Polymer engineering by blending PIM-1 and 6FDA-DAM for ZIF-8 containing mixed matrix membranes applied to CO₂ separations

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ABSTRACT. The preparation of mixed matrix membranes (MMMs) for post-combustion CO₂ capture and biogas upgrading from PIM-1 (10-90 wt%)/6FDA-DAM heterogeneous blends with ZIF-8 as filler (3-20 wt% with regard to the polymer blend) is described. The heterogeneity of the blend, considered here as an advantage for the dispersion of the filler within the MMMs, has been confirmed by the existence of a single glass transition temperature, consistent with that of 6FDA-DAM. The segregation between the two polymeric phases and the filler dispersion has been studied by Raman spectroscopy, SEM

microscopy and EDX analysis. Increasing the amount of PIM-1 in the blend makes the *d-spacing* of the polymer chains higher and increases gas permeability. When embedding filler nanoparticles of ZIF-8, a better compatibility with 6FDA-DAM than with PIM-1 is observed. The filler locates near the interphase between polymers helping its dispersion. The use of small loadings of ZIF-8 enhances the gas separation performance of the MMMs in terms of permeability and selectivity for 50/50 CO₂/CH₄ and 10/90 CO₂/N₂ mixtures. The best performing membranes are the blends PIM-1/6FDA-DAM 10/90 (w/w) with 10 wt% of ZIF-8, showing a CO₂ permeability of 2891 Barrer, a CO₂/CH₄ selectivity of 26.6 and 2802 Barrer of CO₂ with a CO₂/N₂ selectivity of 18.1. Importantly, the CO₂, N₂ and CH₄ permeabilities of the pure polymeric blends can be predicted using both the logarithmic and the Maxwell models. A new coupled Maxwell model has also been developed. This model is able to calculate the flow through the blends containing ZIF-8 and to predict the gas separation properties of the filler itself.

1. Introduction

One of the most common contaminants in the world is CO₂. It can be found in fossil fuels such as natural gas or biogas with concentrations of up to 50 %, which remarkably reduces the calorific value of the fuel and helps to corrode gas transport infrastructure[1]. In addition, the increase in the anthropogenic emissions of CO₂, precisely from the burning of such fossil fuels for power generation, is causing a serious environmental problem due to its contribution to the greenhouse effect[2]. Hence, it is necessary to remove CO₂ from fuels and exhaust gases to obtain a clean fuel and to reduce its environmental impact, respectively. For instance, in the case of natural gas and biogas, the CO₂ level should be reduced to less than 2% to meet the pipeline specifications and to minimize corrosion[3]. The current technologies used for the removal of CO₂ from gas mixtures are absorption, adsorption and membrane technology, among others[4-6]. Membrane technology enjoys inherent advantages such as easy of operation, simplicity, high efficiency, low energy consumption and investment, adaptability and environmental friendliness[7].

Only a few polymers such as polysulfone, cellulose acetate and certain polyimides are used in commercial membranes[8] and there is still interest in developing new polymers with higher permeability and selectivity able to surpass the gas separation trade-off defined by Robeson[9]. The inhibited polymer chain packing and rigid backbone of 6FDA-DAM make it one of the most permeable polyimides for gas separation[10]. Another group of highly permeable polymers are the so-called polymers of intrinsic microporosity (PIMs), a class of rigid ladder-type polybenzodioxins with highly contorted chains. Budd et. al.[11] were the first to report these polymers, of which PIM-1 is possibly the most popular in the literature thanks to its relative ease of preparation with high molecular weight[12]. Both polymers have shown an interesting performance

for the separation of CO₂ from CH₄ (natural gas/biogas upgrade) and from N₂ (post-combustion CO₂ capture). It has been reported that 6FDA-DAM can reach CO₂ permeabilities from 380 to 817 Barrer with CO₂/CH₄ selectivities between 15.9 and 31.0 and CO₂/N₂ selectivities around 15.0[13-15]. PIM-1 has usually shown 2300-5300 Barrer of CO₂ with CO₂/CH₄ and CO₂/N₂ selectivities of around 15 and 20, respectively[11,16-18]. Owing to the potential of these two polymers for the CO₂ separation, it was anticipated that mixtures of 6FDA-DAM and PIM-1 could lead to the formation of blends with superior separation properties. PIM-1 has been previously blended with polyimides (such as Matrimid®[19] or P84®[20]) and polysulfone[21]. In all cases PIM-1 formed heterogeneous blends, where it was considered an organic phase dispersed in the matrix formed by the other polymer. The combination of 6FDA-DAM with polybenzimidazole (PBI) has also been reported, which also led to the formation of an immiscible polymer blend which demonstrated an improved performance for H₂/CO₂ separation[22,23].

