Metal organic framework mixed matrix membranes for gas separations

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ABSTRACT

Mixed matrix membranes (MMMs) for gas separations are traditionally comprised of zeolites dispersed in a polymer matrix in order to improve desired penetrant permeability and selectivity. Zeolites have a variety of drawbacks for this application – chiefly, a limited number of possible zeolite structures – that limit their potential for use in MMMs. Metal organic frameworks (MOFs), a relatively new class of microporous materials, are not well studied for use in MMMs. MOFs are an attractive alternative to the use of zeolites in MMMs because the number of possible structures is effectively infinite. In this work, a MOF of copper and terephthalic acid (CuTPA) was synthesized, characterized, and used to make MMMs. The gas transport properties of these CuTPA MMMs showed improvements over the pure polymer gas transport properties.

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1. Introduction

For decades, researchers have dispersed inorganic filler particles in polymer matrices to improve pure polymeric membrane properties [1–14]. The goal of such mixed matrix membrane (MMM) work is to leverage the superior transport properties of inorganic materials, like zeolites, with the ease of creating and installing polymeric membrane units. There are many reports of improved penetrant permeability and desired penetrant selectivity in MMMs [1–12]. MMMs may overcome the efficiency–productivity trade-offs of polymers if the polymer and filler properties are appropriately matched [13,14].

Traditionally, MMMs are comprised of zeolite particles dispersed in a polymer matrix. Zeolites often exhibit relatively high penetrant sorption capacities and penetrant size-based selectivities compared to polymers due to their large micropore volumes and well-defined, rigid structures. There are several drawbacks to the use of zeolites in MMMs: (1) preparation of defect-free zeolite crystals can be difficult, time consuming, and costly [15]; (2) there are a limited number of possible zeolite structures and compositions [16]; (3) costly surface chemistries are often needed to improve adhesion to polymer matrices [17]. These issues create demand for new filler materials for MMMs.

Metal organic frameworks (MOFs) are a relatively new class of microporous materials comprised of transition metals and transition metal oxides connected by organic linkages to create one-, two-, and three-dimensional microporous structures. MOF particles may be an attractive alternative to zeolite particles in MMM applications. Many MOFs can be synthesized easily and quickly at low cost; moreover, variations of MOF compositions and structures, including high aspect ratio MOFs, may be practically unlimited and the organic linkages provide a useful platform for chemistries that may improve adhesion to polymer matrices [18].

Numerous experimental and computational reports of gas sorption capacity in MOFs have been published [18–32], but few reports of MOF MMM performance have been provided [33–35]. While impressive permeability enhancements for MOF–MMMs were reported, selectivity enhancements were less pronounced [33–35]. Car et al. [33] reported appreciable selectivity enhancements for some gas pairs. However, there is little discussion of experimental details, repeatability, error analysis, or the inconsistent data trends of gases at a given loading and for single gases at various loadings. In the work of Zhang et al. [34], permeabilities are reported from permeation masks that were only vacuum degassed for a few hours before testing with no apparent leak rates reported; thus, these data may be somewhat inaccurate Perez et al. [35] vastly improve the experimental and analytical methods of Zhang et al., but no significant selectivity enhancements were reported therein.

The relative ease of creating defect-free MMMs from low glass transition temperature, Tg polymers and rubbery polymers versus higher Tg polymers is well documented [36–39]. Car et al. addressed this issue by investigating PDMS-based MOF–MMMs, but the high permeabilities of gases through PDMS may have diluted the contribution of the MOFs to overall gas transport [33]. Zhang et al. [34] as well as Perez et al. [35] chose Matrimid® (a widely used polyimide) as the matrix polymer, which resulted in MMMs
with increased permeabilities but little change in pure gas selectivities, a result consistent with void defects at the particle–polymer interface [38]. Matrimid® was an ambitious choice as it is extremely rigid and known to sometimes adhere poorly to filler particles in other MMM investigations [8,37]. However, it must be noted that the SEMs from these works were excellent and showed no obvious voids at particle interfaces [34,35]. Furthermore, the lack of detailed analysis of selectivity enhancements [33] and use of less than optimal experimental methods and data analyses [34] in these pioneering MOF MMM investigations may explain the lack of significant selectivity enhancements rather than inherently low MOF gas separation efficiencies.

