Molecular sieving realized with ZIF-8/Matrimid® mixed-matrix membranes


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Zeolitic imidazolate frameworks (ZIFs), that have the potential for gas separation, were used as additives in mixed-matrix membranes (MMMs). ZIF-8, which exhibits the sodalite topology, is composed of zinc (II) ion clusters linked by imidazolate ligands. The ZIF-8 pore aperture is 3.4 Å allowing it to readily absorb small molecules such as H2 and CO2. ZIF-8/Matrimid® MMMs were fabricated with loadings up to 80% (w/w), which are much higher than the typical loadings achieved with select zeolite materials. Only at the highest loading did the ZIF-8/Matrimid® MMM show a loss of mechanical strength, leading to a decrease in flexibility. The ZIF-8/Matrimid® MMMs permeability properties were tested for H2, CO2, O2, N2, CH4, C2H6, and gas mixtures of H2/CO2 and CO2/CH4. The permeability values increased as the ZIF-8 loading increased to 40% (w/w). However, at higher loadings of 50% and 60% (w/w), the permeability decreased for all gases, and the selectivities increased consistent with the influence of the ZIF-8 additive. The ideal selectivities of gas pairs containing small gases, such as H2/O2, H2/CO2, H2/CH4, CO2/CH4, CO2/C3H8, and H2/C3H8, showed improvement with the 50% (w/w) ZIF-8 loading, demonstrating a transition from a polymer-driven to a ZIF-8-controlled gas transport process. In control experiments using as-synthesized ZIF-8 with filled pores, there was no transition at 50% (w/w) loading. This may be the first example of an MMM wherein molecular sieving is evident and suggests that additive loadings >50% (w/w) may be required to observe this effect in MMMs.

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1. Introduction

Membrane gas separation technology continues to grow in importance due to advantages such as low capital and operating cost, minimum energy requirements, ease of operation, and environmental friendliness [1]. Membranes are now replacing more traditional gas separation processes, such as cryogenic distillation and absorption [2,3], and their current applications include hydrogen separation, nitrogen recovery, oxygen and nitrogen enrichment, and natural gas purification [4]. Some significant membrane requirements include durability, mechanical stability at the operating conditions, and excellent permeability and selectivity [5,6]. However, simultaneously obtaining high permeability and high selectivity remains a challenge. Polymeric membranes have been extensively studied for gas separation applications [7–9] but, despite efforts to improve polymer separation properties, current polymeric membrane materials have reached a limit in the tradeoff between permeability and selectivity [10]. Inorganic membranes, on the other hand, offer good thermal and chemical stability and high gas flux and selectivity, but are limited by fabrication costs [11]. Thus, finding new membrane materials suitable for industrial separations has become an essential research objective in recent years. The advent of inorganic-organic hybrid membranes combines the processability of polymers and the superior gas separation properties of inorganic materials. Such composites are referred to as mixed-matrix membranes (MMMs) [12,13]. A desirable MMM consists of well-dispersed particles with as high a loading as possible. Polymers frequently used for commercial gas separations that may be adapted for mixed-matrix membranes include polysulfones, polyarylates, polycarbonates, poly(aryl ethers), poly(aryletherketones) and polyimides [10]. Polyimides are especially attractive due to their high gas selectivity and high chemical, thermal, and mechanical resistance [14,15]. One such polyimide that has been studied extensively for gas separations and MMMs is Matrimid® (Fig. 1), which has permeability and selectivity properties falling close to the upper bound region of various Robeson plots [16,17].

Many materials have been used as the inorganic phase in MMMs, including carbon molecular sieves [18,19], zeolites [20–22], mesoporous materials [23], activated carbons [24], carbon nanotubes [25], and metal-organic frameworks [26,27]. While these materials have shown promise in MMM applications, there are still many challenges to overcome. A significant problem is the compatibility of the polymeric and inorganic phases for optimum dispersion and interfacial contact [28,29] that only allows for moderate loadings of inorganic materials. For example, loadings only up to
of polymer chains with the zeolite [36]. However, these methods have also provided additional roughness for the interlocking [13,34,35]. Strategies to create better adhesion at the polymer-zeolite interface include silanation using different silane coupling agents [13,34,35]. In addition, whisker-like structures formed on the zeolite surface have provided additional roughness for the interlocking of polymer chains with the zeolite [36]. However, these methods did not result in significant improvement in gas permeability and selectivity.

