Incorporation of benzimidazole linked polymers into Matrimid to yield mixed matrix membranes with enhanced CO_2/N_2 selectivity

Tsemre Dingel M. Tessema,[a] Surendar R.Venna,[b,c], Ganpat Dahe,[b] David P. Hopkinson,[b] Hani M. El-Kaderi,[a]*Ali K. Sekizkardes[b,c] *

[a] *Department of Chemistry, Virginia Commonwealth University, 1001 W. Main St., Richmond, Virginia 23284-2006, United States*
[b] *National Energy Technology Laboratory, 626 Cochrans Mill Road, Pittsburgh, PA 15236, USA*
[c] *AECOM, 626 Cochrans Mill Road, Pittsburgh, PA 15236, USA*

**Email:* ali.sekizkardes@netl.doe.gov, *Phone: (412) 386-7255*
**Email:* *helkaderi@vcu.edu Phone: (804) 828-1298*

Abstract

Two different highly cross-linked benzimidazole linked polymers (BILPs) displaying high surface area were successfully incorporated into Matrimid polymer to form a series of new mixed matrix membranes (MMMs). The surface functionality of the BILPs, BILP-4 and BILP-101, were exploited to assure the interaction with the Matrimid matrix and produce robust MMMs, which displayed significantly improved CO_2 gas permeability. The ideal selectivities for CO_2/N_2 were calculated with enhancements as high as 34% at 15 wt% BILP loading. While BILP-4 and BILP-101 have similar structures and functionality, the two materials have notably different surface areas and CO_2 adsorption capacity. Despite the differences in their gas adsorption properties, MMMs composed of Matrimid/BILP-4 and Matrimid/BILP-101 had very similar gas transport properties. These results suggest that the functional groups of the filler particle and the resulting interaction with the polymer matrix may have had more influence on the gas separation properties of the mixed matrix membrane than the adsorption properties of the fillers.

1. Introduction

With the world still heavily relying on fossil fuel as a source of energy, flue gas composed of 12-15 wt% CO_2 accounts for a significant amount (33-40%) of the global CO_2 emissions.[1, 2] As such, a remarkable effort in development of technologies to separate carbon dioxide (CO_2) from mixtures of gases has occurred for technologies including: absorption, adsorption, cryogenic distillation and membrane separation. Of these technologies, membranes offer several advantages including high energy efficiency, ease of operation and control, scalability and low maintenance costs.[3]

Polymer membranes have been prevalent in gas separation applications through the years due to their easy processability. However, their trade-off between permeability and selectivity as proposed by Robeson presents a drawback.[4] To address this issue, researchers have pursued the incorporation of porous materials ranging from zeolites,[5, 6] metal organic frameworks (MOFs),[7-9] carbon molecular sieves,[10]and silica gel,[11] into a polymer matrix to produce a class of materials known as mixed matrix membranes (MMMs). A common challenge encountered in MMM performance for gas separation is the inadequate adhesion between the polymer matrix and the filler particle. This drawback causes interfacial defects including voids, polymer rigidification, and filler pore blockage. [12]

In order to address this issue, porous organic polymers (POPs) have recently been evaluated as a promising class of material to be implemented as a filler material in a MMM.[13-15] In comparison with MOFs, POPs offer higher chemical and physical stability along with high surface area, tunable functionality, and tunable textural properties. Their purely organic nature combined and desirable surface functionalities needs to be further explored for its potential to enhance the adhesion to polymer matrix and reduce interfacial defects in MMMs.

To date only a few groups have explored the incorporation of porous organic polymers into polymer films to make MMMs, despite promising results. Wu and coauthors used the POP SNW-1 in the polymer PIM-1 and found an increase in CO_2 permeability of 106% and CO_2/N_2 selectivity of 35% up to 10 wt% filler particles, after which selectivity decreased.[16] A similar trend was shown for CO_2/CH_4 selectivity (increased by 23%). In our previous work with PIM-1 and a benzimidazole linked polymer, we demonstrated an increase of 53% in CO_2 permeability at 30 wt% filler particles, but at the expense of a small decrease in CO_2/N_2 selectivity.[14] Cao and coauthors fabricated an MMM from COF-LZU1 filler particles in a poly(vinylamine) matrix and tested in a humidified gas mixture of CO_2 and H_2. They observed a 244% increase in CO_2 permeability and a 36% increase in CO_2/H_2 selectivity over a neat poly(vinylamine) membrane at 0.15 MPa, with reduced performance at higher pressures. [17]

