MIL-96/Polyamide (PA) Mixed-Matrix Membranes with Improved Gas Separation Capabilities

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Abstract

Aromatic polyamide (PA)/MIL-96-(Al) mixed-matrix membrane was fabricated and explored for gas separation (CH_4, N_2, O_2 and CO_2) performances. Mixed-matrix formulation is a promising method to overcome permeability-selectivity trade-off of polymer with incorporation of filler. The filler properties play a key role in determining the performance of mixed-matrix membrane (MMM). MMMs were prepared by nanoscale aluminum trimesate MIL-96-(Al) filler with Semi fluorinated polyamide (PA) at 3%, 6% and 12% weight percent of loading fillers. The 12 wt% nanoscale MIL-96 incorporated MMM showed CO_2 permeability to 120 Barrer and CO_2/CH_4 selectivity to 24. Nanoporous fillers in MMMs contributed to enhance the CO_2/CH_4 separation performance compared to pristine membrane. Nanoscale MIL-96 filler uniformly incorporated into polyamide (PA) matrix confirmed by SEM images. This study provides a feasibly pathway for the development of efficient and high performances separation membranes.

Index Terms - Poly(amide), Mixed-Matrix Membranes, Gas permeability, Nanoscale MIL-96 filler.

1. Introduction:

Membrane technologies of current gas separation through polymeric membranes are cost and energy effective, environmentally benign, as well as simple, versatile and environmental friendly operation.[1] This is due to the attractive combination of low costs with facile processing and innovation that characterizes polymer materials.[2] Polyamide (PA) membranes attracted substantial attention due to their higher CO_2 permeability and CO_2/CH_4 selectivity at laboratory scale, as compared to cellulose acetate membranes. Over the last two decades, inorganic particles e.g. zeolite and inorganic oxides have been used to prepare mixed-matrix membranes (MMMs), also called hybrid membranes.[3] A common strategy to enhance the gas separation performance of PA membranes is the use of fillers and the formation of what is known as mixed-matrix membranes (MMMs).[4] In literature the use of graphene oxide (GO), Metal-organic frameworks MOFs, and zeolitic imidazolate frameworks (ZIFs) are reported.[4] MOFs were recently proposed as fillers due to their outstanding gas separation properties. The periodic aluminum−oxo framework including the coordination sphere of Al centers with microporous aluminum trimesate MIL-96-(Al) are a subclass of porous materials of special interest owing to their pore aperture sizes below 4−7 Å that can potentially address key challenges in separation of CO_2/CH_4 and CO_2/N_2.[4] Rigid framework with relative small pores incorporating diverse potential adsorption sites (Al acid sites, hydroxyl groups, and coordinating water) makes this MOF attractive for the selective capture of CO_2 over N_2. Due to its high thermal and hydrothermal stability, MIL-96-(Al) was envisaged for the processing of mixed matrix membrane (MMM).[5] These mixed matrix membranes which consist of filler particles dispersed into an organic polymer phase potentially combine the gas transport and separation properties of the incorporated particles with the good processability and mechanical properties of the polymers.[6] Fillers of MIL-96-(Al) particles are at the nanoscale thus dispersion of MOF fillers in the polymer matrix take place voids are bypasses.[7] Such a lack of chemical compatibility between both components limits the MOF loading of numerous MMMs and thus their performance. The glassy and high free volume polaimide was selected owing to its high CO_2 permeability, good mechanical properties, and easy processability.[8] Defect-free membranes were prepared that consisted of homogeneously distributed MIL-96-(Al) particles in the polymer matrix with adequate interfacial properties. The prepared MMMs have been tested for single gas permeation tests (CH_4, N_2, O_2 and CO_2) separations. An attempt has been made to understand the structure property correlationship of the MMMs and the role of the Nanoscale MIL-96 filler on the final gas permeability.