To provide for better wetting and dispersion, mesoporous materials have also been combined with polymers to form MMMs. The premise was that the chains of the polymer could penetrate into the large mesopores (2–30 nm) resulting in better interfacial contact. This concept was demonstrated by MCM-41/polysulfone MMMs, wherein gas permeabilities increased but selectivities remained unchanged [37]. A disadvantage of such membranes can be a loss of selectivity due to the large size of the mesopore. The loss in selectivity might be offset by incorporating micropores into mesoporous materials [38]. In these dual pore systems, the mesopores improve interfacial contact and the micropores provide size and shape selectivity. For example, MMMs were fabricated with a carbon aerogel having both micropores and mesopores in a Matrimid® matrix. Higher ideal selectivities for H2/N2, O2/N2, and CO2/CH4 gas pairs relative to pure Matrimid® were observed. The incorporation of nano-sized ZSM-5 embedded in a carbon aerogel to form carbon aerogel-ZSM-5/Matrimid® MMMs also resulted in higher selectivity for CO2/CH4 separation [38].

Another class of porous materials that has been employed in MMMs is the metal-organic frameworks (MOFs). The functional groups of the organic ligands and the metal ions associated with the secondary building units (SBU) may facilitate interactions with the polymer. This new type of zeolitic material is expected to be more flexible in chemical design and diverse in pore size and shape [39–41]. MOFs are being studied extensively owing to their exceptionally high surface area, controlled porosity, functionalizable pore walls, affinity for specific gases, and flexible chemical composition due to the presence of strong chemical bonds and modifiable organic linking units [42]. These properties make them promising materials for gas storage, gas separations, and catalysis [43]. For gas storage and separation, MOFs can act as molecular sieves due to their rigid frameworks and finite pore sizes allowing for size exclusion of gas molecules [44,45]. Our research group has explored the use of MOFs as additives in mixed-matrix membranes for gas separations [27,46]. We fabricated MOF-5/Matrimid® MMMs that showed increased permeability at high loadings while maintaining constant selectivity compared to Matrimid® [46]. Cu-BPY-HFS in Matrimid® showed increased solubility and selectivity for CH4 gas [27].

Zeolitic imidazolate frameworks (ZIFs) are a sub-family of MOFs that also have tunable pore sizes and chemical functionality [47]. Moreover, ZIFs possess the exceptional chemical stability and rich structural diversity found in zeolites. ZIFs are based on metal imidazolates, and their structures are related to many zeolite frameworks [48]. For example, the zeolitic imidazolate framework number eight (ZIF-8) has sodalite (SOD) topology [39]. The structure of this material is shown in Fig. 2. The five-membered imidazolate ring creates a framework by bridging the Zn(II) centers to the N-atoms in the 1,3-positions of the ring. The 145° angle made by the metal-imidazolate-metal bond is similar to the Si–O–Si bond angle found in many zeolites [49]. In contrast to sodalite, which has no accessible pores, ZIF-8 has a pore aperture of 3.4 Å in diameter allowing it to readily adsorb small gas molecules, such as hydrogen and carbon dioxide [41], while the pore cavity has a diameter of 11.1 Å [49]. An attractive feature of ZIF-8 is its apparent thermal stability up to nearly 400 °C. ZIF-8 also exhibits a high surface area of 1300–1600 m²/g [49]. Due to these properties, the ZIF-8 material was chosen as the inorganic additive in Matrimid® polymer membranes. In this work, ZIF-8 was synthesized and ZIF-8/Matrimid® MMMs were prepared and characterized as well as tested for their permeability and selectivity properties. The permeability data showed a shift from a polymer-driven to a ZIF-8-controlled gas transport process at high loadings (>50% (w/w)). Selectivity data showed that the MMMs have an affinity for the transport of small gas molecules due to the sieving effect of ZIF-8.

