Benzimidazole linked polymers (BILPs) in mixed-matrix membranes: influence of filler porosity on the CO₂/N₂ separation performance

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Abstract

The performance of mixed-matrix membranes (MMMs) based on Matrimid® and benzimidazole-linked polymers (BILPs) have been investigated for the separation CO₂/N₂ and the dependency on the filler porosity. BILPs with two different porosities (BILP-101 and RT-BILP-101) were synthesized through controlling the initial polymerization rate and further characterized by several techniques (DRIFTS, ¹³C CP/MAS NMR, SEM, TEM, N₂ and CO₂ adsorption). To investigate the influence of porosity, the two types of fillers were incorporated into Matrimid® to prepare MMMs at varied loadings (8, 16 and 24 wt.%). SEM confirmed the well dispersion of BILP-101 and RT-BILP-101 indicating their good compatibility with polymer matrix. The partial pore blockage in the membrane was verified by CO₂ adsorption isotherms on the prepared membranes. In the separation of CO₂ from a 15:85 CO₂:N₂ mixture at 308 K, the incorporation of both BILPs fillers resulted in an enhancement in gas permeability together with constant selectivity owing to the fast transport pathways introduced by the porous network. It was noteworthy that the initial porosity of the filler had a large impact in separation permeability. The best improvement was achieved by 24 wt.% RT-BILP-101 MMMs, for which the CO₂ permeability increases up to 2.8-fold (from 9.6 to 27 Barrer) compared to the bare Matrimid®.

1. Introduction

The soaring increase in CO₂ emissions has caused great public concern due to its accompanying greenhouse effect. In this sense, the capture of CO₂ from flue gas or natural gas has become necessary from the perspective of energy and the environment [1]. Flue gas is composed of CO₂, N₂, CO, O₂, water vapour and sulfur oxide, where N₂, CO₂ is the main component and the CO₂/N₂ ratio is around 15:85. Traditional technologies using amines or solvents to absorb CO₂ are environmentally unfriendly and energy intensive. Membrane-based gas separation on the other hand is a promising alternative owing to its attractive features, such as smaller footprints, easy operation and energy efficiency. Although many novel membrane materials have been proposed, polymeric membranes still dominate the current membrane market given their good processability, mechanical stability and low price. Nevertheless, conventional polymeric membranes suffer from a universal ‘trade-off’ relation between permeability and selectivity, known as the Robeson upper bound [2, 3]. Extensive efforts have been devoted to improve the gas separation performance (permeability and selectivity) of polymeric membranes, which include polymer blending [4], post-treatment of the membranes via cross-linking [5] or thermal rearrangement [6] and the development of novel nanoporous polymers, such as polymers of intrinsic microporosity (PIMs) [7, 8]. In this line, one of the most promising approaches to overcome polymers’ gas separation performance is to use mixed-matrix membranes (MMMs), consisting of a blend of selected fillers dispersed in a continuous polymeric matrix. This strategy allows to combine into one membrane the better separation performance of the selected fillers with the good processability and low price of polymeric membranes. Numerous porous fillers such as zeolites [9, 10] and Metal-Organic Frameworks (MOFs) [11, 12] have been successfully incorporated

into different polymers to prepare MMMs, resulting in an improved separation performance compared to the bare polymer membranes.

Porous organic frameworks (POFs) [13], such as covalent organic frameworks (COFs) [14, 15], conjugated microporous polymers (CMPs) [16], porous aromatic frameworks (PAFs) [17] and covalent triazine-based frameworks (CTFs) [18], are a relatively new category of porous materials constructed from covalent bonds. Given their diversified porosities, tunable chemical properties, inherent light weight and exceptional chemical and thermal stabilities, POFs are promising candidates to be used as fillers in MMMs for CO₂ separation [19, 20]. For example, Jin *et al.* [21] studied the effect of dispersing COF nanosheets in polyether-block-amide (PEBA) and prepared PEBA-based MMMs, which show 56 % improvement in ideal selectivity towards CO₂/N₂ compared to the pure PEBA membrane with only 1 wt.% COF loading. Zhu *et al.* [22] developed a new synthesis protocol to prepare self-supported PAF-56P@PSF composite hollow fibre membranes with a CO₂ over N₂ selectivity of 38.9 together with good thermal and mechanical stabilities. Recently, our group incorporated ACOF-1 in three different polymers to prepare MMMs for CO₂ separation [23]. The best improvement was observed for Matrimid®-based MMMs, for which a 20% and 87% increase in CO₂/N₂ selectivity and CO₂ permeability was obtained for 16 wt.% COF loading, respectively. These examples underscore the compatibility between POFs with different polymer matrices resulting in MMMs with improved performance when compared to the pure polymers. The fully organic nature of POFs has been reported to account for this good compatibility, in contrast to other inorganic fillers, such as zeolites, for which a poor compatibility resulting in the formation of voids at the filler-polymer interface has often been encountered.