Polyimide based polymer membranes are widely employed in several gas separation applications due to their promising gas transport properties as well as their attractive physical properties. Matrimid is one such commercial polyimide prepared from the polycondensation reaction between 3,3'-4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and diaminophenylindane (DAPI). The DAPI monomer (5(6)-amino-1-(4-aminophenyl)-1,3,3-trimethylindane) contains an isomeric phenyl indane leading to a mixture of 6-amino and 5-amino isomers. Its isomeric nature along with the bent phenyl indane ring bearing four out of plane bulky groups by way of a three methyl and one phenyl group stiffen the polymer backbone and minimize efficient chain packing.[18] These structural details are manifested in Matrimid's solubility in common organic solvents, impressive mechanical strength, and high T_g.[18, 19] Due to its processability and excellent physical properties, we used Matrimid in the fabrication of a new class of mixed matrix membranes.

There is a continuing need to develop filler particle materials for MMMs that have strong interaction with polymer matrices, are able to enhance both permeability and selectivity, and can be produced at low cost. In this study, two benzimidazole linked polymers (BILPs) were studied as filler particles in the commercial polyimide Matrimid. Benzimidazole linked polymers (BILPs) are highly porous nitrogen rich polymers prepared by the acid catalyzed condensation reaction between aryl-*o*-diamine and aryl-aldehyde building blocks.[20, 21] The chemical stability of benzimidazole groups along with their physisorptive affinity for CO_2 through Lewis acid-base ($N\cdots CO_2$) and aryl ($C\text{-}H\cdots O{=}C{=}O$) has garnered interest in BILPs as CO_2 separation materials.[22, 23] BILP-4 is one such polymer with a highly cross-linked structure obtained by a metal free synthesis from simple building blocks.[23] It has a high surface area and high CO_2 uptake at low STP. BILP-101 is composed of similar building blocks as BILP-4, but is structurally unique and has a lower surface area and lower CO_2 solubility.[24] With these considerations in mind, we have prepared a series of MMMs using both BILP-4 and BILP-101, characterized their physicochemical properties as well as gas permeabilities to evaluate their ability to selectively separate CO_2 over N_2 as a function of their physical properties.

2. Experimental Methods and Materials

2.1 Materials and instrumentation

All chemicals for BILP-4 synthesis were purchased from Sigma Aldrich and were used without further purification. Matrimid® 5218 polymer was purchased from Huntsman Chemical. Tetrahydrofuran was purchased from Fisher Scientific. Fourier transformed infra-red (FT-IR) spectra were obtained using a Bruker Vertex 70. Thermogravimetric analysis (TGA) was performed using a TGA Q500 thermal analysis system. Surface area measurements were conducted using a Quantachrome Autosorb iQ_2 gas sorption analyzer. Scanning electron microscopy (SEM) was conducted using an FEI Quanta 600 scanning electron microscope. Tension tests were conducted with a TA instruments model Q800 dynamic mechanical analyzer (DMA). Differential scanning calorimetry (DSC) was from a TA instruments Q2000.

2.2. Synthesis of BILP-4 and BILP-101

BILP-4 was synthesized following a method previously reported.[23] Briefly, a 200 mL Schlenk flask was loaded with 1,2,4,5-benzenetetramine tetrahydrochlroide (55 mg, 0.19 mmol) and anhydrous DMF (30 mL) and stirred to form a homogeneous mixture. A solution of tetrakis(4-formylphenyl)methane (40 mg, 0.1 mmol) in 15 ml anhydrous DMF was added drop-wise to the Schlenk flask at -30 °C. Upon the precipitation of a brown product the mixture was allowed to warm up to room temperature and kept stirring overnight. The reaction mixture was bubbled with air for 15 minutes, capped and incubated at 130 °C for a period of 72 hours. The resulting yellowish brown polymer was isolated by filtration and washed with DMF, acetone, water, 2M HCl, 2M HCl, water and acetone in that order. The product was soaked in acetone/CH_2Cl_2 (1:1, v:v) for 24 hours and dried at 120 °C under vacuum to yield the yellowish brown BILP-4 (54 mg, 91%). BILP-101 was synthesized following the methods mentioned above for BILP-4 using 1,2,4,5-benzenetetramine tetrahydrochloride (100 mg, 0.35 mmol) and 1,3,5-triformylbenzene (40 mg, 0.23 mmol). After drying, the final product BILP-101 was obtained as a yellow brown powder (72 mg, yield 92%).[24] Structures for the two BILPs are shown in Figure 1.

