Tuning the Mixed-Matrix Membranes Gas Separation Performance of Ionic Liquid/MIL-53 (Al) filler in polyamide (PA) Membrane

Barun Kumar Mondal and Soumendu Bisoi*

Assistant Professor,

Department of Chemistry,

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

Abstract

Metal-organic framework (MOF)-containing polymeric membranes have enormous promise for gas separation. To lessen the membrane's flawed structure, it is essential to precisely control the adhesion between MOFs and polymer matrices. The interaction between MOFs and the polymer matrix, which has a tendency to aggregate on the membranes, is restricted by their partially inorganic structure. This article describes an interfacial technique that improves the interfacial interaction between filler and Polyamide (PA) matrices by post-synthetically functionalizing MIL-53 (Al) with ionic liquids (ILs) to create an IL@MIL-53 (Al) composite. IL@MIL-53 (Al) and PA matrices have close contact, which makes uniform dispersion visible in morphological analyses. MMMs were characterized using Fourier transform infrared (FTIR) spectra and scanning electron microscopy (SEM). The behavior of gas separation was investigated by measuring one. The gas permeability of four different gases CH_4, N_2, O_2, and CO_2 was evaluated for both pure and composite membranes using a constant-volume variable pressure method. The CO_2 permeance was 44 barrer at 2 % weight percent of MIL-53 (Al) nanofiller, which was noticeably greater than that of the pure Polyamide (PA) membrane. Because of ILs' strong affinity and CO_2 solubility, introducing them into the MOFs pores will adjust pore size while improving adsorption selectivity. Functionalization of ILs on the cores of the MIL-53 (Al) structure is a successful tactic that allows for a wide variety of fillers to be chosen in terms of commercialization.

Index Terms - Poly(amides), Mixed-Matrix Membranes, Gas permeability, MIL-53 (Al) with ionic liquids (ILs).

1. Introduction:

Membrane-based technology is now regarded as one of the most effective methods for removing CO_2 from natural gas or syngas in order to lower CO_2 emissions into the atmosphere. [1-3] For selective CO_2 separation, membranes composed of polymer materials including polyethersulfone (PES) and polyamide (PA) are used. These polymers, however, have a "trade-off" relationship, meaning that they have poor permeability and high selectivity, or vice versa. In order to get around this issue, scientists have created new MMMs by incorporating inorganic particles into metal–organic frameworks (MOFs), which are continuous polymer matrices. Carbon nanotubes (CNTs) have also been utilized to create extremely permeable and selective MMMs. [4-7] MOFs are materials made up of a transition metal and an organic ligand that have a high crystalline structure. MOFs are perfect filler materials because of a number of properties, including porosity. To create the perfect polymer/MOF hybrid membrane, researchers from all over the world are trying to improve the interface between MOFs and the polymer matrix. For the storage and separation of CO_2, MIL-53 (Al) is regarded as a dependable porous material. Combinations of MIL-53(Al) with CNTs, such as MIL-53(Al)@CNT for bisphenol removal and MIL-53(Al)@MWCNT for CO_2 absorption, have been utilized recently. [7-10] For CO_2/CH_4 separation, Mubashir et al. created a hollow fiber mixed matrix membrane (HFMMM) based on cellulose acetate (CA)/MIL-53(Al). HFMMM that was developed had a maximum selectivity of 16.0. During the film forming process, MIL-53(Al) shows irreversible aggregation. [7-10] Second, the likelihood of agglomeration particles in the polymer network rises with increasing MIL-53(Al) loading. In comparison to other light gases, ILs have a unique combination of features, including low vapor pressure, wide liquid range, good thermal stability, low flammability, and strong CO_2 solubility and selectivity. Because imidazolium cations shown a remarkable inherent solubility of CO_2, 1-butyl-3-methylimidazolum bis(trifluoromethylsulfonyl) imide ([bmim][Tf_2N]) IL was chosen. [1-4] Here, MOF-based composite membranes were prepared using PSf as the continuous polymer phase and MIL-53 (Al) and IL@MIL-53 (Al) as fillers. For CO_2/N_2 and CO_2/CH_4 gas separation, the gas separation performance was examined in terms of MIL-53 (Al) and IL@MIL-53 (Al) loading in the PA matrix.