Benzimidazole-linked polymers (BILPs) were first reported in 2011 [24]. BILPs have shown high CO₂ uptakes (up to ~ 6 mmol·g⁻¹ at 273 K for BILP-19 [25]) together with high CO₂/N₂ and

CO₂/CH₄ adsorption selectivities [26]. This preference for CO₂ has been related to the presence of imidazole functionalities in the POF framework. Further, the excellent thermal and chemical stabilities of BILPs make them desirable for practical separations. Sekizkardes *et al.* [27] successfully incorporated BILP-101 nanoparticles into the high free volume PIM-1 matrix. The obtained MMMs achieved a 53 % enhancement in the CO₂ permeability together with good stability under harsh conditions upon 30 wt.% POF loading, further proving the feasibility of using BILPs as fillers in the MMMs.

In terms of fillers, porosity is an important factor affecting CO₂ uptake and selectivity, playing a key role on the MMMs performance [28, 29]. Several studies have been devoted to the influence of the filler particle size and morphology [12, 30-33] as well as filler functionalities [34] on the membrane performance. However, the role of the fillers' porosity has remained largely unexplored. Herein, therefore, effect of filler porosity on the separation performance of POFs-containing MMMs is studied. BILP-101 particles with different porosities were synthesized by controlling the initial polymerization rate and used as fillers in the polyimide Matrimid® 5218. Matrimid® 5218 was chosen as polymer matrix owing to its good CO₂ selectivity together with high thermal and chemical stabilities and commercial availability. The prepared membranes were tested for CO₂/N₂ separation at 308 K and the effect of filler porosity, filler loading, and feed pressure on membrane performance was assessed.

2. Experimental Section

2.1. Materials

Benzene-1,3,5-tricarboxaldehyde (97 %), 1,2,4,5-benzenetetramine tetrahydrochloride, hydrochloric acid (37 %), sodium hydroxide (99.99 % metals basis), acetone (99.9 %) and tetrahydrofuran (THF, 99.9 %) were purchased from Sigma Aldrich. N,N-Dimethylformamide (DMF, 99.8%, extra dry over molecular sieves) was purchased from Thermo Fisher. All these

starting materials and solvents were used without further purification. Matrimid® 5218 ($M_w \approx 123,000 \text{ g}\cdot\text{mol}^{-1}$, $M_n \approx 11,000 \text{ g}\cdot\text{mol}^{-1}$) was kindly supplied by Huntsman Advanced Materials. Matrimid® was dried prior to use to remove the adsorbed moisture under vacuum at 453 K for 48 h.

2.2. Synthesis of BILP-101 and RT-BILP-101

BILP-101 was synthesized following the same procedure as previously reported by Sekizkardes *et al.* [35] In a typical synthesis, a 100 mL round bottom flask was charged with 1,2,4,5-benzenetetramine tetrahydrochloride (100 mg, 0.35 mmol), 60 mL anhydrous DMF, and a stirring bar. The resultant homogeneous solution was degassed under N_2 for 1 h, cooled to approximately 243 K and treated drop-wise with a solution of 1,3,5-triformylbenzene (40 mg, 0.23 mmol) in anhydrous DMF (15 mL). The temperature was maintained at *ca.* 243 K for 1 h during which a dark-brown solid formed. The resultant slurry solution was then left to warm to room temperature overnight, flushed with air for 30 min, and further heated to 403 K in an oven, temperature at which the reaction mixture was kept for 2 days. The solid was then collected by centrifugation at 5,000 rpm for 10 min for 2 cycles and subsequently washed with DMF, acetone, water, 1 M HCl, 1 M NaOH, water and acetone. Finally, the product was dried overnight at 393 K under vacuum.

RT-BILP-101 was prepared following the same procedure as described for BILP-101, but without the low temperature treatment, *i.e.*, 1,3,5-triformylbenzene was added to the 1,2,4,5-benzenetetramine tetrahydrochloride solution at room temperature (Scheme 1).

Scheme 1. Schematic of the procedure followed for the synthesis of BILP-101 and RT-BILP-101.

2.3. Preparation of mixed-matrix membranes (MMMs)

To prepare the MMMs, the required amount of BILP-101 particles (or RT-BILP-101) was first dispersed in THF and sonicated for 30 min. To this suspension, 0.2 g of dried Matrimid® was added and the casting suspension was further stirred overnight. The solvent/filler-polymer weight ratio was kept at 90/10 in all cases. The amount of BILP-101 in the casting suspension was adjusted to achieve the desired final filler loading of 8 wt.%, 16 wt.% and 24 wt.% in the resulting MMMs.