The present work shows the preparation of membranes for CO₂ separation based on the heterogeneous blend of 6FDA-DAM with PIM-1. In order to improve the gas separation performance of the composites, nanoparticles of the zeolitic imidazolate framework ZIF-8 have been used as porous filler within this polymer mixture. Besides, the filler has located near the interphase between PIM-1 and 6FDA-DAM, helping its dispersion across the membrane section. ZIF-8 is a metal-organic framework (MOF) with a sodalite type zeolitic topology (**sod**), consisting of Zn cations coordinated with the organic linker 2-methylimidazolate, which forms large cavities of 1.16 nm connected through smaller windows of 0.34 nm[24]. Hence, the concept of mixed matrix membrane (MMMs) has been applied, where particles (i.e. fillers, which are often crystalline and porous) are embedded within a suitable polymer matrix to obtain a composite that combines the advantageous properties of both phases. ZIF-8 has actually shown advantageous

properties as filler in several polymers for the separation of CO₂/N₂ and CO₂/CH₄ mixtures[25-29].

2. Experimental

2.1 Membrane preparation

PIM-1/6FDA-DAM blends were prepared in the form of flat dense membranes following a two steps dissolution process. Amounts between 0.04-0.40 g of each polymer were used, being 8 wt% the total polymer concentration in the casting solution. Firstly, PIM-1 was dissolved at room temperature in 4.93 g of chloroform (CHCl₃, anhydrous, Sigma-Aldrich) under stirring. After 3h, a homogenous solution was obtained and 6FDA-DAM (purchased from Akron Polymer Systems, Inc., MW= 418 kDa) was added. The resulting solution was further stirred overnight. The composition of the blend was 0, 10, 20, 35, 55, 90 and 100 wt% of PIM, where the proportions of 0 and 100 wt% correspond to pure 6FDA-DAM and pure PIM-1 membranes, respectively. The following day, the polymer solution was left unstirred for 30 min to release air bubbles and then cast onto a glass Petri dish, allowing it to dry at room temperature for 24 h. The obtained film was immersed in MeOH, (HPLC grade, Scharlau) for another 24 h to remove traces of solvent and dried afterwards at 100 °C for 24 h more. The resulting films had a thickness of around 80 µm. In the case of blended MMMs, ZIF-8 was dispersed in the same volume of CHCl₃ previous to the addition of both polymers in the necessary quantities for obtaining nominal loadings of 1, 3, 10 and 20 wt%. ZIF-8 nanoparticles were synthesized following a route that can be found elsewhere and that uses a MeOH-water mixture as solvent[30].

2.2 Membrane characterization and gas separation analysis

Membrane characterization includes thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) scanning electron microscopy (SEM), Fourier transform

infrared (FTIR) and Raman spectroscopy and X-ray diffraction (XRD). The experimental details as well as those corresponding to the gas separation test can be found in the supporting information.

3. Results and discussion

3.1 Membrane characterization

Figure 1. SEM images of the cross section of PIM-1/6FDA-DAM blends containing (a) 10, (b) 20 and (c) 90 wt% of PIM-1 and (d) EDX analysis of the former.

Several PIM-1/6FDA-DAM blends have been prepared in this work containing PIM amounts of 10, 20 and 90 wt%. Figure 1 shows the SEM images of the cross-section of all these membranes. It can be deduced that 6FDA-DAM and PIM-1 are not full miscible due to the presence of two different morphologies. The two polymers form a heterogeneous blend where the minor component builds the dispersed phase as spheres or lenticular shapes in a matrix consisting of the other polymer. In the case of PIM

loadings of 10 and 20 wt% (Figure 1a and 1b, respectively), PIM-1 was the dispersed phase. This was verified by EDX analysis (see Figure 1d) since the signal of fluor, F (only contained in the 6FDA-DAM chains) appears in spectra 2 and 4, i.e. those corresponding to the polymeric matrix, while it cannot be detected in the dispersed phase of PIM-1 spheres (spectra 1 and 3). Confocal Raman microscopy analysis in Figure S1 also supported this phase segregation, obtaining different spectra for the dispersed phase and the matrix, where PIM-1 showed fluorescence while 6FDA-DAM did not. For the blend containing 90 wt% of PIM-1, the 6FDA-DAM formed the disperse phase with lentil shape particles. The existence of a heterogeneous blend between PIM-1 and 6FDA-DAM has also been verified by DSC analysis (see Table S1), since the same glass transition temperature (T_g) of around 320 °C was found for all the composites and this T_g corresponds to that of 6FDA-DAM[31]. Although typically two different T_g values are obtained in two-component heterogeneous blends, the T_g of PIM-1 cannot be measured because this value is higher than its decomposition temperature, and therefore only one value was obtained (that of 6FDA-DAM).