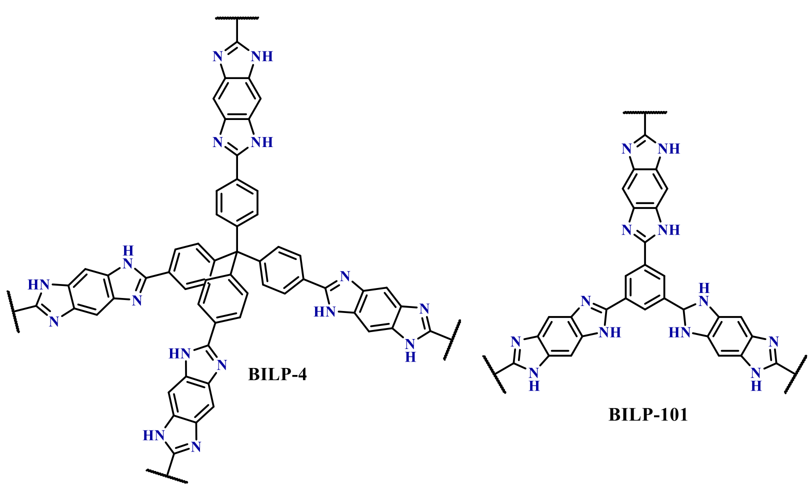

Figure 1. Chemical structures of BILP-4 and BILP-101 polymers.

2.3. Membrane fabrication

The neat Matrimid and BILP/Matrimid MMMs were prepared using a previously reported technique. [8] To prepare the neat polymer film, Matrimid was dried at 120 °C under vacuum for 24 hours. Polymers dissolved in THF and mixed with a roller mixer and left standing overnight to eliminate any gas bubbles. Matrimid membranes were then cast on a glass plate confined in a glove bag purged with N_2 and saturated with THF to minimize humidity and to control the rate of THF evaporation from the membrane. The membrane was then dried at 100 °C overnight, annealed at 225 °C in a vacuum oven for 2 hours and cooled down to room temperature.

The dope solution for the BILP/Matrimid MMMs was prepared by homogenously dispersing activated BILP-4/BILP-101 (120 °C overnight under vacuum) in THF using an ultrasonication water bath for 2 hours. A 30 wt% of Matrimid solution in THF was then added to a BILP dispersion, mixed in a roller mixer and ultrasonicated for 2 hours. This step was repeated for the remaining Matrimid solution at 30 wt% and 40 wt% increments. The BILP/Matrimid MMMs were cast using the same procedure for the neat Matrimid membranes discussed above. BILP loadings of 10 wt%, 15 wt% and 25 wt% were used to fabricate three different BILP/Matrimid MMMs.

2.4 Gas permeance measurements

The CO_2 and N_2 pure gas permeance was measured at 22 °C using a constant volume-variable pressure system as reported previously.[8] The membranes were cut into 2.5 cm diameter coupons and loaded in a Millipore holder creating an effective area of 2.7 cm^2. The upstream and downstream of the membrane were de-gassed using a vacuum pump for 18 hours. The leak rate was measured by isolating the permeation system from the vacuum pump. The leak rate was always at least two orders of magnitude smaller compared to the steady state pressure rise during the gas permeation measurement. The feed gas (pure gas CO_2 or N_2) was then introduced to the upstream side of the membrane, and the pressure rise in the downstream volume was recorded as a function of time. Upstream pressures were measured with a pressure transducer (maximum pressure of 10 bar, Viatran Inc., Model-345). Downstream pressures were measured using a capacitance manometer (maximum pressure of 10 Torr, Baratron 627D, MKS). All membranes were tested at a pressure drop of 207 kPa. The thickness of the membranes was measured using a micrometer several times and the average was used for the permeability calculation. Gas performance data were determined using a minimum of two membranes to ensure the reproducibility of the experimental results.

3. Results and Discussion

3.1. Physical properties of BILP/Matrimid MMMs

The morphology and interaction between the Matrimid polymer and BILP-4 filler particles were assessed using cross-sectional SEM imaging (Figure 2). The MMMs appear to be free of defects, and had evidence of strong polymer/filler particle interfacial interaction. The membrane samples were prepared for SEM analysis by freeze fracturing in liquid nitrogen. During fracturing of the membrane cross section, polymer veins with concentric apertures form due to plastic deformation. For the materials used here, bonds between the polymer and filler particle do not fracture easily because of strong interfacial interaction. As a result, the polymer further from the filler particle undergoes more pronounced plastic deformation before fracturing than would otherwise be seen in the fracture of a neat polymer film. Thus the polymer veins with concentric apertures that were observed here are characteristic of MMMs with strong interaction.[8] The SEM images also reveal that filler particles remain intact upon incorporation into the Matrimid matrix. BILP-101/Matrimid MMMs were very similar in appearance to BILP-4/Matrimid, due to the structural and interfacial similarities of the two filler particles.