The prepared suspensions were then casted onto a clean glass plate with the help of a Doctor Blade knife. The cast membranes were immediately covered with a small watch glass to prevent too fast evaporation of the solvent. The glass plate was further covered with a square box and four small vials containing THF to create a saturated THF atmosphere. All these measures were taken to slow down the evaporation rate of THF, thereby preventing the formation of defects during membrane drying. The membranes were first left to dry overnight at room temperature and then dried under vacuum for 24 h at 423 K.

The pure polymer membranes were prepared following the same procedure as the MMMs, but without the extra step of dispersing BILP-101 or RT-BILP-101 particles. The final thickness of the resulting membranes was the average value of several measurements from various positions individually evaluated by a digital micrometer (Mitutoyo, IP54 Absolute Digimatic Micrometer, MDQ-30, range 0-30 mm, accuracy ± 0.001 mm).

2.4. Filler and membrane characterization

Diffuse Reflectance Infrared Fourier transform (DRIFT) spectra of BILP-101 and RT-BILP-101 powder were acquired in a Nicolet 8700 FT-IR (Thermo Scientific) spectrometer equipped with a high temperature cell with CaF_2 windows. The samples were pretreated in a He flow at 393 K for 5 min prior to collecting the spectra.

One-dimensional ^{13}C CP/MAS solid state NMR spectra were recorded on a Bruker AVANCE III spectrometer operating at 600 MHz resonance frequencies for ^1H . Experiments at 600 MHz employed a conventional double-resonance 3.2 mm CP/MAS probe or a 2.5 mm double-resonance probe. Dry nitrogen gas was used for sample spinning to prevent degradation. NMR chemical shifts are reported with respect to the external references TMS and adamantane. For ^{13}C CP/MAS NMR experiments, the following sequence was used: 90° pulse on the proton (pulse length 2.4 s), then a cross-polarization step with contact time of typically 2 ms, and finally acquisition of the ^{13}C NMR signal under high-power proton decoupling. The delay between the scans was set to 5 s to allow the complete relaxation of the ^1H nuclei, and the number of scans ranged between 10,000 and 20,000. An exponential apodization function corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation. The sample spinning frequency was 15 kHz and 20 KHz.

Powder X-Ray Diffraction (PXRD) patterns of BILP-101 and RT-BILP-101 were recorded using a Bruker-D8 Advanced diffractometer with Co-K_α radiation ($\lambda = 1.78897$ Å). The samples were

scanned in the 2θ range of $5 - 80^\circ$ using a step size of 0.02° and a scan speed of 0.4 s per step in a continuous scanning mode.

Scanning Electron Microscopy (SEM) micrographs were acquired using a JEOL JSM-6010LA InTouchScope microscope equipped with an integrated SDD EDS detector. BILP-101 and RT-BILP-101 particles were directly put on the sample holder and cross-section of the prepared membranes were obtained by cryo-fracturing in liquid nitrogen. All the samples were sputtered with gold for 60 s prior to acquiring SEM micrographs.

N_2 physisorption (77 K) and CO_2 adsorption isotherms (273 K) of BILP-101, RT-BILP-101 and the resulting MMMs were recorded in a Tristar II 3020 (Micromeritics). Argon adsorption isotherm was performed in 3Flex (Micromeritics) instrument. Prior to the gas adsorption measurements, the samples were degassed at 423 K under N_2 flow for 16 h to remove any solvent or moisture trapped in the polymer network. The particle size distribution (PSD) curves of the prepared BILPs fillers and corresponding MMMs was estimated by CO_2 -DFT (Density functional theory) model, using a non-negative regularization method with a factor of 0.03160 . The standard deviation of fit are 0.002057 , 0.001954 , 0.001904 , 0.002594 $mmol\ g^{-1}$ for RT-BILP-101, BILP-101, 16 wt.% BILP-101 MMMs and 16 wt.% RT-BILP-101 MMMs, respectively. For the PSD calculation based on Argon adsorption, a Argon on oxides at 87 K Non Local DFT (NLDFIT) model was employed with the assumption of cylindrical pores, using a non-negative regularization method with a factor of 0.03160 . The standard deviation of fit are 0.36770 and 0.52406 cm^3g^{-1} STP for BILP-101 and RT-BILP-101, respectively.

Thermogravimetric analyses (TGA) were performed in a Mettler Toledo TGA/SDTA851e apparatus by measuring the mass loss of the sample while heating BILPs and the prepared membranes under air ($100\ mL\cdot min^{-1}$) from room temperature to 1073 K at a heating rate of $5\ K\cdot min^{-1}$.