2. Experimental

2.1. Materials

Zinc nitrate tetrahydrate [Zn(NO3)2·4H2O, 98% purity] and 2-methylimidazole (H-MelM, 99% purity) were purchased from EMD and Sigma–Aldrich, respectively, and used as received. Chloroform (CHCl3, 99% purity), N-N-dimethylformamide (DMF, 98% purity) and methanol (MeOH, 98% purity) were purchased from Fisher. Prior to use, all organic solvents were dried with activated 4A nitrogen (N2), oxygen (O2), hydrogen (H2), methane (CH4), carbon dioxide (CO2), and propane (C3H8), as well as gas mixtures of H2/CO2 (50/50 mol%) and CO2/CH4 (10/90 mol%), with purities >99.50% were obtained from Air Liquide.

Fig. 1. Chemical structure of Matrimid®.

Fig. 2. The structure of ZIF-8 calculated from crystallographic data in Ref. [49] using Materials Studio® software.
2.2. Synthesis of ZIF-8 nanocrystals

A modified literature procedure [49] was followed for the synthesis of ZIF-8, wherein a 1:1 mole ratio of Zn(NO₃)₂·4H₂O and H-MeIM was used. Zn(NO₃)₂·4H₂O (3.1 g) and H-MeIM (0.96 g) were dissolved in 120 mL of DMF. Activated 4A molecular sieves were added to the solution, which was allowed to stand for 1 h to remove excess water. The solution was heated to 100 °C, and then 4 mL of TEA was immediately added with constant stirring forming a light brown solution. The solution was further heated to 140 °C for 6–8 h. Upon cooling, the light brown ZIF-8 nanocrystals precipitated. The solution was then suction filtered and the crystals were washed with 50 mL portions of DMF, CHCl₃, and MeOH solvents. Washing with different solvents allowed for activation or evacuation of guest molecules from the pores of the material. After drying in air, the crystals were placed in a vacuum oven at 240 °C for overnight. The typical percent yield of ZIF-8 was 48% based on zinc.

2.3. ZIF-8/Matrimid® mixed-matrix membrane fabrication

ZIF-8/Matrimid® MMMs [0%, 20%, 30%, 40%, 50%, 60% and 80% (w/w)] were fabricated by solution blending [50]. Two solutions, Matrimid® (0.50 g) and ZIF-8 [0.10 g (20%), 0.15 g (30%), 0.20 g (40%), 0.25 g (50%), 0.30 g (60%), 0.40 g (80%)] in chloroform (5 mL) were prepared separately. These solutions were stirred and bath sonicated alternately for 24 h to obtain a homogenous suspension. The ZIF-8 nanocrystals were first “primed” or coated [13,51] by adding a small amount of the Matrimid® solution to the ZIF-8 solution, after which it was further stirred and bath sonicated for another 24 h. After thorough mixing, the remaining bulk polymer solution was added. The chloroform solvent was evaporated to obtain the desired solution viscosity for membrane casting. Membranes were cast in a Pure Aire® laminar flow hood onto a Mylar-covered glass substrate using an AccuLab Jr TM Drawdown casting table with a 2.5 cm² membrane area covered with different solvents allowed for activation or evacuation of guest molecules in the pores after annealing. A Perkin-Elmer Pyris-1 TGA instrument, with a calibrated platinum pan, was used to determine the thermal stability of ZIF-8 and the evacuation of guest molecules in the pores after annealing. A single bounce attenuated total reflectance (ATR) accessory to determine the surface interaction of the ZIF-8 material with the Matrimid® matrix. Tensile testing was performed on a Favimat Textechno instrument to obtain the Young’s modulus and tensile strength of the MMMs. Portions of the membrane films were cut and used for XRD and TGA analyses using the same parameters as previously described.