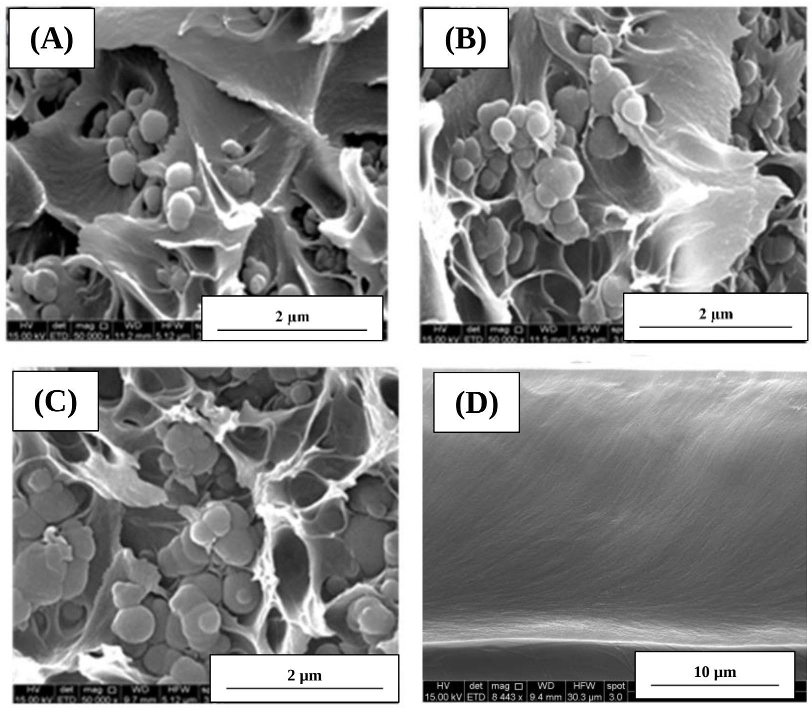

Figure 2. SEM images of (A) 10 wt% BILP-4/Matrimid, (B) 15 wt% BILP-4/Matrimid, (C) 25 wt% BILP-4/Matrimid, (D) neat Matrimid.

The incorporation of BILP into Matrimid was verified by comparing the FT-IR spectra of neat Matrimid membranes and BILP-4/Matrimid MMMs (Figure 3A). A broad peak between 3450-3200 cm^{-1} absent in the pure Matrimid membrane was evident in the membranes loaded with BILP-4.[20] This value is characteristic of free N-H and hydrogen bonded N-H peaks from the secondary amine in the imidazole ring of BILP-4. The thermal stability of the MMMs was assessed by non-oxidative thermogravimetric analyses (Figure 3B). The decomposition onset temperature observed for Matrimid was found to be around 445 °C. With increased filler loadings, a trend of enhanced thermal stability up to 461, 470 and 474 °C for 10, 15 and 25 wt% BILP-4/Matrimid MMMs, respectively was observed. This is caused by a thermal motion inhibition introduced by the interfacial interaction of Matrimid and BILP-4 polymers which increases the thermal energy barrier needed to mobilize the polymer chains.[20, 25] The 10 and 15 wt% BILP-4/Matrimid MMMs showed a small loss in mass starting at about 180 °C, most likely due to the volatilization of unevaporated solvent from the films.