Differential Scanning Calorimetry (DSC) measurements were carried out using a Perkin Elmer DSC 7 equipment to assess the glass transition temperature (T_g) of the neat membrane and the MMMs. The scanning range was 298 K – 698 K at a heating rate of 10 K·min⁻¹ under nitrogen atmosphere. Two consecutive runs were performed. A first DSC cycle was performed to remove thermal history and adsorbed water from the samples. After cooling, a second cycle was performed following the same procedure. The glass transition temperature (T_g) value was calculated as the middle point of the slope transition in the DSC curve.

2.5. Gas permeation experiments

Membrane areas of 3.14 cm² were cut from the casted membrane films, placed on a macroporous support and mounted in a flange between Viton® o-rings. This flange fits in a permeation module, which was placed inside an oven in the permeation home-made setup described elsewhere.[36] The CO₂/N₂ separation measurements were performed employing a 15:85 CO₂:N₂ gas mixture (23 ml·min⁻¹ CO₂ and 130 ml·min⁻¹ of N₂) as feed. Helium (4.6 ml·min⁻¹) was used as sweep gas at the permeate side. The absolute pressure of the feed stream was adjusted in a range of 2 - 5 bar using a back-pressure controller at the retentate side, keeping the permeate side at atmospheric pressure. The temperature in the permeation module was kept at 308 K when collect the data at different feed pressures for fresh membranes. The aged membrane was first undergone the test at different feed pressures (up to 5 bar). After that, the feed pressure was changed back to 2 bar and the membrane was tested at 308, 323 and 353 K, respectively.

An on-line gas chromatograph (Interscience Compact GC) equipped with a packed Carboxen 1010 PLOT (30 m x 0.32 mm) column and TCD detector was used to periodically analyse the permeate stream. Each membrane was fabricated and measured 2-3 times to ensure

reproducibility of the reported data. In all cases, gas separation performance was evaluated after ensuring steady operation.

Gas separation performance was defined by the separation factor (α) and the gas permeability (P) of the individual components. The permeability for the i -component (P_i) was calculated as follows (Equation 1):

$$P_i = \frac{F_i \cdot l}{\Delta p_i \cdot A} \quad (1)$$

where F_i denotes the molar flow rate of compound i , l is the thickness of the membrane measured by a digital micrometer and A is the membrane area. Δp_i is the partial pressure difference of the component i across the membrane and it can be calculated according to Equation 2.

$$\Delta p_i = p_{feed} \times Y_{i,feed} - p_{perm} \times X_{i,perm} \quad (2)$$

where p_{feed} and p_{perm} represent the pressures at the feed and permeate sides and $Y_{i,feed}$ and $X_{i,perm}$ are the molar fractions of the component i in the feed and permeate gas streams, respectively.

The SI unit for the permeability is $\text{mol} \cdot \text{s}^{-1} \cdot \text{m}^{-1} \cdot \text{Pa}^{-1}$. However, gas permeabilities are commonly reported in the widely used non-SI unit Barrer, where $1 \text{ Barrer} = 3.35 \times 10^{-16} \text{ mol} \cdot \text{s}^{-1} \cdot \text{m}^{-1} \cdot \text{Pa}^{-1}$.

The separation factor or mixed gas selectivity (α) was calculated as the ratio of the permeability of the more permeable compound (CO_2) to the permeability of the less permeable compound (N_2) (equation 3).

$$\alpha = \frac{P_{\text{CO}_2}}{P_{\text{N}_2}} \quad (3)$$

3. Results and discussion

3.1. Characterization of BILP-101 and RT-BILP-101

BILP-101 particles were synthesized by a condensation reaction following the synthetic route recently developed for BILP [26, 35, 37]. This approach requires the slow addition of aldehyde at low temperatures (243 K) during the initial polymerization stages to control the overall porosity of the final product (*vide supra*). In this work, we synthesized two different POFs: BILP-101 and RT-BILP-101. BILP-101 was obtained following the procedure previously reported by Sekizkardes *et al.* [35], in which the 1,2,4,5-benzenetetramine tetrahydrochloride solution was cooled to 243 K prior to drop-wise adding the aldehyde-containing solution (see experimental section). Aiming at tuning the polymer porosity, RT-BILP-101 was prepared following the same procedure as described for BILP-101, but at room temperature (Scheme 1). This influences the early stages of the condensation reaction, affecting the initial polymerization rate and ultimately affects the porosity of the resulting product.