Figure 2. SEM images of MMMs with the 10/90 wt% PIM-1/6FDA-DAM blend containing (a) 1 wt%, (b) 10 wt% and (c) 20 wt% of ZIF-8; the MMMs with the 20/80 wt% PIM-1/6FDA-DAM blend containing (d) 3 wt% and (e) 10 wt% of ZIF-8; and 90/10 wt% PIM-1/6FDA-DAM blend with (f) 10 wt% of ZIF-8 and (g) its EDX mapping. (h) A scheme of the MMMs explaining the filler distribution is also included.

Mixed matrix membranes (MMMs) have been prepared with the PIM-1/6FDA-DAM blends containing different loadings of ZIF-8. The cross-sections of all these membranes were observed by SEM and the corresponding images are shown in Figure 2. The blends containing 10 wt% of PIM-1 were loaded with 1, 10 and 20 wt% of ZIF-8. The blends consisting of 20 wt% of PIM-1 contained ZIF-8 amounts of 3 and 10 wt%. And the blends with the highest amount of PIM-1 (i.e. 90 wt%) were prepared with a ZIF-8 loading of 10 wt%. Table S2 summarizes the different membranes prepared, where the actual loadings obtained from TGA analysis are also shown. It can be determined from the SEM

images that the filler is not distributed within the two polymeric phases, but it seems to possess more affinity for 6FDA-DAM. This fact was verified by the EDX analysis in Figure 2g, where it can be seen that the signals of F and Zn, corresponding to 6FDA-DAM and ZIF-8, respectively, are overlapped. Despite being firstly dispersed in PIM-1 for the preparation of the casting solution, ZIF-8 was mainly accumulated in the 6FDA-DAM phase during the film formation. In fact, the filler nanoparticles are allocated near the interphase between polymers, which helped to enhance the filler dispersion across the membrane (see explanatory scheme of Figure 2h). Further characterization of the ZIF-8 nanoparticles comprising SEM images, N₂ adsorption (77 K) and CO₂ adsorption (273 K) is provided in Figure S2.

The thermal stability of the blends was studied performing TGA analysis in air oxidizing atmosphere. The thermograms in Figure S3 show that the pristine PIM-1 possesses two decomposition steps with maximum degradation temperatures of 501 and 617 °C, while the pure 6FDA-DAM membranes only have one at around 571 °C. PIM-1/6FDA-DAM blends show the same behavior as 6FDA-DAM for PIM loadings of 10 and 20 wt% and as PIM-1 when containing a PIM amount of 90 wt%. The absence of a combined pattern between the pure polymers with different decomposition steps is again indicative of the heterogeneity of the blend. Besides, the lack of weight loss below 400 °C proves the good activation of the films with no traces of solvent remaining. FTIR analysis was also performed with the different PIM-1/6FDA-DAM blends. Figure S4 shows that pristine PIM-1 exhibited its typical resonances at 1009 and 1445 cm⁻¹, corresponding to the imide C-N-C and C-N stretching, respectively[19]. Pure 6FDA-DAM membranes, however, showed characteristic peaks at 723 (imide ring deformation), 1101 and 1190 (C-C aromatic), 1356 (C-N stretching) and 1722 cm⁻¹ (C=O

stretching)[32]. As expected, the blends had the vibration modes of both polymers with different intensities depending on the amount of each other in the composite.

Figure 3. XRD patterns of the PIM-1/6FDA-DAM blends. (a) pure polymeric membranes and MMMs with (b) ZIF-8 as filler.

Figure 3a shows the XRD analyses performed on the PIM-1/6FDA-DAM blends without filler. All the XRD patterns form amorphous bands due to the lack of crystallinity in both polymers 6FDA-DAM and PIM-1. All the membranes show a band with a broad maximum in the range from $2\theta = 10$ to 15° , from which the d -spacing of the polymer could be calculated using the Bragg's law. This value was higher for pristine PIM-1 membranes ($7.2 \text{ \AA}$) than for those of 6FDA-DAM ($6.5 \text{ \AA}$) and showed an evolution in

correlation with the amount of PIM in the blend. XRD analyses have also been performed with blends containing ZIF-8 (see Figure 3b and S4), where it can be appreciated how the crystallinity of the filler remains unaltered after the membrane formation. In addition, the intensities corresponding to ZIF-8 became clearer as a function of the increasing loading in agreement with an even distribution of the filler in the MMMs.