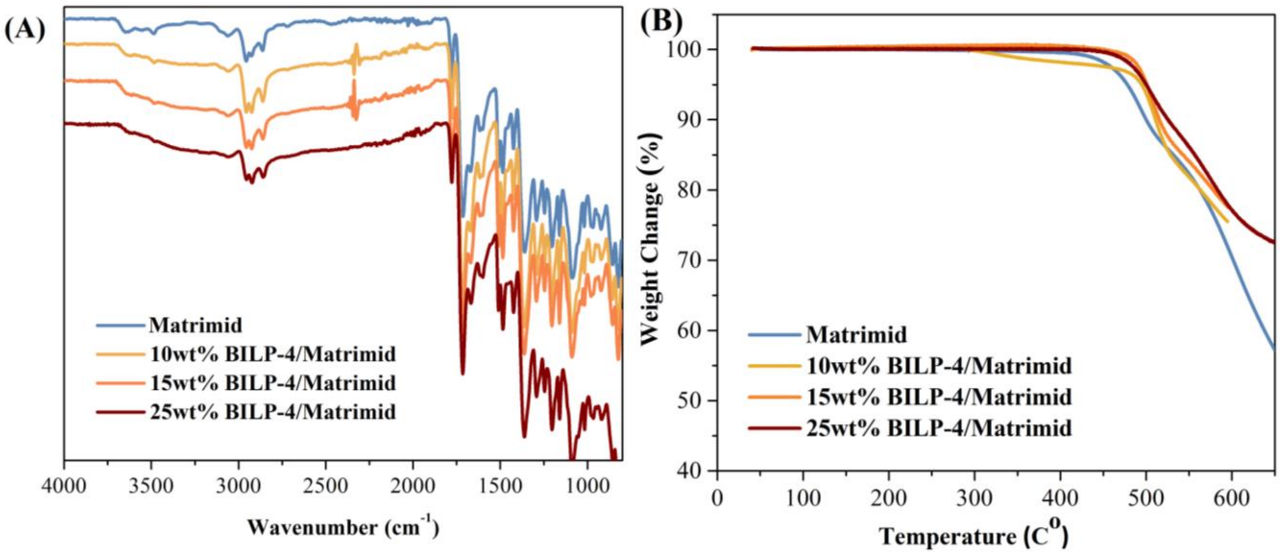

Figure 3. (A) FTIR spectra of Matrimid and BILP-4/Matrimid MMMs, (B) thermogravimetric analysis of Matrimid and BILP-4/Matrimid MMMs (Membranes were treated at 225°C prior to TGA).

Because of the structural similarities between BILP-4 and BILP-101, BILP-101/Matrimid MMMs will have similar spectral and thermal characteristics as demonstrated in Figure 3. The mechanical properties of BILP-4/Matrimid MMMs were evaluated using a tension test (Figure 4A). The Young's modulus values of BILP-4/Matrimid MMMs are higher than the neat Matrimid membrane (1.5 GPa). An increase in the Young's modulus values of MMMs up to 2.1 GPa was recorded. These results are an indication of a strong interfacial interaction between Matrimid and the BILP-4 filler particles, and is similar to trends that were reported on MMMs composed of Matrimid loaded with Cu-BPY-HFS MOFs and carbon molecular sieves.[26, 27] The glass transition temperature (T_g) of MMMs were determined using DSC. The T_g of BILP-4/Matrimid® membranes were slightly higher than pure Matrimid (Figure 4B). MMMs with 15 and 25 wt% BILP-4 have a T_g of 328 °C, 3 °C higher than that of pure Matrimid. This trend is in agreement with previous reports in which the addition of filler particles resulted in rigidification of the polymer matrix and hence a restricted mobility of polymer chains.[28, 29] In the case of BILP-4/Matrimid, this interaction is enhanced by hydrogen bonding between secondary amines of BILP-4 imidazoles and imide oxygens of Matrimid as well as π-π stacking between aromatic groups of the two materials (Figure 4C). N_2 adsorption isotherms of MMMs containing various concentration of BILP-4 in Matrimid are depicted in the Figure 4D. Increasing surface area of MMMs showed that BILP-4, as a filler, enhances the free volume of Matrimid membranes.