In the present work, two-dimensionally coordinated MOF particles (with one-dimensional pore channels) of copper and terephthalic acid (CuTPA) were synthesized for use in MMMs. CuTPA MOFs were characterized by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), cryogenic nitrogen physisorption analysis, thermal gravimetric analysis (TGA), and optical microscopy. The particles were dispersed in poly(vinyl acetate) (PVAc) to create 15% (w/w) CuTPA–PVAc MMMs. PVAc is a low MOF gas separation efficiencies.

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The efficiency of a membrane separation can be described by the gas transport in dense membrane materials is governed by a solution–diffusion mechanism first envisioned by Graham [40]. In solution–diffusion transport, a penetrant first adsorbs to the membrane from a high activity upstream feed, diffuses through the membrane thickness along a chemical potential gradient, and finally desorbs into a low activity downstream feed. Permeability of penetrant \( i \), \( P_i \), can be expressed with the following phenomenological expression:

\[
P_i = \frac{\text{Flux}_i \times l}{\Delta P_i}
\]

(1)

In Eq. (1), \( \text{Flux}_i \) is the molar flux of penetrant \( i \), \( l \) is the thickness of the dense film, and \( \Delta P_i \) is the partial pressure difference across the dense film. Eq. (1) is the expression used to determine permeability in isochoric permeation experiments as conducted in this work. Through Fick’s 1st law Eq. (1) can be rearranged so that permeability is expressed as a product of the diffusivity, \( D_i \), and solubility, \( S_i \), of penetrant, \( i \):

\[
P_i = D_i \times S_i
\]

(2)

The efficiency of a membrane separation can be described by the ideal perme selectivity of a gas pair, \( \alpha_{ij} \). Ideal perme selectivity is expressed as the ratio of pure gas permeabilities:

\[
\alpha_{ij} = \frac{P_i}{P_j}
\]

(3)

Typically, the fast penetrant is denoted with an \( i \) and the slow penetrant with a \( j \) so that selectivities are greater than unity.

In an isochoric permeation experiment where the membrane separates a high pressure feed volume from a low pressure permeate volume, steady-state flux is preceded by a time lag, \( t \), where there is little or no accumulation of penetrant in the permeate volume. For the case of single penetrant permeation through a structurally and compositionally homogeneous film of uniform thickness, \( l \), for which Fickian kinetics apply, the time lag is related to the average diffusivity of penetrant \( i \), \( D_i \), through the film as shown in Eq. (4):

\[
D_i = \frac{l^2}{6h}
\]

(4)

For the case of zero initial permeate pressure, the time lag is simply the time-intercept of a linear fit of the steady-state permeate pressure rise.

Permeation time lag is also observed in MMMs but has a more complex relationship with diffusivity than the case of a pure polymer film. For example, a polymer dispersed with impermeable particles can increase the permeation time lag relative to the pure polymer due to tortuosity effects. These effects can be greatly magnified by use of high aspect ratio particles aligned perpendicular to flow. An increased time lag in such a sample does not mean that diffusivity in the polymer is inherently lower; it simply means that diffusional path lengths have increased due to tortuosity.

The case of permeable filler particles in MMMs is even more complex. Penetrants that permeate readily through the filler particles in a MMM can have longer time lags than impermeable particles due to the relatively high sorption capacities often seen in microporous filler particles relative to the polymer matrix. Higuchi and Higuchi [41] and Paul and Kemp [42] were among the first to explore this “time lag extension” or immobilizing sorption phenomenon. Paul’s work is especially useful as he shows that time lag extension (relative to pure polymer) for a microporous particle filled polymer matrix can be understood with a fairly simple function of filler volume fraction, filler equilibrium sorption properties, and polymer matrix equilibrium sorption properties for the case of total penetrant immobilization (i.e., solubility is much higher and mobility is substantially lower than in the surrounding polymer matrix).

