Performance of Gas Separation in Mixed Matrix Membranes with ZIF-78/Polyamide (PA)

Barun Kumar Mondal *

Assistant Professor,

Department of Chemistry,

Narajole Raj College, Vill: Narajole, PO: Harirajpur, Paschim Medinipore, West Bengal, India, Pin: 721211

Abstract

Recently, ZIF-78 MOF has gained attention as a promising metal-organic framework (MOF) material for the fabrication of mixed matrix membranes (MMMs) for gas separation applications. In order to create Polyamide (PA) mixed-matrix membranes (MMMs) for CO_2/N_2 separation, ZIF-78 MOF was used as a filler in this work to get around the performance trade-off of traditional polymeric membranes. A high aspect ratio and a low one ZIF-78 particles are created and added to a matrix of polyamide (PA). SEM and XRD were used to evaluate the microstructures and physico-chemical characteristics of the ZIF-78 fillers and ZIF-78/PA MMMs. Through the use of a solution-diffusion model and permeation measurements at different input pressures, the CO_2/N_2 transport characteristics through the MMMs were assessed. Due to the ZIF-78 filler's molecular sieving action, the results demonstrated that adding ZIF-78 to PA improved both CO_2 permeability and CO_2/N_2 selectivity. The MMM with the ideal ZIF-78 loading of 15 wt% demonstrated CO_2/N_2 of 25 and CO_2 permeability of 211 barrer, both of which exceeded the 2008 Robeson upper-bound, indicating that a ZIF-78-based membrane would be a viable option for purifying natural gas.

Index Terms - Poly(amides), Mixed-Matrix Membranes, Gas permeability, ZIF-78 MOF.

1. Introduction:

Membranes containing a polymer matrix and a dispersed additive that enhances the membrane's permeability and/or selectivity in comparison to the native polymer are known as mixed matrix membranes, or MMMs. MOFs are one of the additive kinds that have drawn a lot of interest from MMMs because of their matrix compatibility, large surface area, and microporosity.[1-3] Depending on the MOF-matrix system, MMMs often exhibit one of the three selectivity options together with an increase in permeability brought on by the MOF microporosity: 1) Selectivity is reduced due to interfacial defects caused by incompatibility between the MOF and the matrix, 2) selectivity is unaffected by appropriate compatibility between the MOF and the matrix, or 3) the MOF matrix interface becomes denser due to excessive affinity between the MOF and the matrix or pore penetration of the matrix into the MOF, which increases selectivity. Zinc or cobalt cations and various imidazolate linkers make up zeolitic imidazolate frameworks (ZIFs), a subclass of thermally and chemically stable MOFs. Numerous novel ZIF topologies and structures have been discovered since the first ZIFs were announced. [3-7] ZIF-containing membrane structures have been studied for gas separation because of their stability, adaptability, and microporous nature (high gas absorption). Because of the nitro functionality in the KNO pore channel, ZIF-78 (GME structure, built by connecting Zn^{2+} with nIm and 5-nitrobenzimidazolate (nbIm)) exhibited the greatest CO_2 affinity despite having a relatively high pore polarity. Investigations into the ZIF-78 catalytic activity of cyclic carbonate synthesis, the control of the ZIF-78 aspect ratio by triethylamine (TEA) addition and linker ratio, and the separation performance of pure ZIF-78 membranes for both liquid and gas separations were prompted by this nitro functionality and high CO_2 affinity. [2-5] Remarkably, the later work on gas permeation through pure ZIF-78 membranes showed that, in contrast to gases with weaker electrostatic interactions, such as N_2 and CH_4, the enhanced pore polarity of ZIF-78 reduced the permeability of CO_2. [4-7]

