synthesized MMMs for CO_2/CH_4 separation and also to obtain higher thermal stability.

Methods and Materials

Materials

Different single layer MMMs were prepared using Matrimid 5218 (Huntsman Chemical Company, USA, with a chemical structure as shown in Figure 1), P84 (dedicated by HPPolymer, Australia with a chemical structure as shown in Figure 2), nano-sized aerosil silica 200 (dedicated by Evonika Ltd., 12 nm), nanosized zeolite 4A (dedicated by Iranian Research Institute of Petroleum Industries), zeolite ZSM-5 (purchased from Zeochem Co.), homemade carbon nanotubes (CNTs) [45], and carbon molecular sieve (CMS) (dedicated by Activated Carbon Business Division, Japan EnviroChemical). Normal methylpyrrolidone (NMP, \geq 99.5%) was purchased from Merck as solvent, and used as received.

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 10 % 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 and bounded by









Figure 3: Schematic diagram of membranes gas permeability measurement setup.



Figure 4: Cross section SEM images of pristine Matrimid 5218 with average thickness of 45μ m, (10 wt. %), (a) top surface and (b) cross section.

paper tapes (11 by 16 cm). Certain volumes of solutions were chosen in such manner that after solvent evaporation, thin films of 40 - 70 μ m (Mitutoyo digital micrometer, 1 μ m accuracy) were remained on the glass sheet surfaces. Casting of solutions using a film applicator resulted in formation of dropwise agglomerates regions on the glass surface instead of uniform film region in many cases. In order to avoid films rupture during peeling, films were peeled at high temperatures (around 170°C). After peeling of the nascent membranes, they were placed between two stainless steel meshes on oven trays for thermal treatment as reported by Ying Jiang et al. without N₂ purging [44]. The pristine polymeric membranes were also prepared in this manner.

Membranes characterization

Membrane samples were immersed and fractured in liquid N₂, coated with Au/Ag and their morphologies were studied using SEM images prepared by VEGA II TESCAN apparatus. PerkinElmer-pyris diamond TGA apparatus was employed in order to evaluate thermal stabilities of the prepared pristine and MM membranes. The samples were heated from 30 to 600°C at heating rate of 10°C/min under nitrogen environment. T_g of the prepared membrane was measured by a PerkinElmer-pyris6 DSC with heating and cooling rates of 10°C/min.

Permeation measurements

Performances of pristine and MM membranes in gas separation were evaluated using a gas permeation setup as shown schematically in Figure 3. Pure gases of CO_2 (Sabalan Company, > 99%) and CH_4 (Sabalan Company, > 99.9%) were used. Temperature was set at 30°C (PT-100 sensors, accuracy of 0.1°C) and pressure was changed in the range of 5-10 bar (2.600 G BD pressure sensors, accuracy of 0.25 FSO). Steady state conditions were achieved in all cases of gas permeation experiments. After that, gas permeation rates were measured in constant volume mode (17.5 cm3), pressure was measured using a DMP 343 BD pressure sensor (accuracy of 0.175% FSO, 1 mbar) and recorded using NX series control & monitoring program V.1.0.0. Net provided membrane area inside the module was 11.95 cm². After each gas permeation test, the membranes were degassed inside an oven at 100°C for at least 12 h. Permeabilities and selectivity coefficients were calculated according to the following formulas (low permeate side pressure allows application of ideal gas law):

$$V_{\text{Perm}} = \frac{(V\Delta p/T)Ts}{Ps}$$
(1)

$$P = \frac{V_{Perm} 1}{A_{Mem} t \Delta P u_{pst}}$$
(2)

$$V_{i,j} = \frac{P_i}{P_j}$$
(3)

Where V_{Perm} , V, Δp , t, T, T_s, P_s, P, l, A_{Mem} , Δp_{Upst} , α , i and j are permeated volume in cm³, permeate side volume in cm³, pressure increment in time duration of *t* in bar, permeation time in s, operating temperature in K, standard temperature (298.15 K), standard pressure (1 bar), permeability coefficient in Barrer, membrane thickness in cm, membrane area in cm², pressure difference across the membrane in mmHg, selectivity coefficient and subscripts relating to components i and j, respectively.

Results and Discussions

Fillers incorporation inside the polymer matrices

Morphologies of thermally treated pristine and MM membranes were investigated using SEM images. SEM image of pristine Matrimid