In general cases where penetrant mobility in the filler particles is comparable to or greater than the surrounding polymer, gas transport in porous filler–polymer systems is expected to show similar apparent increased sorption and corresponding extended time lag effects. Many researchers studied partial penetrant immobilization in great depth [43–45], resulting in permeation time lag expressions much more complex than Eq. (4). Regardless of complexity of analysis, permeation time lag extension in glassy polymers or polymer-microporous filler systems are the results of the penetrant sorption in non-equilibrium microporoids or filler particles, respectively. In other words, non-equilibrium microporoids and filler particles act as mass sinks during the transient portion of a permeation experiment.

The MMMs studied in this work are unlikely to result in total immobilization due to the large channel windows of the CuTPA MOF and low penetrant diffusivities in PVAc. However, the dispersed CuTPA crystals will still act as mass sinks which must be filled by penetrant diffusion from the PVAc phase during the transient portion of permeation, thereby resulting in time lag extension and apparent diffusivity reductions for the MMMs compared to pure PVAc. While the likelihood of partial penetrant immobilization in these MMMs will make it difficult to understand whether transport enhancements are diffusivity based, solubility based, or combinations of both, use of Eq. (4) will assist in the characterization of the transport properties of the MMMs.

3. Experimental

3.1. CuTPA synthesis and characterization

The copper terephthalate (CuTPA) was synthesized in accordance with a previously published procedure [46]. Equimolar quantities of copper nitrate trihydrate (0.93 g) and terephthalic...
acid (0.664 g) were dissolved in \textit{N,N}-dimethylformamide, DMF (100 mL). This solution was placed in a sealed Erlenmeyer flask in an oven at 110 °C for 24 h. To confirm that the product had the correct crystal structure, the powder diffraction profile was measured with a Panalytical X’Pert Alpha-1 with Cu K\textsubscript{α1} radiation. To verify the thermal desolvation, the thermogravimetric profile was measured with a TA Instruments Q50 Thermogravimetric Analyzer. Detailed discussion of the powder diffraction profile and the thermogravimetric profile, which confirmed the presence of CuTPA-DMF, can be found elsewhere \cite{46}. A Micromeritics ASAP 2020 physisorption analyzer was used to determine specific BET surface areas and cryogenic nitrogen adsorption/desorption isotherms.

3.2. MMM preparation

The MMM samples were prepared via polymer solution processing. CuTPA powder was dried at 230 °C under active vacuum for 36 h in clean glass vials. After cooling to room temperature under active vacuum, the vacuum was broken with a dry nitrogen purge. The vials were quickly capped so their dry mass could be recorded. 9.24 g anhydrous toluene/g dry CuTPA was immediately added to the vials after weighing.

A 130 W ultrasonic probe operating at 80% maximum amplitude was used to disperse the CuTPA particles in toluene. Three 60 s ultrasonic exposures with 30 s cool downs were used to fully disperse the particles. Following the final sonication step, a small amount of PVAc–toluene solution (≤10% of the total amount required) was added to the vial to stabilize (or prime) the dispersion. The vials were then capped, shaken vigorously for a few minutes, and allowed to tumble-roll overnight.

PVAc was then added from the same PVAc–toluene solution to the primed dispersion to make a 15% CuTPA–PVAc MMM on a solvent-free basis. Brief, vigorous shaking was used to quickly mix the bulk PVAc solution with the primed dispersion. The final solution was left to coaxially roll to maintain a homogenous mixture while minimizing the entrainment of air as bubbles. After a few days of gentle rolling, the casting solution was placed in a room temperature vacuum oven under partial vacuum (<19.5 in Hg vacuum) to liberate entrained bubbles without boiling toluene.

The vial was then transferred to a glove bag containing a leveled Teflon\textsuperscript{®} plate to cast a thin film upon. The glove bag was thrice purged with dry nitrogen and backfilled with some nitrogen to ensure a dry casting atmosphere. Films were cast with a 10 mil casting knife and left to partially vitrify in the glove bag overnight. Then the partially vitrified film (still adhered to the Teflon\textsuperscript{®} plate) was transferred to a vacuum oven where the remaining toluene was driven away at 130 °C active vacuum for 36 h. Finally, the film (still adhered to the Teflon\textsuperscript{®} plate) was removed after the oven has cooled to room temperature under vacuum and removed from the plate. Pure PVAc samples were prepared similarly minus all particle dispersion steps.