2. Experimental

2.1. Materials & Equipments

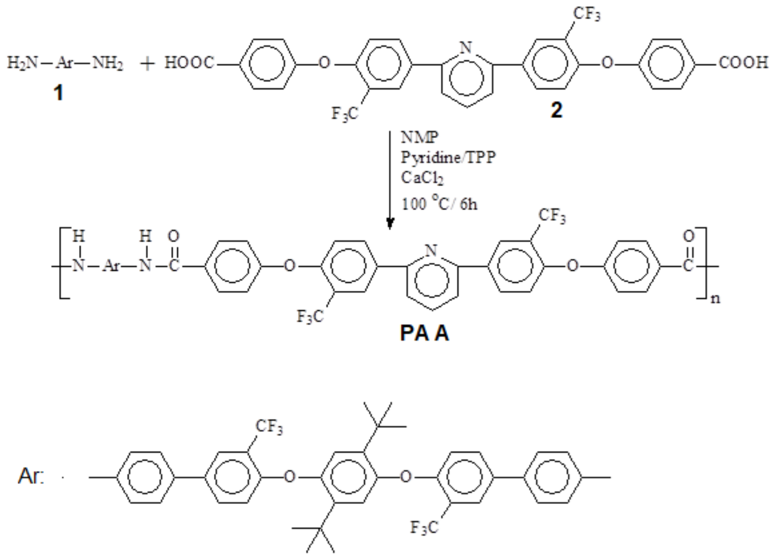
Synthesis of 1,4-bis-[{2'-trifluoromethyl-4'-(4''-aminophenyl)phenoxy}]2,5-di-t-butylbenzene (1), 2,6-bis[3'-trifluoromethyl-4'(4''-carboxyphenoxy)benzyl]pyridine (2) has been reported earlier [4]. 2-Nitroimidazole (nIm, 98% purity) and 5-nitrobenzimidazole (nbIm, 95% purity) were purchased from Fluorochem Ltd. Zinc nitrate hexahydrate ($Zn(NO_3)_2 6H_2O$, 98% purity), triethylamine (TEA, ≥ 99% purity), *N*,*N*-dimethylformamide (DMF, ≥ 99.9%), and tetrahydrofuran (THF, ≥ 99.0% purity, 250 ppm BHT inhibitor) were purchased from Sigma-Aldrich. purchased from Aldrich. 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. [2-4]

2.2. Synthesis of ZIF-78 framework

ZIF-78 LA nIm (0.226 g, 2 mmol) and nbIm (0.163 g, 1 mmol) were dissolved in DMF (20 mL) (2:1 linker ratio). After dissolution, TEA (0.693 mL, 5 mmol) was added to deprotonate the imidazoles and the solution was stirred for 10 min. Meanwhile, Zn(NO3)2 6 H2O (0.300 g, 1 mmol) was dissolved in DMF (10 mL). The zinc solution was added to the imidazole solution and the mixture was heated at 120 °C and stirred at 130 rpm for 18 h. The resulting suspension was centrifuged with a VWR Compact Star CS 4 for 20 min at 6500 rpm and washed with DMF three times. The precipitate was dried with a rotary evaporator and further dried in a vacuum oven at 125 °C and 1 mbar for 24 h. [5-7]

2.3. Polymerization and Dense membrane preparation

The dicarboxylic acid monomer (2) was reacted with aromatic diamine (1) in molar ratio of 1:1 using NMP as solvent and in the presence of triphenyl phosphite (TPP), $CaCl_2$ and pyridine as shown in Scheme 1. A polymerization reaction (PA ‘A’) is as follows: a mixture of dicarboxylic acid, 2,6-bis[3'-trifluoromethyl-4'(4"-carboxyphenoxy)benzyl]pyridine (0.493 g, 7.71 mmol) (2), 1,4-bis-[{2'-trifluoromethyl-4'-(4"-aminophenyl)phenoxy}]2,5-di-t-butylbenzene (1) (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. The off-white fibrous polymer was dried overnight at 80 °C under vacuum [4]. The same method was used for the preparation of other PAs.



Scheme 1. Synthesis of the poly(amide)s (PA 'A'). [2-4]

The polymeric membrane were prepared by casting 10-15% (w/v) homogeneous polymer solution in DMAc solvent onto clean glass Petri dishes. The Petri dishe 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. 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. $FFV = (V-1.3V_w)/W$ 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 [4].

Table 1 Physical properties of the poly(amide)

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^{EXP}**
PA 'A'	0.52	1.32	344.6	451	76.0	0.117

$^a\eta_{inh}$ = 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. EXP =Experimental, SIM = Simulation.

2.4 Membrane preparation

PA and ZIF-78 were dried overnight at 120 °C. 10, 20 and 30 wt% MOF loading were added as determined by

$$\text{MOF loading (wt\%)} = [(\text{wt. MOF})/(\text{wt. MOF} + \text{wt. polymer})] \times 100$$

2.5 Dense membranes

For the films containing 5, 10 and 15 wt% ZIF-78, the corresponding amount of MOFs were dispersed in DMF. The solution was stirred for 1 d and then 10% of the total polymer powder was added into the solution. The solution was allowed to stir for another 6 h, followed by addition of 20% of the total polymer into the solution and stir for 2 h. This step was repeated until the requisite total polymer amount was added. The solution was cast on a flat-bottom Petri dish, maintaining a ratio of 1 ml solution/1 cm diameter of Petri dish. The inner diameter of the petri dish was 10 cm. oven heated at 80 °C overnight, followed by slow heating to 150 °C and then kept for 6h. The dry film was removed by immersing in a solution of H_2O/IPA (1:1) and then dried in an oven. The film was heated to 200 ºC at a rate of 20 ºC/h. The membrane was further dried for 8 h at 200 ºC [4-6]. [2-5]

3. Results and discussion

3.1. Structure characteristic of ZIF-78

The SEM images of ZIF-78 in Fig. show irregular fan-shaped crystal morphologies with an average particle size of less than 4 μm.