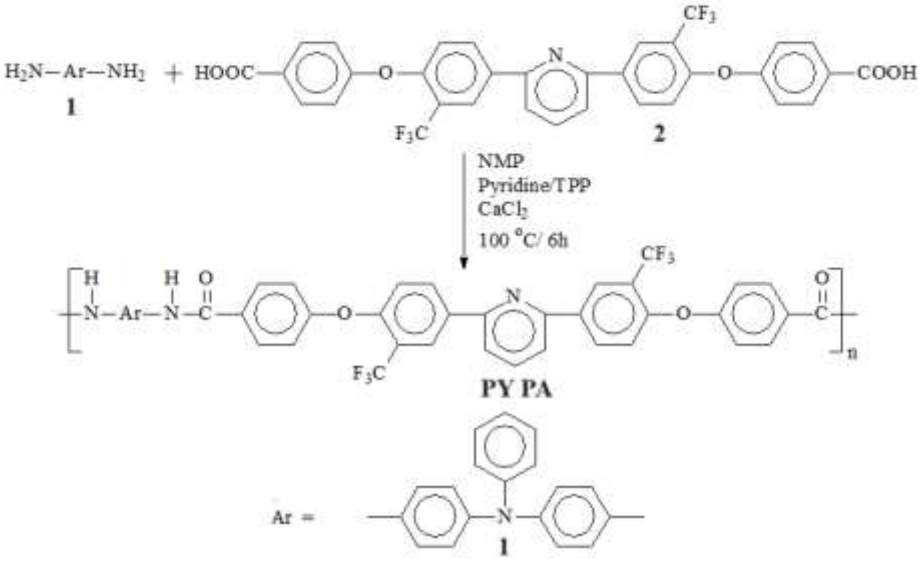
2. Experimental

2.1. Materials, Membrane Characterization & Gas Separation Measurements

Synthesis of MIL-96-(Al) Nanoparticles[4] and 2,6-bis[3'-trifluoromethyl-4'(4"-carboxyphenoxy)benzyl]pyridine (2) acid has been reported earlier.[8] Triphenylamine monomer was purchased from SD Chemicals, India. The permeability of CO_2, O_2, N_2 and CH_4 gases were measured through the polymer membranes (thickness around 60-80 μm) using an automated Diffusion Permeameter (DP-100-A) manufactured by Porous Materials, Inc., USA at 3.5 bar of applied gas pressure and at 35 °C. The permeability coefficient, ideal perm selectivity (α), were determined according to reported procedure.[1,8]

2.2. Polymerization

The aromatic diamine, Triphenylamine (1) was reacted with dicarboxylic acid monomer (2) in molar ratio of 1:1 using 1-Methyl-2-pyrrolidinone (NMP) as solvent and in the presence of triphenyl phosphite (TPP), $CaCl_2$ and pyridine as shown in **Scheme 1.** A polymerization reaction (PY PA) is as follows: a mixture of di amine, m-triphenylamine (0.786 g, 7.71 mmol) (1) and dicarboxylic acid, 2,6-bis[3'-trifluoromethyl-4'(4"-carboxyphenoxy)benzyl]pyridine (2) (0.534 g, 7.71 mmol), calcium chloride (0.36 g), NMP (5 mL), pyridine (1.4 mL) and TPP (1.4 mL, 5.34 mmol) were taken in a 50 mL round bottom flask equipped with reflux condenser. The mixture was heated with continuous stirring (using magnetic stirrer) at 110 °C for 6 h under nitrogen atmosphere. The reaction mixture became highly viscous during this period. The mixture was poured in methanol (500 mL) with constant stirring and obtained fibrous polymer.[8] The off-white fibrous polymer was dried overnight at 80 °C under vacuum.



Scheme 1. Synthesis of the poly(amide)s (PY PA)[4].