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]. Aluminum nitrate nonahydrate, Al $(NO_3)_3{\cdot}9H_2O$, and terephthalic acid for MIL-53 (Al) synthesis were purchased from SRL Pvt Ltd, India. N, N-dimethylformamide (DMF, 99.5% purity), methanol, and Nmethyl-2-pyrrolidone (NMP, 99.5% purity) were supplied by SigmaAldrich, USA. Acetone and n-hexane were procured from Merck, Germany. Dow Chemicals, USA, supplied polydimethylsiloxane (PDMS, Sylgard 184). The 1-Butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ([bmim] [NTf_2], ≥98%) was procured from Sigma-Aldrich, USA. 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.

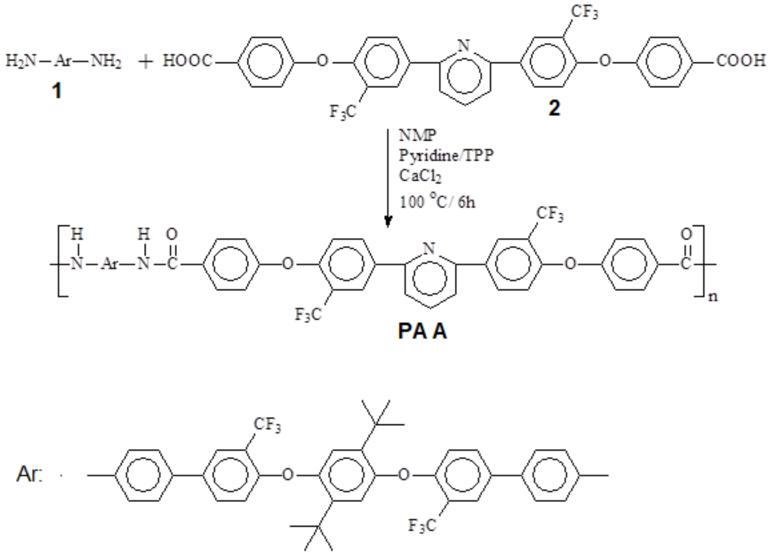
2.2. Synthesis of MIL-53 (Al) and IL@MIL-53 (Al) fillers

As previously reported, a combination of $Al(NO_3)_3{\cdot}9H_2O$ and terephthalic acid in DMF was used to create MIL-53 (Al) filler particles using the solvothermal process [1-4]. After dissolving $Al(NO_3)_3$ and terephthalic acid in DMF at the molar ratios of 1: 1.4: 184.5, respectively, the solution was aged for 24 hours at 30 °C before being moved to a steel autoclave lined with Teflon. For 72 hours, the mixture was cooked to 130 °C in an oven. After 30 minutes at 10,000 rpm, the resultant MIL-53 (Al) white particles were recovered using a centrifuge. Three DMF washes at 130 °C for 24 hours were used to get rid of the remaining acids. Eventually, the solvent was eliminated by acetone in Soxhlet extraction for 20 h and dried in an oven at 100 ◦C for 48 h. [1-4]

MIL-53 (Al) filler particles functionalized with IL were manufactured in an open environment and then vacuum-sealed at 200 °C. After first dispersing 0.13 g of [bmim] [NTf_2] in 15 ml of acetone using magnetic stirring, 0.32 g of MIL-53 (Al) was added to the mixture and continuously swirled (350 rpm) at 40 °C for 6 hours until the solvent had completely evaporated. For ten hours, the resultant mixture was maintained at 100 °C in an oven. Lastly, based on its weight percentage, the resulting white powder is designated as [bmim] [NTf_2]/MIL-53(Al) (20 wt %). [8-10]

2.3. Polymerization

As seen in Scheme 1, the aromatic diamine (1) and the dicarboxylic acid monomer (2) interacted in a molar ratio of 1:1 with NMP acting as the solvent and triphenyl phosphite (TPP), $CaCl_2$, and pyridine present. The following is a polymerization reaction (PA "A"): a combination of 2,6-bis[3'-trifluoromethyl-4'(4"-carboxyphenoxy)benzyl] and dicarboxylic acid1,4-bis-[{2'-trifluoromethyl-4'-(4"-aminophenyl)phenoxy}], pyridine (0.493 g, 7.71 mmol) (2)In a 50 mL round-bottom flask with a reflux condenser, 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 added. For six hours, the mixture was heated to 110 °C while being continuously stirred with a magnetic stirrer in a nitrogen environment. During this time, the reaction mixture became quite viscous. [4-6] 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'). [4]