3.3. Permeation testing and analysis

Masked films were affixed to a permeation cell as described elsewhere \cite{47}. Before affixing the mask to the permeation cell, five thickness measurements were made with a micrometer. The membrane areas were known due to use of standard die-cut circles. MMM thicknesses and areas from sample to sample varied from 58 to 91 \textmu m and 2.2 to 2.9 cm\textsuperscript{2}, respectively. The permeation cell was tightly sealed and loaded into a constant volume permeation system. Vacuum was applied to both faces of the sample until the system leak rate minimizes (typically 4 days of vacuum). Before each gas was tested, 1–2 h of leak data is collected.

In between each gas permeation experiment, vacuum was pulled on each face of the mask to remove sorbed gas until the leak rate returned to its initial minimum value. For most gases this took 1–2 days, but for methane 6–7 days was often necessary since long methane permeation experiments resulted in longer penetrant exposure to the masking adhesive which absorbs substantially and has long path lengths for desorption. Pre-permeation test leak

![Fig. 1. Stereo-model of CuTPA DMF.](please cite this article in press as: R. Adams et al., Micropor. Mesopor. Mater. (2010), doi:10.1016/j.micromeso.2009.11.035)
rates never exceeded 0.87% of the raw, steady-state fluxes. All steady-state fluxes were analyzed from leak-corrected data between 9 and 14 time lags. All gases were tested at 35 °C and 65 psia, except carbon dioxide which was tested at 35 °C and 1.35 psia to avoid plasticization of PVAc. To ensure carbon dioxide had not conditioned the samples, all gases were retested post-CO₂ exposure to validate the original measurements. Reported permeabilities, apparent diffusivities, and selectivities are the average values of two different areas from three unique membranes for pure PVAc and CuTPA MMMs.

4. Results and discussion

4.1. Pure CuTPA

CuTPA is the product of the thermal desolvation of CuTPA-DMF. Before desolvation, the carbonyl groups of the DMF molecules associate with the copper atoms of the CuTPA framework as shown in Fig. 1. An optical micrograph of CuTPA-DMF particles is shown in Fig. 2. The particles in Fig. 2 have the appearance of a crystalline material and X-ray diffraction of CuTPA-DMF confirms the synthesis produced a crystalline material (see Fig. 3).

Thermal gravimetric analysis shows that DMF molecules detach from the apical position on the copper atoms above 200 °C. The TGA results in Fig. 4 suggest that vacuum drying at 230 °C is sufficient to desolvate the as-synthesized CuTPA-DMF since the mass losses from TGA and vacuum drying were equivalent.

The synthesis and crystal structure of CuTPA-DMF, as well as the powder pattern of CuTPA, were recently published [46], although the crystal structure of CuTPA has not been reported. XRD was performed on the desolvated CuTPA – the diffractogram is given in Fig. 5. Although the diffractogram in Fig. 5 shows some noise and broader peaks compared to that of the solvated product shown in Fig. 3, the desolvated CuTPA diffractogram still has the characteristics of an ordered, crystalline material. The structure of desolvated CuTPA is shown schematically in Fig. 6. Analysis of the crystal structure indicates that the pore limiting diameter of the framework is ~5.2 Å. This value is in reasonable agreement with the work of Seki et al. where a slightly different synthetic protocol was used to investigate the structure of CuTPA [48].

![Fig. 2. Optical micrograph of synthesized CuTPA particles.](image1)

![Fig. 3. X-ray diffractogram of CuTPA DMF.](image2)

![Fig. 4. Thermal gravimetric analysis of CuTPA-DMF crystals.](image3)
Cryogenic nitrogen physisorption and BET analyses were performed on desolvated CuTPA. The measured specific surface area of 625 m²/g is further evidence that thermal desolvation does not destroy the porous, ordered nature of the original material. Fig. 7 shows the cryogenic nitrogen physisorption–desorption isotherms. Both the shapes of the curves and the amount of uptake seen in Fig. 7 confirm desolvated CuTPA to be a microporous material.