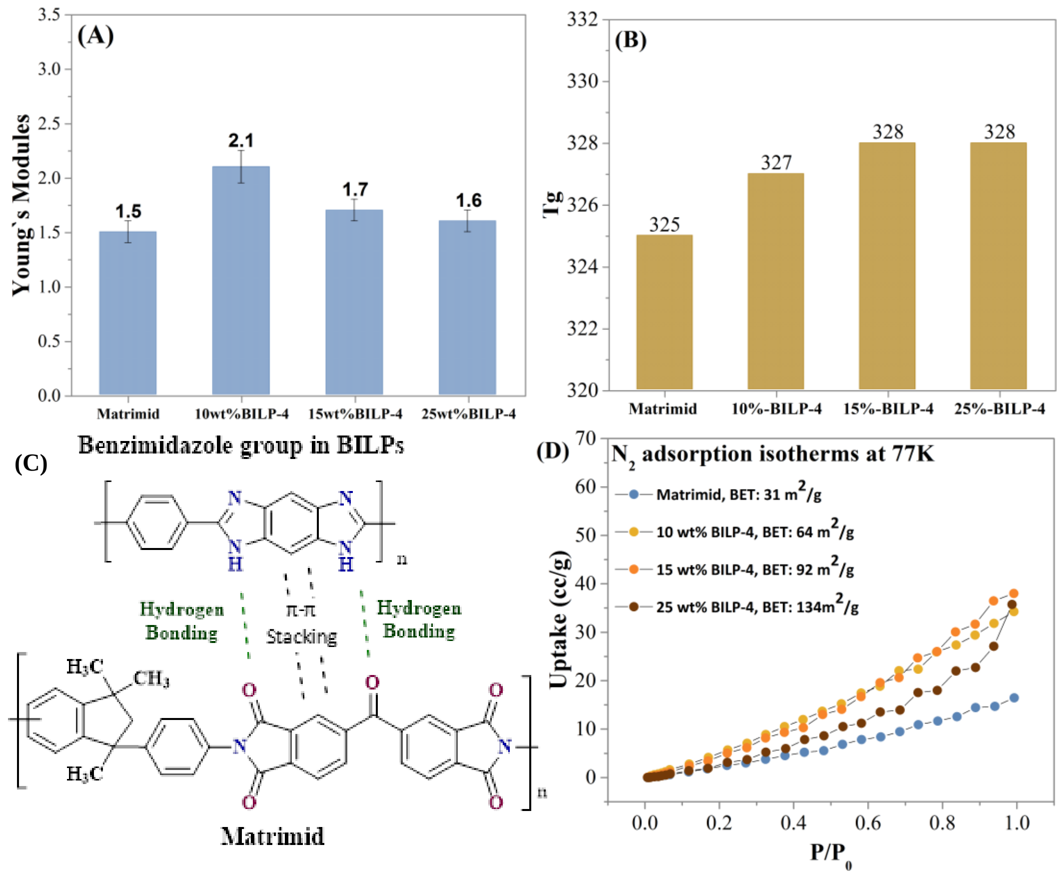

Figure 4. (A) Young's Modulus for BILP-4/Matrimid MMMs, (B) T_g for BILP-4/Matrimid MMMs, and (C) interaction between benzimidazole moiety of BILPs and Matrimid. (D) N_2 adsorption isotherm and BET surface area of neat Matrimid, 10 wt%, 15wt% and 25wt% BILP-4/Matrimid MMMs, respectively.

3.2. Gas adsorption and permeability properties

We evaluated the gas transport properties of MMMs by employing the two different benzimidazole linked porous polymers, BILP-4 and BILP-101. Testing two BILP filler particles achieved these objectives; (i) it confirmed the compatibility of the BILP class of materials with the polymeric matrix, Matrimid and (ii) it allowed us to evaluate the impact of textural properties (pore size, pore volume, surface area) of the filler particles on the gas transport properties of the membrane. Thus, we fabricated MMMs composed of 10, 15 and 25 wt% BILP-4 and BILP-101 in Matrimid.

The BET surface area of BILP-4 and BILP-101 was deduced from a N_2 isotherm at 77 K presented in Figure 5A. The BILP-4 surface area of 1079 m^2/g (Table 1) is in agreement with a previously reported value.[20] The Type-1 isotherm is reversible with a sharp uptake in the pressure range of P/P_0 = 0.01-0.15 indicative of a large portion of micropores.

This observation was supported by pore-size distribution (PSD) curves modeled using nonlocal density functional theory (NLDFT) which showed a dominant pore size of 0.65 nm (Figure 5B). The BILP-4 CO_2 uptake of 158 mg/g at 298 K (1 bar pressure) is also in close agreement with the previously reported value.[14] By contrast, BILP-101 has a smaller pore size of 0.54 nm, which is associated with improved CO_2/N_2 selectivity, and a reduced pore volume and surface area of 536 m^2/g. The reduced surface area caused a related reduction in CO_2 uptake, which was only 108 mg/g at 298 K.