2.3. Fabrication of MIL-53 (Al) and IL@MIL-53 (Al) based composite PA membranes

The composition of the dope solution for asymmetric flat sheet composite membranes was 20 weight percent PA, 40% nonvolatile solvent (NMP), 30% volatile solvent (THF), and 5% nonsolvent (ethanol). To get rid of the water residues, PA and filler particles were first dried for 12 hours at 60 and 100 ◦C, respectively. The NMP-THF solvent combination was supplemented with a predefined quantity of MIL-53 (Al) and IL@MIL-53 (Al) filler particles (0–3 weight percent). Before adding particles to the polymer matrix, the "priming" process involves gradually adding polymer to the filler solution. [1-4] To guarantee the fillers' optimal wetting, the filler solution was first primed for five hours after adding 10% total PA. The remaining 90% of the PA was then added to the dope solution in batches, and it was constantly swirled at 500 rpm and 60 °C until it was fully dissolved. It is anticipated that the uniform thin dense layer would form when ethanol is added as a nonsolvent to the PA and NMP-THF combination. The identical process described for composite membranes without fillers was used to create the pure flat sheet membrane. By dip coating the surface with 5 weight percent PDMS/n-hexane solutions for 15 minutes and then curing at 60 °C for the whole night, the pinholes in the manufactured membranes were sealed. [7-10]

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} (^oC)^d	**T.S.** (MPa)^e	FFV^{EXP}
PA 'A'	0.53	1.34	345.6	451	75.0	0.126

$^a\eta_{inh}$ = 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

Surface morphology PA/IL@MIL-53 (Al) membranes

SEM pictures were used to describe the shape of the neat and composite PA membranes, and the results are displayed in Fig. 1. All of the manufactured membranes had a typical asymmetric membrane structure. The "spongy-like structure"—a finger-like macrovoid encircled by macrovoid-free portions—formed and sustained the thin, selective skin layer devoid of defects. Better gas transport capabilities were ensured by filler particles and PA matrix compatibility, which resulted in smooth and defect-free membranes up to 2 weight percent in the top surface pictures. While the non-solvent ethanol in the dope solution caused instantaneous demixing during the phase inversion, the volatile solvent, THF, quickly evaporates from the outer layer of the PA membranes, causing the polymer-rich phase to undergo rapid vitrification, resulting in the formation of no pinholes or defects in the skin layer. [2-4] A homogeneous, thick skin top surface—which is essential for improved separation performance—could be created by adding a non-solvent, which would lower the NMP-THF solvent mixture's dissolving power and increase polymer-polymer contact and solidification. Due to its chemical nature, the filler was firmly incorporated inside the polymer matrix, and no significant unselective spaces were visible in the cross-sections. However, the dispersion magnitude in the membranes may have been enhanced by appropriate dispersion achieved by priming polymer addition and sonication. [4-8] Furthermore, the [bmim][Tf_2N] modification, which produces the uniform dispersion, was a good reason for the close contact between the PA polymer matrix and IL@MIL-53 (Al) filler. [8-10]

3. Results and discussion

3.1. Fourier transform infrared spectroscopy analysis

The structural changes in MIL-53 (Al) fillers brought on by the physical functionalization with [Bmim][Tf_2N] IL have been identified by FTIR. The Al–O band corresponded to wavenumbers between 470 and 570 cm^{-1}. The carboxylic group of terephthalic acid is represented by vibrational bands about 1420 to 1700 cm^{-1}, whereas asymmetrically –COO– stretching is represented by bands at 1608 and 1518 cm^{-1}. Furthermore, the bands at 1425 and 1430 cm^{-1} matched symmetric –COO stretching. Moreover, the unreacted BDC molecules in MIL-53 (Al) cavities caused the –COOH group's absorption band to be seen at 1672 cm^{-1}. [6-8] The -C-H stretching band of the -CH_2 and -CH_3 vibrations of the alkyl group at the imidazolium ring is shown by the peaks in the 2800 and 3000 cm^{-1} range. The characteristic peaks of –CF3 asymmetric stretching appear around 1243 cm^{-1} in the spectrum of IL@MIL-53 (Al) and may be caused by the vibrations of the [Tf_2N] anion. The peaks at 751 and 781 cm^{-1} correspond to the C–S stretching of the [Tf_2N] anion and –CF_3 symmetric bending, respectively. [2-4]