3.2 Gas separation performance

The membranes were tested for gas separation with mixtures of CO₂/CH₄ (50/50 v/v) and CO₂/N₂ (10/90 v/v), corresponding to the industrial applications of biogas upgrading and post-combustion CO₂ capture, respectively. The gas separation performance of all the membranes is represented in the permeability-selectivity graphs of Figure 4 and the numerical values are collected in Table S3 (see section 2 in the Supporting Information for the calculation details). It can be seen that pristine 6FDA-DAM and PIM-1 are both highly permeable polymers, with CO₂ permeabilities of 1503 and 8994 Barrer, respectively. In addition both CO₂/CH₄ and CO₂/N₂ selectivities in PIM-1 were lower than those in 6FDA-DAM (e.g., 26.0 and 20.1, respectively). The PIM-1 results are consistent with those found in the literature, while the permeability values for 6FDA-DAM are higher[14,16,33,34]. Increasing the amount of PIM-1 in the blend caused enhancement of the CO₂ flow and the resulting permeability is proportional to the polymer composition of the membranes. Both the CO₂/CH₄ and the CO₂/N₂ selectivities followed the opposite trend with values decreasing with a greater amount of PIM-1 in the blend. These results are consistent with the *d-spacing* values obtained from XRD (Figure 3), since the more amount of PIM the blend incorporates, the higher the *d-spacing* value is, and therefore, the gases find it easier to flow through the membrane.

Figure 4. Gas separation performance of the PIM-1/6FDA-DAM blends for (a) CO_2/CH_4 and (b) CO_2/N_2 mixtures at 35 °C and 3 bar of feed pressure. The Robeson upper bounds of 1991 and 2008 are also represented[9,35].

Incorporating ZIF-8 nanoparticles in the matrix of the polymer blends had a positive effect on the gas separation performance of the membranes in comparison with the blends without filler. ZIF-8 was chosen as filler due to its good performance in previous studies[36-38]. The improvement was especially noticeable at low loadings. For example, the blend containing 10 wt% and 90 wt% of PIM-1 and 6FDA-DAM (blend code 10% PIM-10% ZIF in Table S2) demonstrated increased CO_2 permeability from 2135 to 2891 Barrer, while the CO_2/CH_4 selectivity was maintained around 26.0 and the CO_2/N_2 selectivity decreased from 20.1 to 18.1. For the blend with 20 wt% of PIM-1 and 3 wt%

of ZIF-8 (blend 20% PIM-3% ZIF) the CO₂ permeability increased from 2356 to 2586 Barrer and the CO₂/CH₄ selectivity increased from 20.1 to 24.7, while the CO₂/N₂ selectivity remained almost stable at ca. 20. This behavior is typical in MMMs where high filler loadings result in the formation of non-selective voids due to a poor interaction between the filler and the polymeric matrix[39]. On the whole, in Figure 4a-b, although the CO₂/CH₄ selectivity was increased for the increased amount of ZIF-8, the CO₂/N₂ selectivity was decreased. This behavior may be due to the relationship between the pore dimension of ZIF-8 (0.34 nm) and the kinetic diameter of the N₂ and CH₄ molecules (0.36 and 0.38 nm, respectively). While the larger size of CH₄ makes ZIF-8 easier to sieve it, the kinetic diameter of N₂ is similar to the pore dimension of the nanoparticles, making it more difficult to provide an enhanced gas separation. Noteworthy are the blends with 10 and 20 wt% of PIM-1 and 10 wt% of ZIF-8 (empty red circle and triangle, respectively), which showed a better separation performance than the MMMs of 6FDA-DAM with the same amount of ZIF-8 (empty red square). Finally, all the blends prepared in this work surpassed the 2008 Robeson upper bound for the CO₂/CH₄ separation and remained close to that of CO₂/N₂. A comparison with bibliographical values of PIM-1 and 6FDA-DAM MMMs that contain ZIFs is also shown in Table S4. Our best CO₂/N₂ and CO₂/CH₄ selectivity values of 19.0 and 26.6 for PIM-1/6FDA-DAM (20/80 wt%/wt%) and PIM-1/6FDA-DAM (10/90 wt%/wt%), respectively, with 10 wt% ZIF-8 as filler are among the best in the table.

It is also important to consider that the delivery pressure of natural gas is usually very high and the membranes must remain stable under such extreme conditions. 6FDA-DAM has shown no CO₂-induced plasticization effect up to 40 bar, being a perfect candidate for the CO₂/CH₄ separation.[40] However, the plasticization effect is more pronounced for PIM-1, being able to start at 2 bar CO₂ partial pressure.[41] For this reason, a low

amount of PIM in the blend is necessary to obtain membranes with the desirable performance.