4.2. CuTPA–PVAc MMM preparation

Scanning electron micrographs of liquid nitrogen fractured cross-sections of MMMs show good dispersion of CuTPA particles and the absence of void defects at CuTPA–PVAc interfaces. A sample SEM is given in Fig. 8. The overall good dispersion and adhesion seen in Fig. 8 is a promising sign. Since fractures occur along weaknesses in materials, Fig. 8 likely depicts a worst-case scenario. In Fig. 8, some particles are circled in green to aid the eye. Many of the visible particles display an apparently high aspect ratio suggesting the desolvation and dispersion processes may break the large, unity aspect ratio particles seen in Fig. 2 into smaller, higher aspect ratio platelets.

4.3. Pure gas permeation data

Pure gas permeation experiments were performed for three samples each of PVAc and 15% CuTPA–PVAc. Table 1 summarizes the average pure gas permeabilities for pure PVAc and the MMMs. All permeabilities were substantially enhanced. To verify that these enhancements were truly a mixed matrix effect and not the result of voids at polymer–filler interfaces, normalized permeability ($P_{\text{MMM}}/P_{\text{PVAc}}$) is plotted against decreasing penetrant permeability in pure PVAc in Fig. 9.

Permeability enhancements for the MMMs generally decrease with decreasing permeability in pure PVAc. The large enhancement for carbon dioxide permeability is a notable exception and may be attributable to greater solubility enhancement versus that of helium. Interfacial voids would cause the slowest penetrants’ permeabilities to be the most enhanced in relative terms [38].

All relevant gas pairs showed selectivity enhancements for 15% CuTPA–PVAc MMMs as shown in Table 2. Fig. 10 summarizes the normalized selectivity enhancements. As with normalized permeabilities, normalized selectivities are simply $\alpha_{\text{MMM}}/\alpha_{\text{PVAc}}$. Pure gas selectivity of oxygen over nitrogen displayed the weakest enhancement ($3.31 \pm 2.07\%$ over pure PVAc) due to the similar size and shape of these penetrants. The carbon dioxide over methane selectivity enhancement was the largest of all ($15.8 \pm 7.02\%$ over pure PVAc). This is a promising result since selective removal of carbon dioxide from natural gas is of great industrial relevance [49]. Selectivity enhancement was also observed for carbon dioxide over nitrogen ($10.3 \pm 5.23\%$ over pure PVAc). This selectivity enhance-
The permeation time lag behavior of the MMMs also suggests good PVAc–CuTPA adhesion as well as easy penetrant access to the channels of CuTPA. The apparent gas diffusivities of the MMMs, \(D_{\text{MMM}}\), as well as the apparent gas diffusivities in pure PVAc, \(D_{\text{PVAc}}\), are provided in Table 3. The apparent gas diffusivities of the MMMs are consistently lower than the apparent diffusivities in pure PVAc. Note that apparent helium diffusivities are excluded since accurate measurement of helium time lags in such thin samples is infeasible with the methods used.

In Fig. 11, the apparent gas diffusivities of the MMMs are normalized by division of pure PVAc apparent gas diffusivities, \(D_{\text{MMM}}/D_{\text{PVAc}}\), and plotted against decreasing penetrant permeabilities. Due to the large channel window size of CuTPA; these apparent diffusivity reductions are likely a result of transient penetrant sorption saturation (or, penetrant immobilization) and not caused by low gas permeabilities in CuTPA or tortuosity imparted by the high aspect ratio particles. These apparent diffusivity reductions also suggest that the penetrants are accessing the CuTPA particles and not bypassing them through voids. The combined observations of enhanced permeabilities and decreased apparent diffusivities in these MMMs are strong evidence that a true mixed matrix effect was achieved.