2.5. Permeability analysis

Single gas permeation measurements were carried out using a custom-built gas permeameter described previously [37]. The permeameter allows permeability and diffusion coefficients to be determined simultaneously by recording the increase in downstream pressure with time. The permeameter consists of a stainless steel permeation cell that separates the upstream and downstream pressure transducers. The system is controlled by Labview 7.1 software (National Instruments). For each experiment, a 1.2 cm² membrane was mounted into the stainless steel cell and both sides of the membrane were evacuated for several hours at 35 °C following a leak rate test. Afterwards, permeability experiments were conducted by introducing a single gas at an upstream pressure of 2000 Torr. Upstream and downstream pressures were recorded, and the steady-state-slope of the downstream pressure versus time was determined from the acquired data. The time-lag (θ), which is the time required for the gas penetrants to diffuse through the membrane, was calculated from the steady-state-slope. The permeability, P, was evaluated from 30 to 70θ of the steady-state-slope region. The ideal selectivities were calculated from the ratio of the permeabilities of the gases according to the solution-diffusion model [4]. The diffusivity, D, was calculated from the relationship $F/θθ$ where I is the thickness of the membrane, while solubility, S, was calculated using the equation $S = P/D$. For each loading, a minimum of 4 membranes, 2 pieces from each of 2 separately cast membranes, were tested.

For gas mixture analysis, the permeameter uses a MKS PPT 200 Quadrupole Residual Gas Analyzer (RGA, mass range 1–200 amu), and a MKS type 249 sampling valve. For each experiment, the RGA was made to thermally stabilize and achieve low pressure (10⁻⁵ Torr). Uniform feed compositions were used for the mixed gas experiments. The mixture, with an upstream pressure of 2000 Torr, was allowed to permeate through the membrane into the downstream volume for a minimum of 6 h to achieve steady-state composition. The downstream volume was then briefly evacuated, and the subsequent steady-state permeate was sampled by the RGA. Mass spectra of the permeates were acquired by recording the response of the RGA from 1 to 50 amu. The most intense molecular ion peak was used, except for CH₂ in the CH₄/CO₂ mixture, for which the $m/z=15$ peak was used due to interference at $m/z=16$ resulting from CO₂ fragmentation. Ten to thirteen RGA data points at pressures ranging from $2 \times 10^{-6}$ to $1 \times 10^{-6}$ Torr were recorded for each gas mixture to produce a linear plot. The corresponding gas concentrations in the permeates were calculated using calibration curves as previously described by Perez et al. [46].
3. Results and Discussion

3.1. Synthesis and Characterization of ZIF-8

The ZIF-8 material was synthesized using a hydrothermal method producing 50–150 nanometer-sized crystals shown in Fig. 3. It is expected that these small nanoparticles, as well as the presence of organic ligands, will afford better contact with the polymer matrix allowing for improved dispersion and reduction of interfacial voids. The nanometer-sized crystal synthesis of ZIF-8 material was achieved by adding a base, triethylamine (TEA), in the synthesis procedure. This base deprotonates the 2-MeIM allowing it to react faster by producing more nucleation sites, and acts as a buffering ligand for easy release of metal ions [53]. This approach was previously demonstrated by Huang et al. [54] for the nanocrystal synthesis of MOF-5, wherein fast addition of amine to a constantly stirred solution generated a large number of nuclei during crystallization. Recently, nano-sized ZIF-8 was also synthesized rapidly at room temperature by using MeOH as the solvent [55].