3.2. Polymer synthesis and their properties

The usual phosphorylation polycondensation of the aromatic diamine monomer (1) with the dicarboxylic acid monomer (2) produced polyamides (Scheme 1). FTIR-ATR, NMR spectroscopy, and elemental studies were used to confirm the architectures of polymer repeat units. In the FTIR-ATR spectra, these poly(ether amide)s displayed distinctive amide group absorption bands in the region of 3338-3291 cm^{-1} (N-H stretching) and 1653-1661 cm^{-1} (carbonyl group stretching). The significant conversion of diamines to polyamides was substantiated by the lack of an absorption peak caused by the diamine above 3400 cm^{-1}. [4-6]

Additionally, there was good agreement between the polymer repeat unit structures and their ^1H-NMR spectra. An example of PA 'A' s ^1H-NMR spectra in pyridine-d_5. The amide proton for all PAs is represented by the singlet above 11.36 ppm. These PA were dissolved in DMAc to produce transparent and flexible membranes. Tensile strength values of 82 MPa were displayed by the membrane (Table 1). The polymer's TGA thermograms are performed in air. All of the PA had good thermal stability in air, according to TGA thermograms, with 10% breakdown temperatures falling between 458 and 458 °C. [3-7]

3.3. Surface morphology studies

MIL-53(Al) and IL@MIL-53(Al) nanofillers' SEM images revealed homogeneous crystals with the agglomerates (Fig. 1). Following IL functionalization of MIL-53 (Al) fillers, it was discovered that the degree of agglomeration was somewhat reduced (Fig. 1). The IL-modified MIL-53 (Al), on the other hand, has a comparable particle form, indicating that IL did not substantially change the shape. When IL was added, the

MOF crystal's sharp edges vanished, and the IL layer covering on the surface of the artificial MOF crystals filled the gap between the MIL-53 (Al) crystals. [5-9]

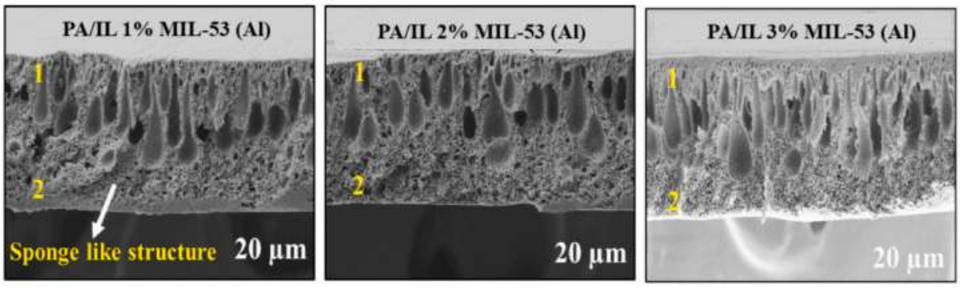


Fig. 1. Cross-sectional morphology f membranes. 1 represents dense skin layer, and 2 represents porous sublayer.

3.4. Gas transport properties

3.4.1. Effect of chemical structures on gas transport properties

Compared to plain PAmembranes, MIL-53 (Al) and IL@MIL-53 (Al) integrated membranes demonstrated noticeably greater CO_2 gas permeability. Table 2 lists the MMMs' ideal permselectivity values and mean gas permeability coefficients for the four distinct gases (CO_2, O_2, N_2, and CH_4). $P (CO_2) > P (O_2) > P (N_2) > P (CH_4)$ is the order in which four distinct gases pass across these MMMs membranes. This is basically the opposite of their kinetic diameter, which is CO_2 (3.3 Å) < O_2 (3.46 Å) < N_2 (3.64 Å) < CH_4 (3.8 Å). [3-6] Since MIL-53 (Al) is porous and provides extra permeation channels, the addition of MIL-53 (Al) nanofillers increased the permeance of all three CO_2, CH_4, and N_2 gases. This may be because CO_2 gas passes through the membrane due to its condensability and small kinetic diameter of 3.30 Å. First, dense membranes were used to assess the MOFs' contribution to the membrane separation performance of the resultant MMMs. Measurements were made of fillers in PA membranes at 3 bar and 35 °C. Additionally, for the three IL @% MIL-53 (Al)-filled PA-membranes at 3 weight percent loading, selectivity increased as filler loading increased. [4-7] Both MIL-53 (Al) and IL@MIL-53 (Al) filler particles cause the polymer chain packing to be disrupted, and interchain space increases the membrane matrix's fractional free volume. The gas pair selectivities rose in tandem with CO_2 permeance. A noteworthy outcome in comparison to previous research is the improvement in both selectivity and permeability, which suggests positive interactions between the filler and the polymer matrix. Interestingly, despite the fact that the structure and physical characteristics of these three MOFs differ greatly, the percentage of loading MOFs that exhibit permeance and selectivity is the same. [6-8] Similar competitive behavior between the two gases for the available adsorption sites in the MOF framework is indicated by comparable selectivities values for any filler loading of the three MOF-based MMMs. The MOFs' selectivities, similar to those of the polymer, can be attributed to the ways in which different gas molecules interact electrostatically with the membrane constituents. For example, CO_2 has a strong quadrupole moment, whereas CH_4 has none. This results in increased interactions, and consequently sorption, in a polar environment like the MOF framework. [5-8]