Both products were characterized by DRIFTS, solid-state ^{13}C cross-polarization magic-angle spinning (CP/MAS) NMR spectroscopy, XRD and N_2 and CO_2 adsorption. The DRIFT spectra acquired for BILP-101 and RT-BILP-101 (Fig. 1a) indicate the same chemical connectivity for these two polymers and confirmed the imidazole ring formation. Particularly, the bands at 1611 cm^{-1} ($-\text{C}=\text{N}-$) and 1499 and 1440 cm^{-1} (assigned to the skeleton vibration of the imidazole ring) [26, 38] point to the successful imidazole ring closure upon poly-condensation. These observations are further supported by the bands at 1362 cm^{-1} (C-N stretching) and 1641 cm^{-1} (N-H bending), which confirmed the formation of the benzimidazole ring. Also, the absence of a band at 1700 cm^{-1} , which could be ascribed to the residual C=O stretching of the aldehyde moieties, points to a complete consumption of the starting aldehyde functional groups. This was corroborated by ^{13}C CP-MAS NMR spectroscopy. For both materials, BILP-101 and RT-BILP-101, the ^{13}C CP-MAS NMR spectra show a peak at $\delta = 151\text{ ppm}$ (Fig. 1b), corresponding to the N=C-N imidazole carbon.

The thermal stability of BILP-101 and RT-BILP-101 was supported by TGA under air atmosphere. The results show that BILP-101 and RT-BILP-101 are stable up to 635 K (Fig. S1), while the initial weight losses, before 373 K, can be attributed to the removal of the adsorbed moisture. Scanning electron microscopy (SEM) micrographs (Fig. 3a) reveal the formation of homogenous spherical-shaped particles for both BILP-101 and RT-BILP-101. In the case of RT-BILP-101, however, a decrease in the particle size can be observed compared to BILP-101 (from 235 ± 3 nm to 310 ± 4 nm, for the former and the latter case, respectively, Fig. 2c and d). We relate this to the higher initial reaction rate at room temperature than at 243 K, favouring nucleation and resulting in the observed decrease of particle size. As expected, both BILPs are amorphous as determined by powder X-ray diffraction (Fig. S2).

Fig. 1. (a) DRIFT spectra of BILP-101 and RT-BILP-101 acquired at 393 K under He atmosphere and (b) assignments of the ¹³C CP-MAS NMR spectra obtained for BILP-101 and RT-BILP-101.

BILPs' porosity was investigated via N₂ adsorption acquired at 77 K (Fig. 2e). The isotherms exhibit a steep uptake at low relative pressures ($p/p_0 < 0.1$), indicating the microporous nature of the two prepared polymers. The calculated Brunauer-Emmett-Teller (BET) areas of BILP-101 and RT-BILP-101 are 460 and 180 m²·g⁻¹, respectively. As expected, BILP-101 possesses a higher BET surface area, which can indeed be ascribed to its slower initial formation rate (*vide*

supra), preventing the premature precipitation of oligomers during the initial polymerization stages and allowing for a better pore formation resulting in an overall enhanced porosity [39, 40]. Furthermore, Fig. 2f shows the low-pressure CO₂ adsorption isotherms acquired for RT-BILP-101 and BILP-101 acquired at 273 K. At 1 bar, the CO₂ uptake observed for BILP-101 reach up to 3.2 mmol·g⁻¹, which is comparable to other POFs [26, 41-45]. RT-BILP-101 on the other hand exhibits relatively lower CO₂ adsorption capacity (2.2 mmol·g⁻¹ at 1 bar and 273 K), in line with N₂ adsorption results. The Inset in Fig. 2f presents the pore size distribution (PSD) curves calculated from the adsorption branch of CO₂ isotherm. Both BILPs show a bimodal pore structure with pores centered around 5.2 Å and a broader range of pores between *ca.* 7 and 9 Å. BILP-101 presents more open pore volume than RT-BILP-101 which is more easier for polymer chain penetration as discussed below.

All in all, two different BILPs were successfully synthesized with the same chemical connectivity, but with different textural properties. This was achieved by tuning the temperature in the early polymerization stages, influencing the initial reaction rate and allowing for a certain degree of control over the overall BILP porosity. In order to further evaluate the potential of these two BILPs for post-combustion CO₂ capture, the adsorption selectivities of CO₂/N₂ were calculated using initial slop method. As shown in Fig. S8, BILP-101 and RT-BILP-101 revealed a CO₂/N₂ selectivity of 89 and 60 at 273 K, respectively. These results are in line with previous reported values [35] and demonstrate that BILP-101 and RT-BILP-101 are promising fillers for the preparation of MMMs for CO₂/N₂ separation.

Fig. 2. TEM micrographs (a and b), particle size distribution (c and d) of BILP-101 and RT-BILP-101, respectively. N_2 (e) and CO_2 (f) Adsorption / desorption isotherms of BILP particles. Closed symbols represent the adsorption and open symbols represent the desorption branches. Black and red correspond to BILP-101 and RT-BILP-101, respectively. Inset in (f) shows the pore size distribution (PSD) of BILP-101 and RT-BILP-101 calculated from the CO_2 adsorption isotherms.