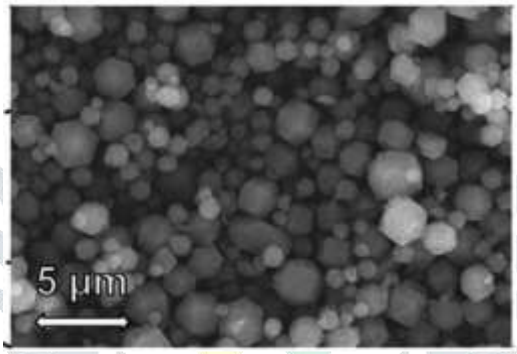


Fig. 1. SEM image of synthesized ZIF-78. [5-7]

3.2. Polymer synthesis and their properties

Polyamides were 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 3338-3291 cm^{-1} (N-H stretching) and 1653-1661 cm^{-1} (carbonyl group stretching) in the FTIR-ATR spectra. The absence of absorption peak due to the diamine above 3400 cm^{-1} supported high conversion of diamines to polyamides. The polymer repeat unit structures were also in good agreement with their ^1H-NMR spectra. Representative ^1H-NMR spectrum of PA 'A' in pyridine-d_5. The singlet above 11.36 ppm (corresponds to the amide proton for all the PAs). [2-5]

Transparent and flexible membranes were obtained from these PA from their solution in DMAc. The membrane showed tensile strength values of 82 MPa (Table 1).

The TGA thermograms of the polymer are done under air. TGA thermograms indicated that all the PA have high thermal stability in air with 10% decomposition temperatures were in the range of 468 °C.

3.2.1. Characterization of MOF-filled PI dense membranes

Morphology

The surfaces and cross-sectional morphology of MMMs are shown in Fig. 2 The surface morphology of MMMs showed that ZIF-78 fillers possessed a homogeneous distribution and increased gradually with the increase in ZIF-78 content. [5-7]

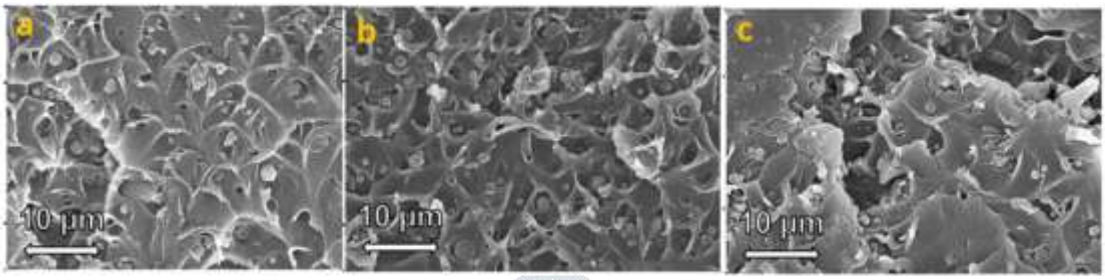


Fig. 2. SEM images of the surfaces (a–c) of the MMMs [5-7]

Mechanical properties

Table 2 shows the mechanical properties of the dense MOF filled PA-membranes at 5, 10 and 15 wt% loadings. It can be seen that with increasing MOF loading, the Young's modulus of the MMMs increases significantly. The significant improvement in Young's modulus of PA/MOFs indicates a good dispersion of the MOFs throughout the PA matrix, as well as a good interaction between the fillers and the PA matrix. It is also interesting to observe that both tensile strength and elongation at break decrease with an increase in MOF loadings. This could be due to agglomeration of fillers in the polymer matrix. Even then, the agglomerates were distributed randomly in the polymer matrix as indicated in SEM images and increased Young's modulus [4-6].

Table 2 Mechanical properties of MOF filled PA-membranes at different loading

MOF/PA	MOF loading (w/w)	Young modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
PA/ ZIF-78	0	2.6	101	110
	5	2.7	83	104
	15	3.2	74	90

3.3. Gas transport properties

3.3.1. 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 3. 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). The contribution of the MOFs to the membrane separation performance of the resulting MMMs was evaluated first using dense membranes. Fillers in PA membranes at 3 bar and 35 °C was measured. Moreover, increase in selectivity with increasing filler loading for the three MOF-filled PA-membranes at 15 wt% loading. The increase in both permeance and selectivity indicates good interactions between the filler and the polymer matrix, which is a remarkable result compared to existing literature. It is also interesting to note that although these three MOFs vary significantly in structure and physical properties, the permeance and selectivity of all the % of loading MOFs. Comparable selectivities values for any filler loading of the three MOF-based MMMs indicate a similar competitive behavior among the two gases for the available adsorption sites in the MOF framework. Just like for the polymer, the selectivities in the MOFs 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 MOF framework. [3-7]