3.3 Membrane modeling

The gas transport through the bare polymeric blends is easy to predict since the permeabilities of both individual phases (6FDA-DAM and PIM-1) can be tested empirically. The permeability of the blends has been found to fit the logarithmic model of Hopfenberg and Paul[42]. This empirical model explains that the logarithm of the permeability of a blend consists of the linear combination of the logarithm of the permeability of each polymer. The formula for the blends in this study is shown in Equation 1:

$$\ln P_{blend} = \Phi \ln P_{PIM-1} + (1 - \Phi) \ln P_{6FDA-DAM} \quad (1)$$

where Φ is the volume fraction of PIM-1 in the composite ($\Phi = V_{PIM-1} / (V_{PIM-1} + V_{6FDA-DAM})$), and P_{blend} , P_{PIM-1} and $P_{6FDA-DAM}$ are the respective permeabilities of the blend, PIM-1 and 6FDA-DAM. The volume fraction of PIM-1 was calculated with the polymer density values of 6FDA-DAM and PIM-1 (1.33 and 0.93 g cm⁻³, respectively) obtained from the literature[43,44].

Figure 5. (a) Logarithmic and (b) Maxwell models for the permeability of CO₂, N₂ and CH₄ through the different PIM-1/6FDA-DAM blends. Scatters represent the empirical values and dashed lines those predicted by the models.

Figure 5a represents the logarithm of the mixed-gas permeabilities of CO₂, N₂ and CH₄ against the volume fraction of PIM-1 in the blends, showing that they follow a linear tendency. For CO₂ there are results available for the CO₂/CH₄ and the CO₂/N₂ separation, but only the gas permeability values from the former were chosen. The validity of the linear regression is shown in Table S5, with R^2 values higher than 0.99 and where the calculated permeabilities for the pure polymers can also be seen. They agree with the empirical values previously explained (see Figure 4 and Table S3), validating the model.

The Maxwell model[45] can also describe the gas transport through systems consisting in random distributed and non-interacting homogeneous solid spheres in a continuous matrix. It can be therefore used to model the gas flow through heterogeneous blends. In this case, the PIM-1 spheres were considered the disperse phase of the composite, providing the gas permeability described as seen in Equation 2.

$$P_{blend} = P_{6FDA} \left[\frac{P_{PIM} + 2P_{6FDA} - 2\Phi_{PIM}(P_{6FDA} - P_{PIM})}{P_{PIM} + 2P_{6FDA} + \Phi_{PIM}(P_{6FDA} - P_{PIM})} \right] \quad (2)$$

Figure 5b shows the Maxwell prediction together with the empirical values. A good agreement between the empirical and calculated permeabilities of all gases was found, highlighting the suitability of the Maxwell model for this type of blend.

For the case of the blends containing ZIF-8 (giving rise to MMMs), according to the previous definition, these composites represent a ternary system, where the ZIF-8 nanoparticles were dispersed in the 6FDA-DAM continuous phase, while at the same time PIM-1 spheres were also distributed within the same 6FDA-DAM matrix. For this model it is necessary to consider the dispersion of two different phases within a continuous polymeric matrix. To predict the flow across such membranes, the following model based on the Maxwell equation is proposed. This model is going to be called “coupled Maxwell model” since the Maxwell equation is used twice. Something similar was applied by Chung *et al.*[46] to consider the non-ideal performance of MMMs induced by interface voids.

Firstly, the Maxwell equation is used to describe the flux through the phase based on a mixture of 6FDA-DAM and the ZIF-8 nanoparticles (P_{2MM}) with Equation 3:

$$P_{2MM} = P_{6FDA} \left[\frac{P_{ZIF} + 2P_{6FDA} - 2\Phi_{ZIF}(P_{6FDA} - P_{ZIF})}{P_{ZIF} + 2P_{6FDA} + \Phi_{ZIF}(P_{6FDA} - P_{ZIF})} \right] \quad (3)$$

Secondly, the permeability defined by the previous equation is introduced as that of the continue phase in the Maxwell equation, providing the gas permeability though the three-phase system (P_{3MM}) with Equation 4:

$$P_{3MM(6FDA)} = P_{2MM} \left[\frac{P_{PIM} + 2P_{2MM} - 2\Phi_{PIM}(P_{2MM} - P_{PIM})}{P_{PIM} + 2P_{2MM} + \Phi_{PIM}(P_{2MM} - P_{PIM})} \right] \quad (4)$$

When the PIM phase is the major component in the blend, P_{2MM} is considered as the permeability of the disperse phase and Equation 5 is used instead:

$$P_{3MM(PIM)} = P_{PIM} \left[\frac{P_{2MM} + 2P_{PIM} - 2\Phi_{6FDA}(P_{PIM} - P_{2MM})}{P_{2MM} + 2P_{PIM} + \Phi_{6FDA}(P_{PIM} - P_{2MM})} \right] \quad (5)$$

Figure 6. Gas permeabilities of CO₂, N₂ and CH₄ calculated with the coupled Maxwell model as a function of the ZIF-8 loading for the blends with (a) 10, (b) 20 and (c) 90 wt% of PIM. Scatter stands for the empirical values and lines for the model predictions.