2.3. Synthesis of MIL-96-(Al) Nanoparticles

Aluminum nitrate nonahydrate (4.5 g, 12 mmol) and trimesic acid (2.52 g, 12 mmol) were dissolved in 300 mL of a H_2O/DMF (1/1 (v:v)) mixture. Acetic acid (1.68 mL, 30 mmol) was added, and the mixture was heated under reflux for 16 h. The resulting white mixture was centrifuged at 14500 rpm for 15 min and then washed once with deionized water (30 mL) and one more time with a H_2O/EtOH (1/1) mixture (30 mL) and finally with EtOH (30 mL).[7] The obtained white powder was dried at RT.[4]

2.4. Polymeric Membrane Preparation

The polymeric membranes were prepared by casting 10-15% (w/v) homogeneous polymer solutions in DMAc solvent onto clean glass Petri dishes. The Petri dishes were placed in an oven heated at 80 °C overnight, followed by slow heating to 150 °C and then kept for 6h. The polymer membranes were removed by immersing the Petri dishes in hot water. Finally, the membranes were kept again under vacuum at 160 °C for 4h for the removal of any trace of solvent and moisture. Free standing flexible membranes were obtained for all the polymers varying thickness from 60-80 µm.[6]

The physical properties of the membrane are summarized in **Table 1.** The density values (ρ) of the polymers were used to determine the fractional free volume (FFV) of the polymers by using the following Eq. $FFV = (V-1.3V_w)/V_w$ where V is the specific volume ($V = 1/\rho$). The vander Waals volume (V_w) was estimated using the Hyperchem computer program, version 8.0.[9]

2.5. Preparation of MIL-96-(Al)-PY -PA MMMs

A polymer solution was prepared by dissolving 0.4 g of polymer in 3 mL in dimethylformamide (DMF). MIL-96 was dispersed in DMF by ultrasonication and stirring for 30 min. Then, 10% of the volume of the polymer solution was added to the MOF suspension followed by further stirring for 2 h. The remaining volume of polymer solution was added to the MOF suspension and stirred overnight. The membranes were prepared by casting homogeneous polymer solution in DMF solvent onto clean glass Petri dishes. The Petri dishes was placed in an oven heated at 80 °C overnight, followed by slow heating to 150 °C and then kept for 6h. Free standing flexible membrane were obtained for all the polymer varying thickness from 60-80 µm. MOF loading were determined by, MOF loading (wt) = [Amount of MOF (wt)/(Amount of MOF (wt) + Amount of polymer (wt)] x 100%, was kept for all MMMs. MMMs were prepared with a MOF loading of 3%, 6% and 12% weight percent of loading fillers.[4]

3. Results and discussion

3.1. Polymer synthesis and their properties

Polyamide was synthesized by the typical phosphorylation polycondensation of the dicarboxylic acid monomer (2) with aromatic diamine monomer (1) (**Scheme 1**). Polymer repeat unit structures were confirmed by elemental analyses, FTIR-ATR and NMR spectroscopic methods. These poly(ether amide)s showed characteristic absorption bands for amide group in the range of 3325-3276 cm^{-1} (N-H stretching) and 1644-1671 cm^{-1} (carbonyl group stretching) in the FTIR-ATR spectra. The absence of absorption peak due to the diamine above 3410 cm^{-1} supported high conversion of diamines to polyamide.[8] The polymer repeat unit structures were also in good agreement with their ^{1}H-NMR spectra. ^{1}H-NMR spectrum of PY-PA in pyridine-d_5**.** The singlet above 11.39 ppm (corresponds to the amide proton for all the PAs).[8]

Table 1. Physical properties of the polyamide

Polymer	η_{inh} (dL g^{-1})^a	Density (g cm^{-3})^b	V_w (cm^3 mol^{-1})^c	T_{d10} (°C)^d	T.S. (MPa)^e	FFV
PY-PA	0.34	1.228	313.7	410	75.0	0.112

$^a\eta_{inh}$ = inherent viscosity at 30 °C. ^{b}Density (g cm^{-3}) measured at 30 °C. ^cV_w = Vander Waals volume, ^{d}10% degradation temperature measured by TGA. ^{e}Tensile strength. FFV = Fractional Free Volume.