The XRD pattern of the activated ZIF-8 nanocrystal in Fig. 4b matches the theoretical pattern (Fig. 4a) [48]. The addition of TEA did not change the crystallinity of the ZIF-8. Immediate washing of as-synthesized ZIF-8 with DMF, CHCl₃, and MeOH was carried out to activate the material by displacing guest molecules from the surface and pores so that they would be available to absorb gas molecules. After the solvent exchange, the ZIF-8 nanocrystals were dried under vacuum at 240°C for overnight. The TGA plot of as-synthesized ZIF-8 nanocrystals (Fig. 5a) revealed a ~10% weight loss starting at 150°C and plateauing at 300°C, which was attributed to the presence of residual solvent or guest molecules in ZIF-8. Between 400 and 500°C, the decomposition of the ZIF-8 material occurred. Only 40% of the material remained after 500°C, resulting from ZnO. The calculated ZnO percent composition of this material resulted in the same amount. The activated and annealed ZIF-8 material (Fig. 5b) showed no immediate weight loss until 400°C, indicating that it was free from guest molecules. The TGA plot also showed that the activated ZIF-8 material was thermally stable up to 400°C, and the framework decomposition occurred in the range of 400–500°C, which is similar to literature observations [49].

The pore size and surface area of the ZIF-8 nanocrystals that had been washed with DMF, CHCl₃, and MeOH were determined by N₂ adsorption at 77K. A Type I isotherm was obtained, which is indicative of a microporous material. Multipoint BET (1300 m²/g) and Langmuir (1500 m²/g) surface areas were calculated by using the P/P₀ data points ranging from 0.01 to 0.10 along the curve of the isotherm plot, which correspond to the formation of a monolayer of adsorbate molecules [56]. The HK pore size of the ZIF-8 nanocrystalline material was determined to be 6.2 Å. This value, which does not agree with the literature value of 3.4 Å determined from crystallographic data [49], was not surprising since N₂ molecules may not fit through the ZIF-8 pore apertures. Also, the HK method may lead to larger values since it calculates the pore size distribution from the adsorption isotherm data of a slit-shaped pore using an approximation of an idealized model. Finally, surface heterogeneity of the material may cause a shift in pore size distribution leading to a larger value [52]. An Argon (Ar) adsorption analysis was also performed to determine if this discrepancy in pore size could be explained. Since Ar has a kinetic diameter of 3.4 Å, it would likely fit better into the theoretical pore size of the ZIF-8 material (3.4 Å) as compared with N₂, which has a kinetic diameter of 3.6 Å. The Ar isotherm resulted in a BET surface area of 1200 m²/g and a Langmuir surface area of 1500 m²/g. The Ar isotherm also showed a two-step feature that is slightly separated by a hysteresis loop, making it a Type IV isotherm. Mesoporous materials that can exemplify capillary condensation exhibit this type of isotherm [53]. For ZIF-

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Fig. 3. SEM image of ZIF-8 nanocrystal.

Fig. 4. Normalized XRD plots of ZIF-8: (a) theoretical, (b) synthesized with TEA and activated, and (c) 60% (w/w) ZIF-8/Matrimid® MMM.

Fig. 5. TGA plots of ZIF-8: (a) as-synthesized ZIF-8 without solvent exchange, and (b) activated ZIF-8 synthesized with TEA and annealed at 240°C.
8, the hysteresis loop could represent the reorganization [57] or phase change of the Ar adsorbate molecules at certain threshold pressures because the pore size of ZIF-8 is very close to the size of Ar gas molecules. The reorganization and distribution of the Ar adsorbate molecules could be due to its difference in polarizability, which leads to the formation of the hysteresis loop [49]. The HK pore size obtained from the Ar isotherm is also 6.2 Å. A density functional theory analysis of the isotherms gave a pore cage diameter of 10.8 Å, which correlated well with the literature value of 11.1 Å [49].

An infrared spectroscopy study of ZIF-8 was conducted to determine the functionalities present in the material, and the spectrum is shown in the Supporting information section. The absorption bands at 3135 and at 2928 cm$^{-1}$ are for the aromatic C–H stretch and the aliphatic C–H stretch of the imidazole, respectively. The 1606 cm$^{-1}$ band is for the C=C stretch, and the peak at 1580 cm$^{-1}$ is for the C=N stretch. The C–N absorption bands are found in the 1100–1400 cm$^{-1}$ region. The absorption band at 421 cm$^{-1}$ is associated with the Zn–N stretching mode. This spectrum also correlates well with the literature data [49].