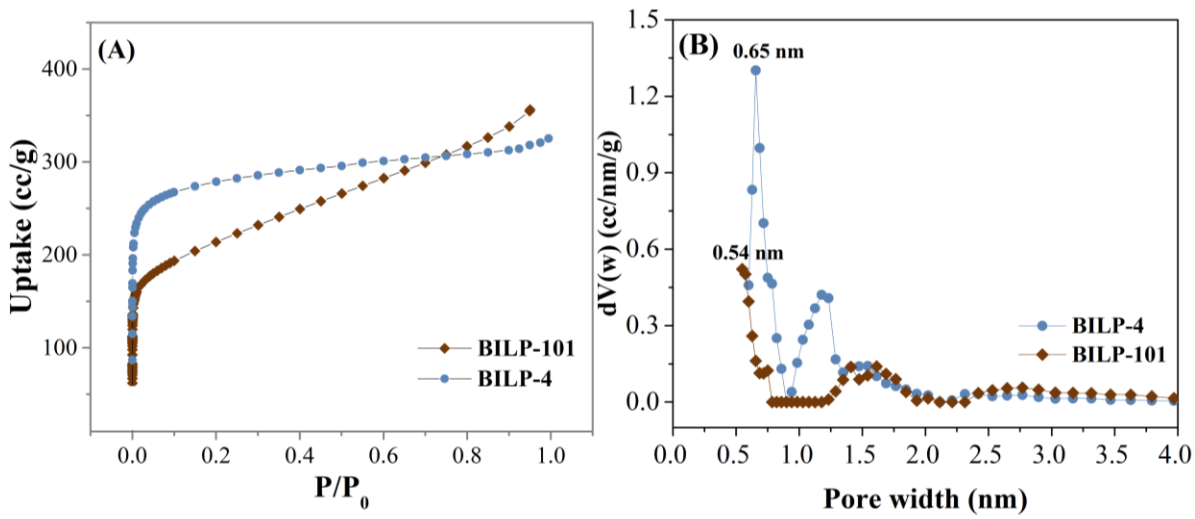

Figure 5. (A) N_2 isotherm of BILP-4 and BILP-101 at 77 K, (B) PSD of BILP-4 and BILP-101 from NLDFT.

Table 1. Textural and CO_2 adsorption properties of BILP-4 and BILP-101

Polymer	*BET Surface Area*	*Pore Volume*	*Pore Size*	*CO_2 uptake at 1 bar, 298K*
BILP-4	1079 m^2/g	0.65 cc/g	0.65 nm	158 mg/g
BILP-101	536 m^2/g	0.41 cc/g	0.54 nm	108 mg/g

The gas permeability properties of neat Matrimid and BILP/Matrimid membranes were obtained from pure gas CO_2 and N_2 permeation measurements (Figure 6A). The ideal selectivity for CO_2/N_2 is defined as the ratio of the permeability of the individual gases. In agreement with literature reports, the CO_2 permeability of the pure Matrimid membrane was measured as 8.7 Barrer with an ideal CO_2/N_2 selectivity of 29.[8] For the BILP-4/Matrimid MMMs, the CO_2 permeability values increase to 13.2, 14.9 and 63.6 Barrer for BILP-4 loadings of 10, 15, and 25 wt%, respectively. BILP-101/Matrimid MMMs showed a similar trend with permeability values of 13.4, 14.0, and 48.0 at the same loading values. These enhancements in CO_2 permeability are attributed to a resulting increase of fractional free volume in the MMMs introduced by the pore space inherently present in BILP-4.

The large increase in permeability at 25 wt% BILP loading indicates a high level of defect formation caused by agglomeration of filler particles in the membranes.

The ideal selectivities of the MMMs were 32.0, 38.9 and 25.3 for 10, 15 and 25 wt% BILP-4 loadings, while BILP-101 MMMs had very similar selectivities of 31.1, 34.5, and 26.0 at the same loadings. This trend suggests that the 15 wt% MMM provided the optimum increase in free volume coupled with an ideal polymer/filler particle interface. However, a different scenario occurs at 25 wt% BILP-4 loading where the dense concentration of the filler particle in Matrimid creates aggregates which results in defect formation and reduced gas selectivity. While the lower loadings of BILP filler particles move the MMM towards the more desirable upper right of the Robeson plot compared with neat Matrimid (Figure 6B), the 25 wt% only increase the gas permeability.