3.2. Morphology: Synthesis of Nanoparticles of MIL-96-(Al)

MIL-96-(Al) was first prepared from a mixture of trimesic acid (BTC) and aluminum nitrate. The structure of MIL-96 (Al), presents four non-equivalent aluminum sites. The characteristic morphology of MIL-96-(Al) crystals was truncated hexagonal bipyramid. Formation of trimesate Al-based MOFs strongly depends on the speciation of molecular Al complexes in solution. Acetic acid impacts the nucleation and growth of MIL-96-(Al) crystals and thus its morphology. Nanoparticles of MIL-96-(Al) (from 160 to 55 nm) solvothermal synthesis in a mixture of H_2O/DMF solvents.[7] As observed by SEM (Figure 2), hexagonal nanorods with a dimension up to 500 nm are formed by this route. SEM images (Figure 2), MIL-96-(Al) consists of pure nanocrystals with a diameter of 200 ± 30 nm. It is worth noting that synthesis conditions without acetic acid led to MIL-96-(Al) nanocrystals with a similar size and shape.[4]

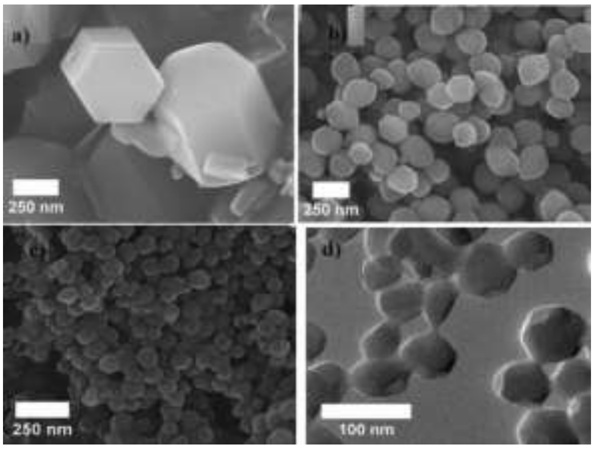


Figure 1. (a) nanoparticles in water MIL-96-(Al); (b) nanoparticles from reflux in H_2O/DMF (MIL-96-(Al)); (c) SEM image of MIL-96-(Al); (d) TEM-bright field image of MIL-96-(Al).

3.3. Processing of Mixed Matrix Membranes

Due to the excellent colloidal stability of MIL-96 in DMF, MMMs with a high MOF content (3, 6, 9 and 12 wt %) could be prepared by dispersing both MIL-96 in a solution of PY-PA in DMF. PXRD superimpose well with the one of MIL-96-NP, confirming that the crystalline structure of MIL-96 is preserved upon its association with PY-PA matrix.[7] SEM images (Figure 2) of the top surface of MMMs show the excellent dispersion of MIL-96-PY-PA-12% in the polymer matrix with the absence of any significant aggregation.[4] Such results are confirmed by cross-sectional SEM images, showing a homogeneous distribution of MIL-96 nanocrystals in the volume of the membranes. The thickness of the supported membranes lies between 70 and 75 µm.[4] Similar results were obtained with MMMs based on MIL-96-PY-PA-3%, MIL-96-PY-PA-6%, MIL-96-PY-PA-9%. According to SEM images, no defects or voids of about a few nanometers in size could be observed at the interface between the MIL-96 and PY-PA polymer.