3.2. Preparation and characterization of ZIF-8/Matrimid$^\circledR$ membranes

Using CHCl$_3$ as the solvent, the ZIF-8 nanocrystalline material was cast into MMMs [0%, 20%, 30%, 40%, 50%, 60% and 80% (w/w) loadings] with Matrimid$^\circledR$ as the polymer matrix. The membranes were annealed at 240° C in a vacuum oven for overnight. The 80% (w/w) ZIF-8/Matrimid$^\circledR$ MMM was not tested for permeability because it cracked in the cell upon exposure to the upstream pressure. XRD plots acquired from the MMMs (see Fig. 4c) showed that the ZIF-8 material was still intact after membrane fabrication and annealing. SEM images (Fig. 6) were acquired from the air-surfaces and cross-sections of the membranes with different ZIF-8 loadings. The surface images showed the incorporation of the ZIF-8 particles into the polymer matrix, wherein there was increased ZIF-8 content with increased loading. Due to their large surface area, the nanosized ZIF-8 particles will theoretically yield better polymer/particle interfacial contact that can lead to a higher percentage loading in the polymer matrix. Also, the inorganic/organic hybrid nature of the ZIF-8 nanoparticle can result in an increased interaction with the...
polymer. Even so, the ZIF-8 nanocrystals tended to aggregate into sub-micrometer particles that were evenly dispersed in the polymer. The SEM images of the membrane cross-sections also showed uniform dispersion of the ZIF-8 material in the polymer matrix. The presence of the concentric cavities in the MMMs, especially at low loadings of ZIF-8, showed that there was strong interfacial contact between Matrimid® and the ZIF-8 nanoparticles, although it was not strong enough to break up the aggregated nanocrystals. Debonding of the nanoparticles from the matrix due to interfacial stress concentration would have also resulted in the formation of fibrillated matrix circles [58]. In addition, freeze fracturing of the membranes to produce the cross-sections could have resulted in debonding of the agglomerates leading to the formation of the cavities [59,60]. At higher loadings of ZIF-8 [e.g. 80% (w/w)], the concentric cavities become less evident because there is less interfacial contact of the ZIF-8 with Matrimid®. The aggregated ZIF-8 particles are more prominent at this loading. The SEM images of the pure Matrimid® membranes revealed a smooth surface and cross-section (images not shown). SEM was also used to measure the thickness of the fabricated MMMs, which averaged 40 ± 10 μm.

The mechanical properties of the ZIF-8/Matrimid® MMMs were obtained from tensile testing (Table 1), and the data showed an increase in the Young’s modulus at 20% (w/w) ZIF-8 loading, followed by a decrease at 30% (w/w) and higher loadings. These results indicate that there was good interfacial contact between the ZIF-8 nanoparticles and Matrimid® at low loadings, specifically at 20% (w/w), resulting in an increase in Young’s modulus. However, at higher loadings the MMMs become more brittle resulting in a decrease in Young’s modulus. This effect could be due to the aggregation of ZIF-8 particles at high loadings resulting in less contact between the ZIF-8 nanoparticles and the polymer matrix [61]. The tensile strength of the MMMs showed a similar trend. The strength is generally degraded due to aggregation [62] and the formation of a more rigid mixed-matrix membrane with the increasing presence of ZIF-8 nanocrystals [27].