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)**	**Ref.**
PA/IL 0% MIL-53 (Al)	10.00	3.40	0.55	0.45	36.00	7.30	This study
PA/IL 1% MIL-53 (Al)	17.00	6.30	0.75	0.80	24.50	7.00	do
PA/IL 2% MIL-53 (Al)	49.00	13.00	1.87	1.50	38.50	6.50	do
PA/IL 3% MIL-53 (Al)	88.00	23.00	3.40	1.90	48.50	7.70	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

Most gas separation membranes based on IL and MOF were described as dense membranes. The synergistic action of [bmim][Tf_2N] and MIL-53 (Al) filler particles led to the fabrication of IL@MIL-53 (Al) composite membranes. The increased molecular sieving characteristic of membranes due to the fine-tuned porous structure of MIL-53 (Al) fillers particles functionalizing with [bmim][Tf_2N] IL is confirmed by the improvement in gas separation performance. Other commercially available polymers (such as Matrimid®, Extem®, and Ultem®) and some previously published polymers (3g, 3h, and P3) were compared to the gas permeability and permselectivity values of these MMMs PAs (PSf/IL 0-3% MIL-53 (Al)) [4–7]. Robeson plots [6,7] have been used to better compare the CO_2/CH_4 permselectivity vs. CO_2 gas permeability (Fig. 2). These MMMs often exhibited good permeability and selectivity that was on par with or better than that of the previously described polyamides. In comparison to other structurally similar PAs, PSf/IL 3% MIL-53 (Al) exhibits very excellent permeability of CO_2 gases with an improvement in permselectivity. Higher diffusivity selectivity values were attributed to PSf/IL 0-3% MIL-53 (Al) for CO_2/CH_4 gas couples' excellent permselectivity values. As seen by their trade-off points around the upper bound of Robeson, the current PAs demonstrated good advances in gas-separation performance.

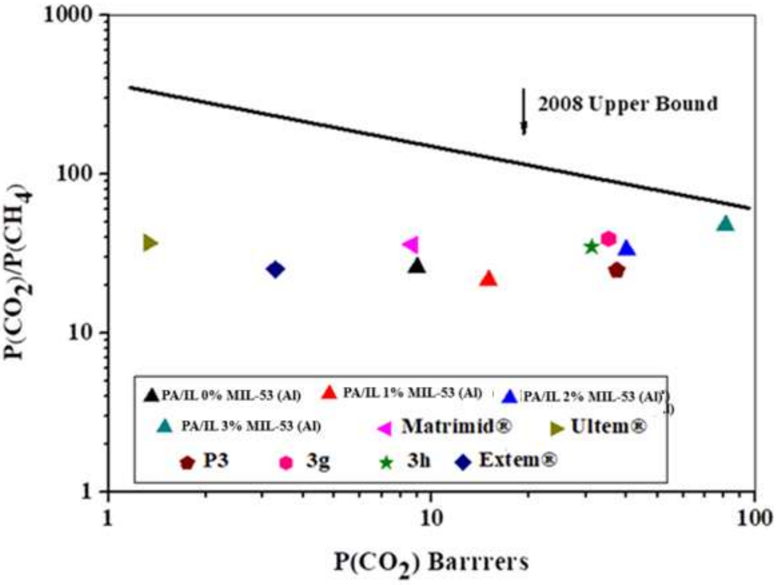


Fig. 2. Robeson plot for a comparison of CO_2/CH_4 selectivity vs. CO_2 permeability coefficients of the MMMs under this investigation and some other reported polymers.