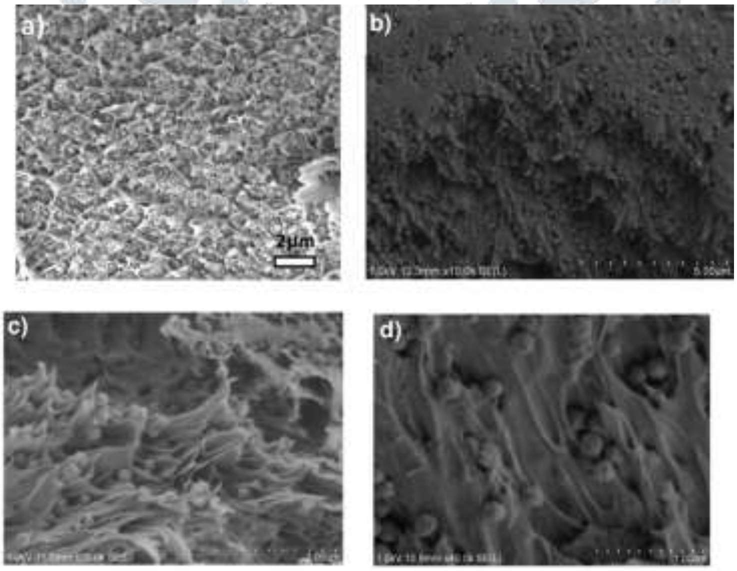


Figure 2. SEM images of MIL-96-PY-PA membranes. a) cross-sectional image; b-d) section of the membrane showing the homogeneous distribution of MIL-96-PY-PA-12%.

3.2. Gas transport properties

3.2.1. Effect of chemical structures on gas transport properties

The mean gas permeability coefficients and ideal permselectivity values for four different gases (CO_2, O_2, N_2 and CH_4) of the MMMs are tabulated in the **Table 2.** The gas permeability of four different gases through these MMMs membranes follow the order of P (CO_2) > P (O_2) > P (N_2) > P (CH_4); which is essentially the reverse order of their kinetic diameter, CO_2 (3.3 Å) < O_2 (3.46 Å) < N_2 (3.64 Å) < CH_4 (3.8 Å).[4,8,10] The contribution of the MIL-96 filler to the membrane separation performance of the resulting MMMs was evaluated first using dense membranes. MIL-96 in PA membranes at 3 bar and 35 ºC was measured. Moreover, increase in selectivity with increasing filler loading for the MIL-96 -filled PA-membranes at 12 wt% loading. We believe that PA have trifluoromethyl group (-CF_3) in polymer chain endowed better particle dispersion in PA matrix and enhanced polymer/filler interfacial affinity, which avoided the nonselective void formation resulting in high selectivity for gas pairs.[11] This is tentatively attributed to a better dispersion of the MIL-96 naoparticles in the polymer and thus a higher accessibility to gas molecules. It is also interesting to note that although these MIL-96 naoparticles have same in structure and physical properties, the permeance and selectivity of all the % of loading MIL-96 naoparticles. Comparable selectivities values for any filler loading of the three MIL-96 naoparticles-based MMMs indicate a similar competitive behavior among the two gases for the available adsorption sites in the MIL-96 naoparticles framework.[4] Just like for the polymer, the selectivities in the MIL-96 naoparticles can be ascribed to the differences in the electrostatic interaction of different gas molecules with the membrane constituents: CO_2 has a strong quadrupole moment, while CH_4 has none, thus showing increased interactions, hence sorption, in a polar environment like the MIL-96 naoparticles framework.[4]

Table 2. Gas permeability coefficients (P) measured at 35 °C (3.5 bar) and permselectivities (α) values of the MMMs and their comparison with other reported polymers.

MMMs	P(CO_2)	P(O_2)	P(N_2)	P(CH_4)	α(CO_2/CH_4)	α(O_2/N_2)
PY-PA	9.00	2.40	0.45	0.35	26.00	5.30
MIL-96-PY-PA-3%	15.00	4.30	0.85	0.70	21.50	5.00
MIL-96-PY-PA-6%	40.0	11.0	1.60	1.20	33.50	6.90
MIL-96-PY-PA-9%	48.0	14.0	1.85	1.32	31.20	6.70
MIL-96-PY-PA-12%	38.0	09.0	1.45	1.16	39.30	8.02
Matrimid®	8.70	1.90	0.27	0.24	36.00	7 .00
Ultem®	1.33	0.41	0.05	0.03	36.90	8.00
Extem®	3.28	0.81	0.13	0.13	25.20	6.20

[a]P = gas permeability coefficient in barrer. 1 barrer =10^{-10} cm^3 (STP) cm cm^{-2} s^{-1} cm^{-1} Hg^{-1}.