Figure 6 represents the prediction of the coupled Maxwell model for the blends with the three PIM loadings used in this work together with the corresponding empirical

values. It can be seen that the model is able to predict with reasonable accuracy the behavior of the blends with 10 and 20 wt% of PIM-1, but the calculated values differ for the highest PIM loading (90 wt%). This may be due to the high concentration of ZIF-8 (10 wt%) for the low amount of 6FDA-DAM in the blend (also 10 wt%), since all the filler is located within this polymer and the original Maxwell model is only accurate for low filler loadings. Finally, Table S6 summarizes the quality of the different models used, showing the corresponding errors between the empirical and the calculated values for the different blends. The calculated gas permeability of ZIF-8 as filler according to the coupled Maxwell model is also provided, with CO₂, N₂ and CH₄ permeabilities of 136483, 1553 and 415 Barrer, respectively.

4. Conclusions

Membranes based on heterogeneous blends of polymers 6FDA-DAM and PIM-1 have been prepared in this work. The SEM microcopy revealed that the disperse phase formed spheres and lenticular particles (3-5 μm) evenly distributed along the membrane cross-section. The *d-spacing* of the membranes was calculated, finding that values became higher as the amount of PIM-1 in the blend increased. ZIF-8 nanoparticles were embedded in the blends to build MMMs where it was found that the heterogeneity of the blend contributed to achieving an even and efficient dispersion of the filler. This resulted in the filler positioned preferably in the interphase between both polymers and embedded in 6FDA-DAM.

When testing the membranes for the CO₂/CH₄ and CO₂/N₂ separations, the increase in the amount of PIM-1 in the blend led to higher gas permeabilities, while the selectivity for both mixtures decreased. The addition of ZIF-8 at low loadings led to the enhancement of the gas separation performance, especially for the blends PIM-1/6FDA-DAM 10/90 (w/w) with 10 wt% of ZIF-8. The gas separation performance of the membranes was

predicted using the logarithmic and Maxwell models, providing successful fittings with the data and allowing the determination of the separation properties of the ZIF-8 filler. This work demonstrates that even when thinking of highly permeable and moderately selective polymers as PIM-1 and 6FDA-DAM there remains some room to obtain additional performance enhancements by doing “polymer engineering” using MOFs as fillers.

The next step in this research would be the development of thinner defect-free membranes without compromising the gas separation performance since the actual permeance for these 80 μm dense MMMs is still low.

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REFERENCES

- [1] M. Harasimowicz, P. Orluk, G. Zakrzewska-Trznadel, and A. Chmielewski. Application of polyimide membranes for biogas purification and enrichment. *J. Hazard. Mater.*, 144 (2007) 698-702.
- [2] F.M. Orr Jr. CO₂ capture and storage: are we ready? *Energy Environ. Sci.*, 2 (2009) 449-458.
- [3] W. Burgers, P. Northrop, H. Khashgi, and J. Valencia. Worldwide development potential for sour gas. *Energy Procedia*, 4 (2011) 2178-2184.
- [4] G. Qi, Y. Wang, L. Estevez, X. Duan, N. Anako, A.A. Park, et al. High efficiency nanocomposite sorbents for CO₂ capture based on amine-functionalized mesoporous capsules. *Energy Environ. Sci.*, 4 (2011) 444-452.