4. Conclusions

Fluorinated PA membranes with a pyridine moiety and a diamine moiety with a pendant tert-butyl group ring were connected in the polymer backbone to examine their properties. A solvent evaporation process was utilized to generate Mixed-Matrix Membranes (MMMs) using semi-fluorinated polyamide (PA) as the base polymer and Ni-MIL-53 (Al) as a filler. For gas separation investigations, PA-based membranes were created using the metal-organic frameworks MIL-53 (Al) and post-synthetic [bmim][Tf_2N] functionalized MIL-53 (Al) nanofillers. The membranes were constructed using the solution casting process at different loadings (0–3 weight percent). The effect of MOFs on MMMs gas separations was examined by creating a thick membrane filled with PA/IL@MIL-53 (Al). The priming process utilized to create the MMMs produced a suitable distribution of fillers in the polymer matrix. The defects seen in the SEM were attributed to artifacts created during sample preparation. The inclusion of bulky tert-butyl groups improved the gas permeability and permselectivity of these polymer membranes, according to the gas transport experiments. The high CO_2 solubility and affinity of [Bmim][Tf_2N] combined with the organic bridges of MIl-53 (Al) fillers may be the source of the simultaneous improvement in permeance and selectivities of IL@MIL-53 (Al) based PA membranes. It was believed that the higher permeances with increasing MOF-loadings were caused by the structural properties of the MOFs. MMMs were composed of the PA polymer matrix and a metal-organic framework (IL@MIL-53 (Al)) that demonstrated a high level of compatibility with PA. Pure gas measurements were used to examine a number of MMMs, and mixed gas measurements were then performed on IL@MIL-53 (Al) /PA.

5. Acknowledgment

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6. References

[1] Kavak, S., Polat, H.M., Kulak, H., Keskin, S. and Uzun, A., 2019. MIL-53 (Al) as a versatile platform for ionic-liquid/MOF composites to enhance CO_2 selectivity over CH_4 and N_2. *Chemistry–An Asian Journal*, *14*(20), pp.3655-3667.

[2] Sezginel, K.B., Keskin, S. and Uzun, A., 2016. Tuning the gas separation performance of CuBTC by ionic liquid incorporation. Langmuir, 32(4), pp.1139-1147.

[3] Banerjee, S., 2015. Handbook of specialty fluorinated polymers: Preparation, Properties, and Applications. William Andrew.

[4] Bisoi, S., Bandyopadhyay, P., Bera, D. and Banerjee, S., 2015. Effect of bulky groups on gas transport properties of semifluorinated poly (ether amide) s containing pyridine moiety. European Polymer Journal, 66, pp.419-428.

[5] Bisoi, S., Mandal, A.K., Singh, A., Padmanabhan, V. and Banerjee, S., 2017. Soluble, optically transparent polyamides with a phosphaphenanthrene skeleton: synthesis, characterization, gas permeation and molecular dynamics simulations. *Polymer Chemistry*, *8*(29), pp.4220-4232.

[6] Mubashir, M., Yeong, Y.F., Chew, T.L. and Lau, K.K., 2019. Optimization of spinning parameters on the fabrication of NH_2-MIL-53 (Al)/cellulose acetate (CA) hollow fiber mixed matrix membrane for CO_2 separation. *Separation and Purification Technology*, *215*, pp.32-43.

[7] Anbia, M. and Hoseini, V., 2012. Development of MWCNT@ MIL-101 hybrid composite with enhanced adsorption capacity for carbon dioxide. *Chemical Engineering Journal*, *191*, pp.326-330.

[8] Rahmani, E. and Rahmani, M., 2018. Al-based MIL-53 metal organic framework (MOF) as the new catalyst for Friedel–Crafts alkylation of benzene. *Industrial & Engineering Chemistry Research*, *57*(1), pp.169-178.

[9] Ullah, S., Shariff, A.M., Bustam, M.A., Elkhalifah, A.E., Murshid, G., Riaz, N. and Shimekit, B., 2014. Effect of modified MIL-53 with multi-wall carbon nanotubes and nanofibers on CO_2 adsorption. *Applied Mechanics and Materials*, *625*, pp.870-873.

[10] Majumdar, S., Tokay, B., Martin-Gil, V., Campbell, J., Castro-Muñoz, R., Ahmad, M.Z. and Fila, V., 2020. Mg-MOF-74/Polyvinyl acetate (PVAc) mixed matrix membranes for CO_2 separation. *Separation and Purification Technology*, *238*, p.116411.