Table 1

<table>
<thead>
<tr>
<th></th>
<th>(P_{\text{He}})</th>
<th>(P_{\text{O}_2})</th>
<th>(P_{\text{N}_2})</th>
<th>(P_{\text{CH}_4})</th>
<th>(P_{\text{CO}_2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAc</td>
<td>15.1 ± 0.8</td>
<td>0.514 ± 0.034</td>
<td>0.0783 ± 0.0064</td>
<td>0.0679 ± 0.0034</td>
<td>2.44 ± 0.32</td>
</tr>
<tr>
<td>MMMs</td>
<td>19.0 ± 0.5</td>
<td>0.624 ± 0.026</td>
<td>0.0912 ± 0.0032</td>
<td>0.0806 ± 0.0035</td>
<td>3.26 ± 0.23</td>
</tr>
</tbody>
</table>

5. Conclusions

CuTPA MOF particles were successfully synthesized, characterized, and incorporated into a PVAc matrix for MMM analysis. Pure gas permeabilities and selectivities of 15% CuTPA–PVAc MMMs showed improvements over pure PVAc properties. Careful attention to the permeability trends from gas to gas and the time lag behavior of the MMMs suggest that the MMMs are free of interfa-

![Fig. 9. Averaged normalized permeabilities of 15% CuTPA–PVAc MMMs.](image1)

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{He}/\text{CH}_4}$</th>
<th>$\lambda_{\text{O}_2/\text{N}_2}$</th>
<th>$\lambda_{\text{N}_2/\text{CH}_4}$</th>
<th>$\lambda_{\text{CO}_2/\text{N}_2}$</th>
<th>$\lambda_{\text{CO}_2/\text{CH}_4}$</th>
</tr>
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<tr>
<td>PVAc</td>
<td>212 ± 1.75</td>
<td>6.57 ± 0.143</td>
<td>1.09 ± 0.0433</td>
<td>32.1 ± 1.36</td>
<td>34.9 ± 2.86</td>
</tr>
<tr>
<td>MMMs</td>
<td>237 ± 11.8</td>
<td>6.79 ± 0.136</td>
<td>1.14 ± 0.0191</td>
<td>35.4 ± 1.68</td>
<td>40.4 ± 2.45</td>
</tr>
</tbody>
</table>

![Fig. 10. Averaged normalized gas pair selectivities of 15% CuTPA–PVAc MMMs.](image2)

<table>
<thead>
<tr>
<th></th>
<th>$D_{\text{CO}_2}$</th>
<th>$D_{\text{O}_2}$</th>
<th>$D_{\text{N}_2}$</th>
<th>$D_{\text{CH}_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVAc</td>
<td>$6.2 \times 10^{-9} \pm 6.8 \times 10^{-10}$</td>
<td>$4.6 \times 10^{-8} \pm 1.9 \times 10^{-9}$</td>
<td>$1.2 \times 10^{-8} \pm 4.0 \times 10^{-10}$</td>
<td>$2.9 \times 10^{-9} \pm 2.7 \times 10^{-10}$</td>
</tr>
<tr>
<td>MMMs</td>
<td>$5.1 \times 10^{-9} \pm 1.5 \times 10^{-9}$</td>
<td>$2.0 \times 10^{-8} \pm 1.0 \times 10^{-9}$</td>
<td>$4.1 \times 10^{-9} \pm 2.9 \times 10^{-9}$</td>
<td>$5.7 \times 10^{-10} \pm 1.5 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

![Fig. 11. Averaged normalized apparent diffusivities of 15% CuTPA–PVAc MMMs.](image3)

cial voids, that the gases have easy access to the CuTPA crystals, and that real mixed matrix effects were observed. Future work will determine if these enhancements continue into higher CuTPA loadings in PVAc as well as various CuTPA loadings in industrially viable polymers.

MMM transport enhancements witnessed in this work suggest a promising future for MOFs in membrane applications. While this MOF shows a high aspect ratio morphology in MMM cross-sectional images (a desirable trait for MMM filler particles) and performs well in MMMs, its large channel window is likely not ideal for size exclusive molecular sieving. Modifying the organic linkages to restrict channel access may result in better molecular sieving. Such a modification could also be designed to improve CO2 solubility to further enhance performance.

Acknowledgments

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References