3.2. Characterization of BILPs MMMs

In order to study the influence of the filler porosity on the performance of MMMs in gas separation, MMMs were prepared with both BILP-101 and RT-BILP-101 particles. SEM micrographs of the surface (Fig. S5) and cross-section (Figs. 3 and 4) of the prepared membranes were acquired. The images show that both BILP-101 and RT-BILP-101 are

randomly dispersed in the polymer matrix at low weight loading (8 wt.%) and began to undergo slightly aggregation at higher loadings. No evident interfacial voids or pinholes could be observed even at 24 wt.% BILP loading. In addition, both fillers retain their spherical morphology upon membrane preparation. In comparison with BILP-101 MMMs, RT-BILP-101 MMMs exhibit better filler dispersion and a more integrated morphology where RT-BILP-101 particles wrapped by the polymer chains are observed. Fig. S6 presents the thermogravimetric analyses (TGA) acquired for the bare Matrimid® membranes together with those obtained for the BILP-101 and RT-BILP-101-based MMMs. The TGA results of BILP-101 and RT-BILP-101 were also included for comparison. As mentioned above, BILP-101 and RT-BILP-101 were stable up to 635 K, temperature at which it starts decomposing. This decomposition temperature is higher for the pure Matrimid® and the resulting MMMs for which decomposition starts at around 750 K. Further, the lack of weight loss at lower temperatures, for both MMMs and pure membranes, ensures the complete removal of solvents after membrane drying procedure.

Fig. 3. SEM micrographs of (a) BILP-101 and the cross-section of (b) 8 wt.% BILP-101@Matrimid®, (c) 16 wt.% BILP-101@Matrimid® and (d) 24 wt.% BILP-101@Matrimid®.

Fig. 4. SEM micrographs of (a) RT-BILP-101 and the cross-section of (b) 8 wt.% RT-BILP-101@Matrimid®, (c) 16 wt.% RT-BILP-101@Matrimid® and (d) 24 wt.% RT-BILP-101@Matrimid®.

DSC and CO₂ adsorption measurements were performed on the MMMs to gain further insight into the filler-polymer interface. DSC results show that the T_g of all the MMMs are similar to that of bare Matrimid® (~ 594 K), suggesting that there is no significant rigidification of the polymeric chains around the BILP particles, like previously reported results on POF-MMMs. [20, 46] To check whether the BILP pores are still available in the MMMs. CO₂ adsorption isotherms were acquired at 273 K for both bare Matrimid® and the prepared MMMs. The incorporation of BILP-101 and RT-BILP-101 into the polymeric matrix results in an enhanced CO₂ uptake, achieving higher CO₂ uptakes compared to pure Matrimid® in all cases (Fig. S7). As expected, the higher the filler loading, the higher the maximum amount of CO₂ that can be adsorbed, indicating that the filler pores are still accessible to CO₂ once the BILP particles have been embedded in the polymeric matrix. In addition, the RT-BILP-101 MMMs can reach almost the same CO₂ uptake compared to BILP-101 MMMs at the same loading. In order to gain further the influence of the filler on the adsorption capacity of the resulting MMMs, the

estimated CO₂ uptake for the 16 wt.% MMMs calculated as a linear combination of those uptakes for the pure components according to their weight loading ($q_i = q_{i\text{ polymer}} \times 0.84 + q_{i\text{ filler}} \times 0.16$) is shown in Fig. 5, together with the experimentally measured isotherms for that filler loading. Experimentally obtained CO₂ uptakes are somewhat lower than those calculated for both BILP-101 and RT-BILP-101 MMMs, pointing to a partial pore blockage of BILP-101 and RT-BILP-101 by the polymer chains [23, 46]. The difference between the estimated CO₂ uptake and the experimental one is larger for BILP-101 MMMs (33.1% porosity loss for BILP-101) than for RT-BILP-101 MMMs (25.8 % loss), suggesting that the bigger porosity of BILP-101 is more easily blocked by the polymer. This is further supported by the pore size distribution curves of the MMMs calculated from the adsorption branch of CO₂ isotherms (Fig. S9). Both, BILP-101 and RT-BILP-101-based MMMs showed a drastic reduction in the pore volume once the filler is embedded in Matrimid®, given the dense nature of the latter. However, Fig S9 shows a more pronounced reduction of the pore volume for BILP-101 than for RT-BILP-101 once incorporated in the polymeric matrix. We hypothesized that this, together with a reduction in the size of the bigger pores and in the expected CO₂ uptake (*vide supra*), points to the partial blockage of the filler pores, which may take place together with a partial collapse of the BILP-101 porous polymer. As already observed for the CO₂ isotherms, this effect is more prominent for BILP-101.