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5218 membranes is shown in Figure 4 as a clean integrated surface which can be considered as characteristics of the pristine polymer membrane. The main probable defect in MMMs structures, as mentioned above, is void formation around fillers. As SEM micrographs indicate (Figure 5 Figure 10), there are no (connected) voids around the dispersed fillers. This claim can be confirmed using gas permeation experiments. SEM images also showed a homogeneous distribution of gooddispersed fillers in the matrix, while a simple method of mixing was used in suspension preparation and there was a wide filler particle size distribution for almost all used fillers. Nano-sized aerosil silica 200 was used to check propriety of filler dispersion. Many sub-micron particles can be observed in cross-section SEM images of P84-nano-sized aerosil silica 200 MMMs (Figure 5), indicating the filler agglomeration since nominal ~10 nm aerosil silica 200 was incorporated inside the polymer matrix. SEM results showed that, as filler content increases from 5 to 10 wt. %, some filler agglomeration occurs and there are loss homogeneity in filler distribution, but the agglomerated particles are still in the range of submicron (Figure 6). MMMs structures prepared using Matrimid 5218 and nano-sized zeolite 4A, were also investigated (Figure 7). As it can be seen, although the zeolite particles are not uniform in size, but the particles are homogeneously distributed and no connected voids can be observed. Micro-sized CMS (~ 50 Å in aperture, as reported by its manufacturer) was also incorporated in Matrimid 5218. Although these particles are relatively large in size, but their continuity (affinity) with the polymer matrix are acceptable and there are no defects around the fillers (Figure 8). CMS has lower mass density and its weight force is partially balanced by its buoyant force and better distribution of CMS is expected. As SEM images show, although the employed CMS has wider particle size distribution but its distribution inside Matrimid 5218 is acceptable. Micro-sized zeolite ZSM-5 (5 wt. %) was also incorporated into tje both polymer matrices. Although the used filler is micro-sized, good distributions can also be observed (Figures 8 and 9).

As mentioned above, thermal treatment was selected as a probable defect-correcting method. In order to check the performance of this method, some MMMs were prepared using P84 and homemade CNTs [45]. SEM micrographs before and after thermal treatment of MMMs



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(Figure 10), showed that the selected thermal treatment method could effectively repair the defects. The ability of this method was also confirmed by gas permeation tests, where there was no unusual permeability increase or selectivity decrease. Probable defects can be attributed to drying or shrinkage stresses [19]. Thermal treatment of the prepared MMMs at temperatures around T_g of their polymer matrices, increases movements of the polymer chains, especially those connected to the fillers and may be rigidified and this results in annealing of the stresses. The annealed stresses result in better connection between the two phases of polymer and filler after natural cooling [46].

DSC analysis

Pristine and some MM membranes were investigated using DSC analysis. As it can be seen in Table 1, T_g values of MMMs increase due to the presence of fillers within polymer matrices. It can be attributed to the inhibition of polymer chain mobility near the polymer-filler interface by their attachment to the filler or the polymer chains rigidification and/or the chain entrance to the filler particles [46]. Acceptable contact between polymer and zeolite interface can be concluded from this analysis.

TGA analysis

TGA analysis was also performed on the pristine and MM membranes. Effects of filler content and filler type on thermal stability of the MMMs were investigated. Figure 11 shows the weight loss of different membranes as functions of temperature. As observed, there are no significant weight loss at temperatures below 500°C. A little weight loss of Matrimid 5218 - zeolite 4A MMM at ~ 275°C can be attributed to removal of the remained solvent in the MMM body. Weigh losses of pristine Matrimid 5218, Matrimid 5218-zeolite 4A and Matrimid 5218-CMS membranes at 594°C are 33.15, 32.23, and 27.86%, respectively. This result confirms more thermal stabilities of the prepared MMMs than those of the pristine polymeric membranes. This can be explained by considering interactions of the fillers and the polymer matrices (polymer chains rigidification around the fillers and/ or their entrance into the filler pores) resulting in more stable matrix formation, as discussed before in DSC analysis [7, 19]. Higher thermal stability of Matrimid 5218 - CMS MMM (Figure 11), can be attributed to the wider apertures of CMS channels (~ 50 Å) and more polymer chains entrance into filler particles and more affinity between CMS and



Figure 8: SEM image of Matrimid 5218 (10 wt. %) - CMS (10 %) MMM with average thickness of 55 $\mu m,$ (a) top surface, (b) cross section.

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the polymer chains, while zeolite 4A pore aperture is 3.8 Å and this causes less polymer chains entrance into the filler particle pores [46].

Gas permeation

Polyimides are known to exhibit high permselectivity for various gas pairs, specially for CO₂/CH₄ (pseudo molecular sieves [47]), and high chemical resistance, thermal stability and mechanical strength [1]. Many researchers reported polyimide of Matrimid 5218 as one of the best material choices for membrane based CO₂/CH₄ separation due to its attractive combination of gas permselectivity and high T_a [16, 43]. Another polyimide, named P84, was also investigated for gas permeation measurements. Measured permeation rates of single gases through the prepared membranes are reported in Table 2. As observed, incorporation of different fillers in polymer matrices resulted in slightly better performances of MMMs comparing to those of pristine polymer membranes. As mentioned, more polymer chains entrance into filler particles was observed in the prepared MMMs especially for Matrimid 5218 - CMS MMM. In the case of zeolite 4A, as reported by the other researchers, polymer chains entrance into filler particles (pore blockage) may abort the zeolite incorporation inside the polymer