- [5] M. Mikkelsen, M. Jørgensen, and F.C. Krebs. The teraton challenge. A review of fixation and transformation of carbon dioxide. *Energy Environ. Sci.*, 3 (2010) 43-81.
- [6] Y. Xiao, T. Chung. Grafting thermally labile molecules on cross-linkable polyimide to design membrane materials for natural gas purification and CO₂ capture. *Energy Environ. Sci.*, 4 (2011) 201-208.
- [7] E. Favre. Carbon dioxide recovery from post-combustion processes: can gas permeation membranes compete with absorption? *J. Membr. Sci.*, 294 (2007) 50-59.
- [8] W.J. Koros, R.P. Lively. Water and beyond: Expanding the spectrum of large-scale energy efficient separation processes. *AIChE J.*, 58 (2012) 2624-2633.
- [9] L.M. Robeson, Correlation of separation factor versus permeability for polymeric membranes, *J. Membr. Sci.*, 62 (1991) 165-185.
- [10] W. Qiu, L. Xu, C. Chen, D.R. Paul, and W.J. Koros, Gas separation performance of 6FDA-based polyimides with different chemical structures, *Polymer*, 54 (2013) 6226-6235.
- [11] P.M. Budd, B.S. Ghanem, S. Makhseed, N.B. McKeown, K.J. Msayib, and C.E. Tattershall. Polymers of intrinsic microporosity (PIMs): robust, solution-processable, organic nanoporous materials. *Chem. Commun.*, (2004) 230-231.
- [12] N.B. McKeown, P.M. Budd. Polymers of intrinsic microporosity (PIMs): organic materials for membrane separations, heterogeneous catalysis and hydrogen storage. *Chem. Soc. Rev.*, 35 (2006) 675-683.
- [13] Sabetghadam, B. Seoane, D. Keskin, N. Duim, T. Rodenas, S. Shahid, et al. Metal Organic Framework Crystals in Mixed-Matrix Membranes: Impact of the Filler Morphology on the Gas Separation Performance. *Adv. Funct. Mater.*, 26 (2016) 3154-3163.
- [14] L. Xu, C. Zhang, M. Rungta, W. Qiu, J. Liu, and W.J. Koros, Formation of defect-free 6FDA-DAM asymmetric hollow fiber membranes for gas separations, *J. Membr. Sci.*, 459 (2014) 223-232.
- [15] C.K. Yeom, J.M. Lee, Y.T. Hong, K.Y. Choi, and S.C. Kim, Analysis of permeation transients of pure gases through dense polymeric membranes measured by a new permeation apparatus, *J. Membr. Sci.*, 166 (2000) 71-83.
- [16] P. Li, T. Chung, and D. Paul. Gas sorption and permeation in PIM-1. *J. Membr. Sci.*, 432 (2013) 50-57.
- [17] C.R. Mason, L. Maynard-Atem, N.M. Al-Harbi, P.M. Budd, P. Bernardo, F. Bazzarelli, et al. Polymer of intrinsic microporosity incorporating thioamide functionality: preparation and gas transport properties. *Macromolecules*, 44 (2011) 6471-6479.

- [18] S.J. Smith, B.P. Ladewig, A.J. Hill, C.H. Lau, and M.R. Hill. Post-synthetic Ti exchanged UiO-66 metal-organic frameworks that deliver exceptional gas permeability in mixed matrix membranes. *Sci. Rep.*, 5 (2015) 7823.
- [19] W. Yong, F. Li, Y. Xiao, P. Li, K. Pramoda, Y. Tong, et al. Molecular engineering of PIM-1/Matrimid blend membranes for gas separation. *J. Membr. Sci.*, 407 (2012) 47-57.
- [20] P. Salehian, W.F. Yong, and T. Chung. Development of high performance carboxylated PIM-1/P84 blend membranes for pervaporation dehydration of isopropanol and CO₂/CH₄ separation. *J. Membr. Sci.*, 518 (2016) 110-119.
- [21] L. Hao, P. Li, and T. Chung. PIM-1 as an organic filler to enhance the gas separation performance of Ultem polyetherimide. *J. Membr. Sci.*, 453 (2014) 614-623.
- [22] N.P. Panapitiya, S.N. Wijenayake, D. Nguyen, Y. Huang, I.H. Musselman, K.J. Balkus, et al. Gas Separation Membranes Derived from High Performance Immiscible Polymer Blends Compatibilized with Small Molecules. *ACS Appl. Mater. Interfaces*, (2015) 18618.
- [23] N.P. Panapitiya, S.N. Wijenayake, Y. Huang, D. Bushdiecker, D. Nguyen, C. Ratanawanate, et al. Stabilization of immiscible polymer blends using structure directing metal organic frameworks (MOFs). *Polymer*, 55 (2014) 2028-2034.
- [24] K.S. Park, Z.N. Ni, A.P. Côte, J.Y. Choi, R. Huang, F.J. Uribe-Romo, et al. Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. *PNAS*, 103 (2006) 10186-10191.
- [25] S. Shahid, K. Nijmeijer, Performance and plasticization behavior of polymer–MOF membranes for gas separation at elevated pressures, *J. Membr. Sci.*, 470 (2014) 166-177.
- [26] Q. Song, S. Nataraj, M.V. Roussanova, J.C. Tan, D.J. Hughes, W. Li, et al. Zeolitic imidazolate framework (ZIF-8) based polymer nanocomposite membranes for gas separation. *Energy Environ. Sci.*, 5 (2012) 8359-8369.
- [27] M.J.C. Ordonez, K.J. Balkus Jr., J.P. Ferraris, and I.H. Musselman. Molecular sieving realized with ZIF-8/Matrimid (R) mixed-matrix membranes. *J. Membr. Sci.*, 361 (2010) 28-37.
- [28] A.F. Bushell, M.P. Attfield, C.R. Mason, P.M. Budd, Y. Yampolskii, L. Starannikova, et al. Gas permeation parameters of mixed matrix membranes based on the polymer of intrinsic microporosity PIM-1 and the zeolitic imidazolate framework ZIF-8. *J. Membr. Sci.*, 427 (2013) 48-62.
- [29] L. Xu, L. Xiang, C. Wang, J. Yu, L. Zhang, and Y. Pan. Enhanced permeation performance of polyether-polyamide block copolymer membranes through incorporating ZIF-8 nanocrystals. *Chin. J. Chem. Eng.*, 25 (2017) 882-891.