Fig. 5. CO₂ adsorption isotherms acquired for BILP-101, RT-BILP-101 and the prepared membranes at 273 K. The calculated value was obtained by a linear combination of those uptakes for the pure components.

3.3. Gas separation performance

The flat sheet bare Matrimid® membranes and MMMs containing different loadings (0, 8, 16 and 24 wt.%) of BILP-101 and RT-BILP-101 particles were shaped in the form of flat sheets membranes and tested in the separation of CO₂ from a 15:85 CO₂/N₂ gas mixture at 308 K. Besides the effect of the filler porosity on the membrane performance, the influence of the feed pressure was also investigated, and thus varied between 2 and 5 bar. At least 2-3 membranes were tested for each BILP loading in order to provide reliable error estimations. All the prepared membranes can withstand the permeation test conditions, indicating a good mechanical stability of the membranes under relevant conditions. Further, the membranes remain flexible upon 24 % BILP-101 and RT-BILP-101 loading (Fig. S10). Upon addition of BILP particles, the membranes showed an increase in the CO₂ permeability preserving the original CO₂/N₂ mixed gas selectivities (Fig. 6). In this situation the enhanced CO₂ permeability can be attributed to the incorporation of porous fillers into the polymeric matrix, providing additional transport pathways for the permeating gases [46]. Further, the CO₂ adsorption isotherm curves of all the prepared membranes were fit from the adsorption data to the dual-mode model (See Fig. S11 and Table S1)). The results indicate that the incorporation of both BILP fillers lead to the increase of k_D , C'_H , and b simultaneously. The increase in C'_H is more significant (~30% increase were achieved for 24 wt.% loading MMMs compared to pure Matrimid®), indicating the more free volume introduced by the BILP fillers.

It is noteworthy that MMMs fabricated with BILP-101, which possesses a higher BET surface area, showed a lower CO₂ permeability than the RT-BILP-101 MMMs at the same loading. This

may originate from the pore blocking by the polymer chains as indicated by CO₂ adsorption (Fig. 5), being more significant for BILP-101 than RT-BILP-101 due to the big porosity and more open pore volume.

The gas permeability increases with increasing BILP loading, for both BILP-101 and RT-BILP-101, attributed to the additional transport pathways introduced by the incorporation of the filler. Particularly, for the 24 wt.% RT-BILP-101 MMMs, the CO₂ permeability increased by a factor of 2.8 (from 9.6 to 27 Barrer) as compared to bare Matrimid® with constant CO₂/N₂ selectivity. Fig. 7 shows the influence of feed pressure on the gas permeation performance of the membrane. Both the CO₂ and N₂ permeability of the BILP MMMs are higher than the pure Matrimid® through the whole pressure range except for 8 wt.% loading, which is close to Matrimid®. The CO₂ permeability decreases with increasing feed pressure. This is a well-known for components adsorbing in the nonlinear pressure range. Saturation of Langmuir adsorption sites in zeolites [47, 48] and glassy polymers [23, 46, 49] at higher pressures results in a decrease in the membrane permeability. For the case of 24 wt.% loading BILP-101 MMMs (see Table S2 for the detailed value, only one low pressure data was put in Fig. 7a for clarity), the presences of small defects play a role at high pressures, leading to the fast diffusion of N₂ and thereby decrease the CO₂/N₂ selectivity significantly.

Fig. 6. Performance of MMMs with different BILP-101 and RT-BILP-101 loadings in the separation of CO_2 from a 15:85 CO_2/N_2 mixture at 308 K and a feed pressure of 2 bar. Grey, green and purple colour correspond to the pure Matrimid®, BILP-101 and RT-BILP-101 MMMs, respectively. Error bars correspond to the standard deviation of different membranes.

Fig. 7. Effect of the feed pressure on the gas permeation performance of the prepared (a) BILP-101 and (b) RT-BILP-101 membranes. Results obtained in the separation of CO_2 from a 15:85 CO_2/N_2 mixture at 308 K. $\square$ Pure Matrimid®, $\circ$ 8 wt.% MMMs, $\star$ 16 wt.% MMMs, and ∇ 24 wt.% MMMs.