3.2.2. Comparison of gas permeabilities of MMMs with structurally related polymer membranes

The gas permeability and permselectivity values of these MMMs PAs (MIL-96-PY-PA-0-12%) was compared with other commercially available polymers (e.g., Matrimid®, Extem® and Ultem®).[8] A better comparison of the CO_2/CH_4 permselectivity vs. CO_2 gas permeability (**Figure 4**) have been obtained in terms of the Robeson plots.[12] In general, these MMMs showed good permeability with comparable or higher selectivity than the previously reported polyamides. Although the Robeson upper bound is not exceeded, the addition of the filler significantly improved the overall performance of the neat polymeric membrane MIL-96-PY-PA-12% shows permeability of CO_2 gases with an improvement in permselectivity than other structurally analogous PAs. The good permselectivity values of MIL-96-PY-PA-12% for CO_2/CH_4 gas pairs were credited to their higher diffusivity selectivity values. The present PAs showed good improvements in gas-separation performance as proved by their trade off points close to the Robeson's upper bound.[8]

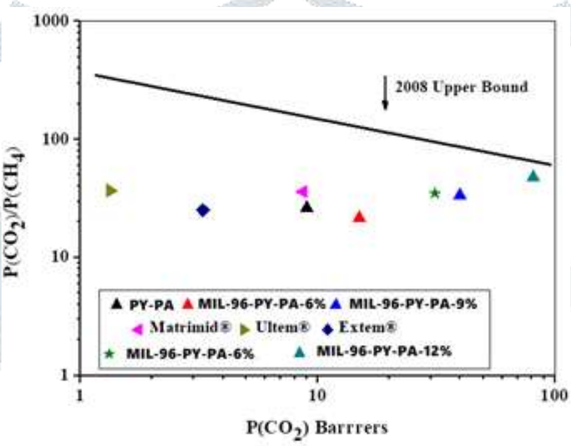


Figure 4. Robeson plot for a comparison of CO_2/CH_4 selectivity vs. CO_2 permeability coefficients of the MMMs under this investigation and some other reported polymers.

4. Conclusions

In this study, a strategy to improve the long-term performance of PA by the addition of nanoporous Al trimesate MIL-96-(Al) (anhydrous or hydrated) nanofillers have been reported, and chemistry and the porosity of the nanofiller play an important role in the performance of the MMMs. A fluorinated PA membranes comprising pyridine moiety and diamine moiety was combined in polymer backbone to studied their properties. Mixed-Matrix Membranes (MMMs) were prepared by solvent evaporation with Semi fluorinated Polyamide (PY-PA) as base polymer and MIL-96-(Al) as filler. Nanoporous MIL-96-(Al) with PY-PA is required to achieve higher loadings of the nanofillers in the polymer matrices. The priming protocol to prepare the MMMs resulted in a good distribution of fillers in the polymer matrix. The gas transport studies showed that the incorporation of the MIL-96-(Al) improved both the gas permeability and permselectivity of these polymer membranes. The increasing permeances with increasing MIL-96-(Al)-loadings were attributed to the structural properties of the MIL-96-(Al). Such properties are likely to be due to the excellent chemical compatibility between MIL-96-(Al) and PY-PA and the absence of any defects or voids at the MOF/polymer interface. Such results pave the way for the processing of composite membranes with a higher MOF content (>30 wt %).

5. Acknowledgment

The authors acknowledge Narajole Raj College for providing opportunity to carry out this work.

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