- [30] N. Liédana, A. Galve, C. Rubio, C. Téllez, and J. Coronas. CAF@ ZIF-8: one-step encapsulation of caffeine in MOF. *ACS Applied Mater. Interfaces*, 4 (2012) 5016-5021.
- [31] W. Xu, D.R. Paul, and W.J. Koros, Carboxylic acid containing polyimides for pervaporation separations of toluene/iso-octane mixtures, *J. Membr. Sci.*, 219 (2003) 89-102.
- [32] M. Safak Boroglu, A.B. Yumru, Gas separation performance of 6FDA-DAM-ZIF-11 mixed-matrix membranes for H₂/CH₄ and CO₂/CH₄ separation, *Sep. Purif Technol.*, 173 (2017) 269-279.
- [33] B. Zornoza, C. Téllez, J. Coronas, O. Esekhile, and W.J. Koros. Mixed matrix membranes based on 6FDA polyimide with silica and zeolite microsphere dispersed phases. *AIChE J.*, 61 (2015) 4481-4490.
- [34] C.L. Staiger, S.J. Pas, A.J. Hill, and C.J. Cornelius. Gas separation, free volume distribution, and physical aging of a highly microporous spirobisindane polymer. *Chem. Mater.*, 20 (2008) 2606-2608.
- [35] L.M. Robeson. The upper bound revisited. *J. Membr. Sci.*, 320 (2008) 390-400.
- [36] W. Zheng, R. Ding, K. Yang, Y. Dai, X. Yan, and G. He, ZIF-8 nanoparticles with tunable size for enhanced CO₂ capture of Pebax based MMMs, *Sep. Purif. Technol.*, 214 (2019) 111-119.
- [37] N. Nordin, A.F. Ismail, and A. Mustafa. Synthesis and preparation of asymmetric PSf/ZIF-8 mixed matrix membrane for CO₂/CH₄ separation. *J. Teknol*, 69 (2014) 73-76.
- [38] J. Sánchez-Laínez, B. Zornoza, S. Friebe, J. Caro, S. Cao, A. Sabetghadam, et al. Influence of ZIF-8 particle size in the performance of polybenzimidazole mixed matrix membranes for pre-combustion CO₂ capture and its validation through interlaboratory test. *J. Membr. Sci.*, 515 (2016) 45-53.
- [39] R. Mahajan, R. Burns, M. Schaeffer, and W.J. Koros. Challenges in forming successful mixed matrix membranes with rigid polymeric materials. *J. Appl. Polym. Sci.*, 86 (2002) 881-890.
- [40] M.Z. Ahmad, M. Navarro, M. Lhotka, B. Zornoza, C. Téllez, W.M. de Vos, et al, Enhanced gas separation performance of 6FDA-DAM based mixed matrix membranes by incorporating MOF UiO-66 and its derivatives, *J. Membr. Sci.*, 558 (2018) 64-77.
- [41] R. Swaidan, B.S. Ghanem, E. Litwiller, and I. Pinnau, Pure- and mixed-gas CO₂/CH₄ separation properties of PIM-1 and an amidoxime-functionalized PIM-1, *J. Membr. Sci.*, 457 (2014) 95-102.
- [42] D. Paul. S. Newman Eds., *Polymer Blends*. Academic Press, New York, (1978).

- [43] J.H. Kim, W.J. Koros, and D.R. Paul, Physical aging of thin 6FDA-based polyimide membranes containing carboxyl acid groups. Part I. Transport properties, *Polymer*, 47 (2006) 3094-3103.
- [44] H. Frentrup, K.E. Hart, C.M. Colina, and E.A. Müller. In silico determination of gas permeabilities by non-equilibrium molecular dynamics: CO₂ and He through PIM-1. *Membranes*, 5 (2015) 99-119.
- [45] C. Choy, K. Young. Thermal conductivity of semicrystalline polymers—a model. *Polymer*, 18 (1977) 769-776.
- [46] T. Chung, L.Y. Jiang, Y. Li, and S. Kulprathipanja. Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation. *Prog. Polym. Sci.*, 32 (2007) 483-507.