To gain further insight into the long-term membrane performance, 16 wt.% loading MMMs (BILP-101 and RT-BILP-101) were re-tested after 4 months (Table S4). Results show that the

separation performance was maintained. As expected, a slight decrease in the membrane permeability was observed, from 17.0 to 15.1 Barrer and from 13.0 to 11.3 Barrer for RT-BILP-101 and BILP-101-based MMMs, respectively, which took place at relatively constant selectivity. The decrease in permeability are believed to be the lower free volume after physical aging, which is common for glassy polymers. Considering the practical post-combustion CO₂ capture process, the flue gas need to be reheated to prevent corrosion problems caused by water vapour condensation in the stack. [50] Thus, the effect of temperature (308 – 358 K) on gas separation performance was further investigated to better understand the actual performance of BILP MMMs in real industrial applications. As shown in Table S4, the gas permeability increases with increasing temperature while this is accompanied by the decrease in CO₂/N₂ selectivity for both BILP MMMs. To better understand this, the Arrhenius equation was applied to calculate the activation energy (E_p) for permeation (Fig. 8).

$$P_i = P_{i,0} \exp\left(\frac{-E_{p,i}}{RT}\right) \quad (4)$$

Where $E_{p,i}$ is the activation energy of gas component i . P_i (Barrer) represents the gas permeability of component i , $P_{i,0}$ is the pre-exponential factor of gas component i , T is the absolute temperature (K) and R is the ideal gas constant, 8.314 J mol⁻¹ K⁻¹.

As shown in Table 1, the activation energy for N₂ is higher than CO₂ for both BILP MMMs. The E_p of gases are determined by two principle factors: the penetrants molecular size (influence the diffusivity) and the interaction with the polymer matrix (solubility). Diffusion activation energy usually increases with molecular size. Thus, increasing the temperature can enhance the diffusivity of gas molecule with large kinetic diameter more than that for small molecules. [51, 52] In addition, CO₂ has a large negative heat of adsorption which lead to a significant decreases in solubility when increasing the temperature. Thus, the increase in temperature

has a larger impact on N₂ than CO₂, leading to a decrease in selectivity. As diffusivity is stronger influenced than solubility [51] and thus permeability increased for both gases.

Fig. 8. Effect of operating temperature on CO₂ and N₂ permeability of aged (a) 16 wt% BILP-101 and (b) RT-BILP-101 @ Matrimid® at 2 feed bar pressure. (The lines are representative of Arrhenius plot)

Table 1 Activation energies for the permeation of CO₂ and N₂ in aged 16 wt.% BILP MMMs at 2 bar feed pressure.

Membrane	E _p (kJ mol ⁻¹)	
	CO ₂	N ₂
Aged 16 wt.% BILP-101 MMMs @ Matrimid®,	7.06	22.61
Aged 16 wt.% RT-BILP-101 @ Matrimid®,	7.65	21.87

Finally, the separation performance of BILP-101 and RT-BILP-101 MMMs were compared with the Robeson upper bound together with other POF-containing MMMs, as shown in Fig. 9 with the representative data in Table S6. As can be observed from the Figure, the performances of our membranes are located in the same region as other POF fillers (like ACOF-1, BILP-4) in Matrimid®. Although the significant increase in CO₂ permeability was achieved by incorporating RT-BILP-101 fillers in Matrimid®, the overall performance are still stay below the upper bound limit due to the very low separation performance of pure Matrimid®, which is similar as other POF – containing MMMs. In most cases, the incorporation of POF fillers in polymer matrix could increase the gas permeability while scarify or maintain the selectivity.

Fig. 9. Robeson plot for CO₂/N₂ separation, showing the gas separation performance of two BILPs based MMMs (with 16 and 24 wt% filler loading in Matrimid®). Most relevant results reported in the literature for POF-based MMMs have also been included for comparison. The black line corresponds to the 2008 Robeson bound line and the arrows indicate the trend of separation performance from pure polymer to POF based MMMs.

4. Conclusions

Porous BILPs with different porosities (BILP-101 and RT-BILP-101) were prepared and dispersed in Matrimid® to prepare MMMs. Their structures and performance were compared in this study. Through controlling the initial polymerization rate, RT-BILP-101 with lower porosity was synthesized than BILP-101. DRIFTS and ¹³C CP-CMS NMR measurements confirms the same chemical connectivity of two BILPs. In the MMMs, a good dispersion and adhesion between the fillers and the polymer matrix was obtained. No rigidification was observed for the polymer chains after incorporating both BILPs. The incorporation of both BILPs into Matrimid® enhanced the gas permeability for both CO₂ and N₂, while keeping the mixed gas selectivity constant. The permeability increases with increasing the filler loading attributed to

the fast diffusion pathways introduced by the porous BILP network, while the polymer still controls the selectivity. Besides, MMMs fabricated with RT-BILP-101 exhibits higher gas permeability than BILP-101 MMMs at the same loading, due to the lower partial pore blockage of the porosity by the polymer in the MMMs.

Overall, our results demonstrate that the porosity of the filler has an impact on the MMM's permeation performance and should be helpful for the design of POF-based MMMs considering that the relatively large POF pores for gas separation.

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