Table 3 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)**	**Ref.**
PA A	9.00	2.40	0.45	0.35	26.00	5.30	This study
PA@5% ZIF-78	15.00	4.30	0.85	0.70	21.50	5.00	do
PA@10% ZIF-78	40.00	11.00	1.60	1.20	33.50	6.90	do
PA@15% ZIF-78	81.00	20.00	3.00	1.70	47.50	6.70	do
Matrimid®	8.70	1.90	0.27	0.24	36.00	7 .00	[5]
Ultem®	1.33	0.41	0.05	0.03	36.90	8.00	[5]
Extem®	3.28	0.81	0.13	0.13	25.20	6.20	[5]
P3[a]	37.40	9.80	1.70	1.50	24.93	5.76	[5]
3g[a]	35.30	7.35	1.36	0.91	39.00	5.40	[5]
3h[a]	31.20	7.23	1.30	0.90	35 .00	5.50	[5]

[a]Gas permeability coefficient (P) values taken from ref. [5]. 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 (PA@0-15% ZIF-78) was compared with other commercially available polymers (e.g., Matrimid®, Extem® and Ultem®) and some previously reported polymer (3g, 3h and P3) [4-7]. A better comparison of the CO_2/CH_4 permselectivity vs. CO_2 gas permeability (Fig. 3) have been obtained in terms of the Robeson plots [6,7]. In general, these MMMs showed good permeability with comparable or higher selectivity than the previously reported polyamides. PA@15% ZIF-78shows very good permeability of CO_2 gases with an improvement in permselectivity than other structurally analogous PAs. The good permselectivity values of PA PA@0-15% ZIF-78 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. [3-7]

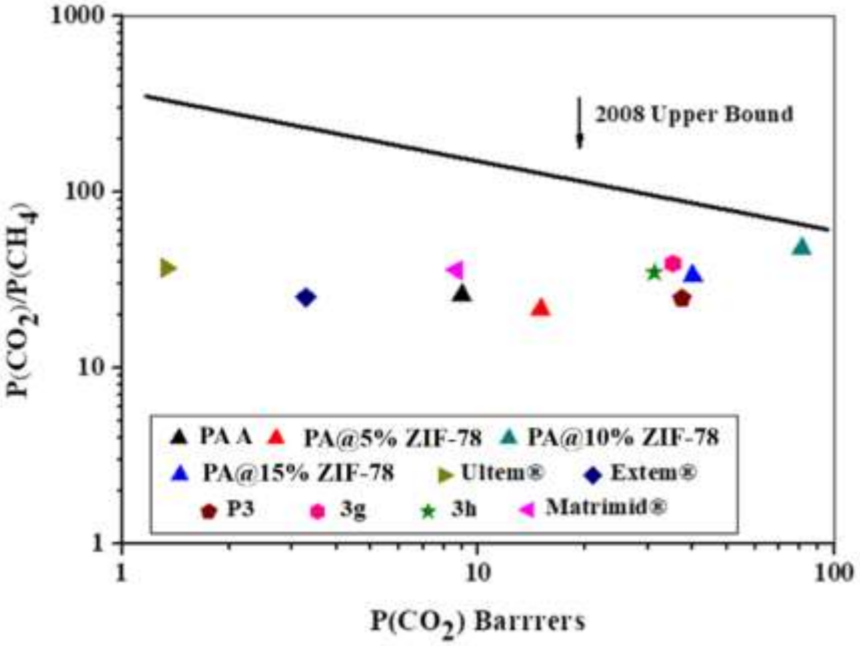


Fig. 3. Robeson plot for a comparison of CO_2/CH_4 selectivity vs. CO_2 permeability coefficients of the MMMs under this investigation and some other reported polymers.

4. Conclusions

To investigate their characteristics, fluorinated PA membranes with a pyridine moiety and a diamine moiety with a pendant tert-butyl group ring were joined in the polymer backbone. Semi-fluorinated polyamide (PA) was used as the basis polymer and ZIF-78 as a filler to create Mixed-Matrix Membranes (MMMs) by solvent evaporation. Through the preparation of a thick membrane packed with PA@0-15% ZIF-78, the impact of MOFs on MMMs gas separations was investigated. A proper distribution of fillers in the polymer matrix was the outcome of the priming procedure used to manufacture the MMMs. Artifacts produced during sample preparation were blamed for the flaws shown in the SEM. According to the gas transport investigations, these polymer membranes' gas permeability and permselectivity were enhanced by the addition of bulky tert-butyl groups. The structural characteristics of the MOFs were thought to be responsible for the increased permeances with increasing MOF-loadings. The PA polymer matrix and a metal-organic framework (ZIF-78), which shown high compatibility with PA, made up MMMs. Pure gas measurements were used to examine a number of MMMs, and mixed gas measurements were then performed on PA@0-15% ZIF-78.

5. Acknowledgment

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6. References

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