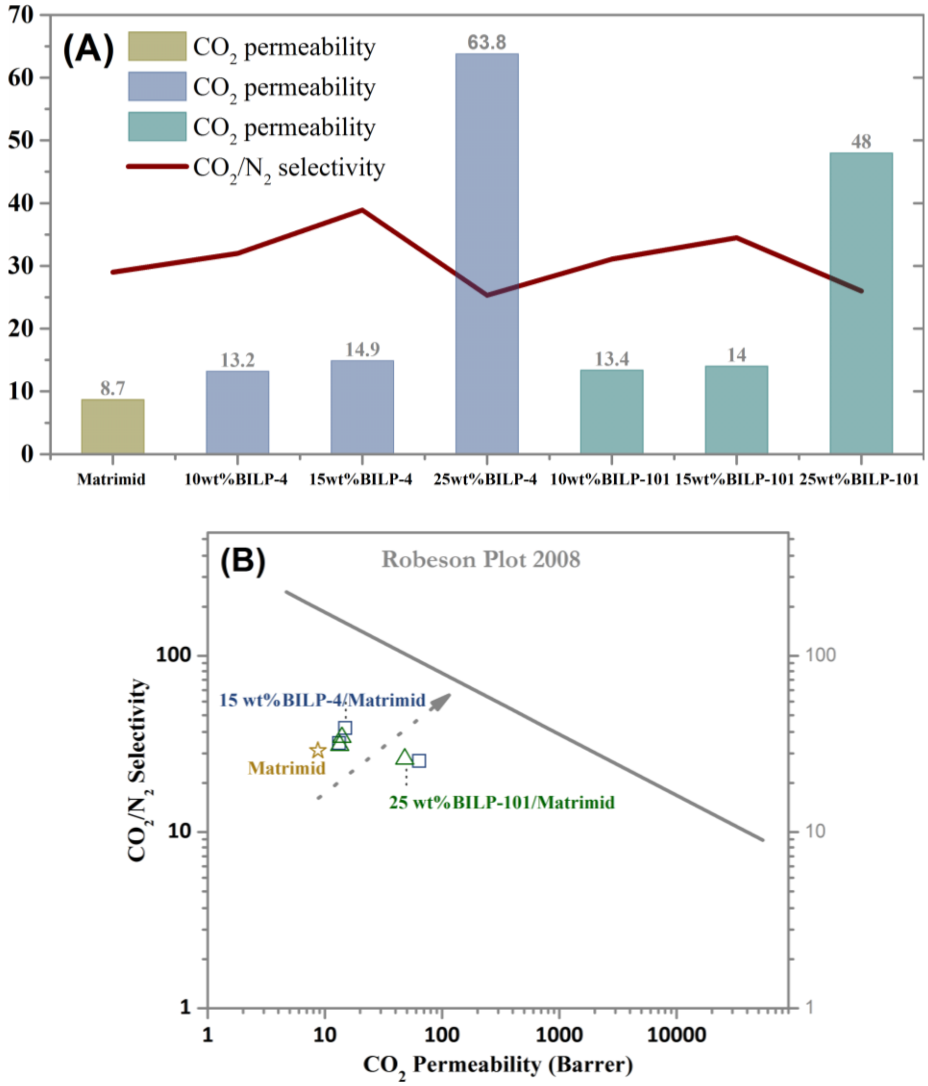

Figure 6. (A) Gas transport properties of Matrimid-BILP MMMs and (B) CO_2 permeability and CO_2/N_2 selectivity properties of membranes in respect to Robeson Plot 2008.

Two different polybenzimidazole filler particles, BILP-4 and BILP-101, were tested in order to relate the gas transport properties of the membranes with their textural properties. Both BILPs are constructed from imidazole linkages within a highly conjugated porous scaffold. BILP-4, however, features nearly two times the surface area of BILP-101 and its pore size is considerably larger. Because of its larger pore size, BILP-4 has lower CO_2/N_2 adsorption selectivity and a larger CO_2 adsorption capacity compared to BILP-101.[24] We expected BILP-4 based MMMs to exhibit lower CO_2/N_2 selectivity compared to BILP-101/Matrimid membranes. However, the gas permeability and selectivity performance was essentially the same for the MMMs regardless of which BILP filler particle was used. While the two filler particles have different textural properties, they are structurally similar and have the same functional groups. Therefore, it is likely that the polymer/particle interface is similar for both MMMs. It is possible that the interfacial properties played a more significant role in the bulk gas transport properties of the MMM than the particle itself.

4. Conclusion

In this study, we have successfully fabricated MMMs by incorporating benzimidazole linked porous polymers (BILPs), which were synthesized by a facile polycondensation reaction, into the commercial organic polymer Matrimid. The resultant MMMs display excellent thermal stability, which is critical for industrial applications. The chemical functionalities of the BILP framework facilitate a strong interaction with the Matrimid polymer matrix. This feature of BILPs was manifested in the defect-free and uniform distribution of two different BILPs, BILP-4 and BILP-101, into the matrix as well as improvements in gas permeability and selectivity of MMMs as compared to the neat Matrimid film. Perhaps due to the structural similarities of the BILPs, MMMs with BILP-4 and BILP-101 had similar performance, despite the notable difference in surface area and pore characteristics of the two filler materials. This findings suggests that the impact of gas diffusion through the particle/matrix interface may be more significant in this case than transport through the pore space of the particles.

Acknowledgments

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