J Membra Sci Technol ISSN:2155-9589 JMST an open access journal matrix [46]. As Y. Li et al. reported, incorporation of zeolite 3A (3 Å) and 4A (3.8 Å) into polyethersulfone (PES) exhibits approximately the same performance, as their blocked apertures are smaller than CO, kinetic diameter (3.3 Å), while originally they have different aperture sizes [46]. As presented, the same phenomenon is observed in the case of zeolite ZSM-5 with pore size of ~ 5.5 Å. As it can be seen from the table, incorporations of 5 and 15 wt. % zeolite ZSM-5 are nearly the same in the separation performance point of view. The behavior is in agreement with the clogged filler case (IV case) of different cases may be encountered in MMM preparation as reported by T. T. Moore and W. J. Koros [48]. In this case permeation rate is lowered by filler incorporation, while selectivity remains nearly constant. Generally it can be concluded that smaller aperture size (compared with the gas kinetic diameter) and less interconnection of filler pores result in nearly abortive incorporation of different fillers inside polymer matrices [36]. Employed CNTs was also used as synthesized without further washing and purification, and a better performance was recorded relative to the other fillers (separation factor was increase up to 11). Employed CMS was trade grade and its pores were not interconnected and separation



thermal treatment based on Ying Jiang et al. procedure [44].



Figure 11: TGA analysis of pristine Matrimid 5218 (10 wt. %), Matrimid 5218 (10 wt. %) - zeolite 4A (15 %), and Matrimid 5218 (10 wt. %) - CMS (15 %) membranes.

Polymer (wt. % in NMP)	Filler (wt. %)	T _c (°C)
Matrimid 5218 (10)	-	293
Matrimid 5218 (10)	zeolite 4A (5)	304
Matrimid 5218 (10)	zeolite 4A (10)	305
Matrimid 5218 (10)	zeolite 4A (15)	306
Matrimid 5218 (10)	CMS (10)	296

 Table 1: DSC analysis of prepared pristine and zeolite 4A filled Matrimid 5218 membranes.

Polymer	Filler	Pressure	Permeability	(Barrer ^a)	Ideal
(wt. % in MP)	(wt. %)	(bar)	CO ₂ (S. D. ^b)	CH ₄ (S. D. ^b)	selectivity
Matrimid 5218 (10)	-	7.5	4.60 (0.45)	0.16 (0.04)	29
		10	4.45 (0.42)	0.12 (0.03)	37
Matrimid 5218 (10)	Zeolite 4A (15)	7.5	4.66 (0.20)	0.13 (0.04)	36
		10	5.98 (0.60)	0.14 (0.03)	43
Matrimid 5218 (10)	ZSM-5 (5)	7.5	4.43 (0.41)	0.15 (0.09)	30
		10	4.28 (0.29)	0.17 (0.06)	25
Matrimid 5218 (10)	ZSM-5 (15)	7.5	4.24 (0.59)	0.15 (0.04)	28
		10	4.87 (0.48)	0.17 (0.05)	29
Matrimid 5218 (10)	CMS (10)	7.5	4.99 (0.51)	0.11 (0.04)	45
		10	4.76 (0.46)	0.10 (0.03)	48
P84 (10)		7.5	0.92 (0.18)	0.13 (0.03)	7
		10	0.83 (0.16)	0.12 (0.03)	7
P84 (10)	ZSM-5 (5)	7.5	0.92 (0.22)	0.12 (0.06)	8
		10	0.83 (0.11)	0.14 (0.03)	6
P84 (10)	CNT (10)	7.5	1.05 (0.38)	0.12 (0.04)	9
		10	1.09 (0.20)	0.10 (0.04)	11

^a1 Barrer = 10⁻¹¹ cm³.cm/cm².s.mmHg

^bS. D.: Standard Deviation

Table 2: $\rm CO_2$ and $\rm CH_4$ permeation rates through the prepared pristine and MM membranes 30°C.

performance of the CMS incorporated MMMs was not changed sharply. Matrimid 5218 was found better than P84 in the case of permeation rates and separation factor. Considering their structure in Figures 2 and 3, it seems that a so called d-spacing of P84 is smaller than that of Matrimid 5218 [47].

Although the results do not reflect sharp performance increment, they confirm good contact between the two phases of fillers and polyamides. Incorporation of the other zeolites and modified CNTs is under investigation in order to improve separation performances of MMMs, while keeping the connectivity between two phases of fillers and polymers.

Conclusion

As many researchers emphasized on superior separation properties of MMMs, the prepared MMMs also showed better performances with respect to those of pristine polymeric membranes to some extent. Selectivities increased, while permeabilities remained nearly constant. Although no filler surface modifying agent was used, good contact was observed between fillers and polymer matrices, as confirmed by SEM, DSC, TGA analysis and gas permeation tests. Employed thermal treatment procedure was found as an appropriate solution for modifying probable defects formed in MMMs preparation. MMMs are promising as a new generation of membranes in order to combine desired properties of polymeric and inorganic membranes to pass the Robeson upper bound limit. Achieving this goal, makes membranes as a more powerful rival of current amine absorption processes in gas sweetening and enhances their chance of totally replacement.

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