The ATR-FTIR spectra of the MMMs are shown in Fig. 7. The Matrimid® film (Fig. 7a) exhibited peaks at 2956, 1788, 1715, 1672, 1510, 1485, 1363, and 1089 cm⁻¹. The band at 2956 cm⁻¹ is attributed to the C–H stretching mode of the methyl group. Peaks at 1778 and 1715 cm⁻¹ are assigned to the symmetric and asymmetric stretching of the C=O groups of the imide. The band at 1672 cm⁻¹ is assigned to the benzophenone C=O stretching mode. The bands at 1510 and 1488 cm⁻¹ have been assigned to the aromatic stretching of the para-disubstituted phenyl group. The 1363 and 1089 cm⁻¹ absorption bands are for the stretching modes of the C–N–C of the imide 5-membered ring. The bands for ZIF-8 (Fig. 7b) at 1580 cm⁻¹ (C=N stretch) and 1145 and 990 cm⁻¹ (C–N stretch) grow in intensity as the ZIF-8 loading increases. For the ZIF-8/Matrimid® MMMs, the FTIR spectrum (Fig. 7c) shows features that are present for both ZIF-8 and Matrimid®. However, the C=N band for ZIF-8 at 1580 cm⁻¹ is not well pronounced because it is masked by the C=O and C=C bands of Matrimid® [63]. No apparent shifts in the bands were observed for the MMMs when compared with ZIF-8 or pure Matrimid® suggesting that a strong chemical interaction had not occurred.

<table>
<thead>
<tr>
<th>ZIF-8 loading (%)</th>
<th>Young’s modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
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<tbody>
<tr>
<td>0</td>
<td>2.5 ± 0.2</td>
<td>109.0 ± 3.5</td>
</tr>
<tr>
<td>20</td>
<td>3.5 ± 0.3</td>
<td>98.1 ± 13.3</td>
</tr>
<tr>
<td>30</td>
<td>3.2 ± 0.2</td>
<td>93.4 ± 5.6</td>
</tr>
<tr>
<td>40</td>
<td>3.1 ± 0.1</td>
<td>85.4 ± 11.5</td>
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<tr>
<td>50</td>
<td>2.9 ± 0.1</td>
<td>67.1 ± 5.0</td>
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<tr>
<td>60</td>
<td>2.2 ± 0.1</td>
<td>47.6 ± 3.1</td>
</tr>
</tbody>
</table>

Table 1 Young’s modulus and tensile strength of ZIF-8/Matrimid® MMMs.

The numerical values of permeability, given in Table 1 (Supporting information), are reported as the arithmetic mean of 4 or more membranes plus or minus the standard deviation. In the lower half of the table, the individual permeability values are reported for each pure Matrimid® [0% (w/w) ZIF-8 loading] and 40% (w/w) ZIF-8 membrane tested. The kinetic diameters of the gases increase in the order of H2 (2.89 Å) < CO2 (3.3 Å) < O2 (3.46 Å) < N2 (3.64 Å) < CH4 (3.8 Å) < C3H8 (4.3 Å), and the permeabilities of the gases in pure Matrimid® increased with decreasing kinetic diameter. The condensability of the gases increases in the order of H2 < N2 < O2 < CH4 < C3H8 < CO2 according to their critical temperatures. The permeability values obtained for Matrimid® are comparable to those reported in the literature [18,19,27,64]. Figs. 8 and 9 graphically show the gas permeability trends for the ZIF-8/Matrimid® MMMs at the different % (w/w) ZIF-8 loadings, where the height of the column represents the mean and the error bar reflects the standard deviation. The standard deviation provides a quantitative description of the spread or dispersion of the individual permeability values about the mean. Typically, the percent standard deviation for permeability measurements of pure polymers is on the order of 10% or less, as reflected by Matrimid® in Table 1 (Supporting information), and is attributed to the error.
in the permeability measurement (see above) as well as the variation in thickness within a given membrane and its associated measurement error. In contrast, the percent standard deviation for permeability measurements of MMMs is higher, for example, up to 20% for the 40% (w/w) ZIF-8 loading (see Table 1, Supplementary Information). Compared to pure Matrimid®, the additional error for the MMMs is likely caused by the incomplete dispersion of ZIF-8 nanoparticles in the polymer matrix that becomes even more pronounced at higher loadings. At the low loading of 20% (w/w) ZIF-8, gas permeabilities for the MMM were comparable to those of Matrimid®. However, there was a measurable increase in permeability at 30% (w/w), and at 40% (w/w) a significant increase in permeability was observed for all gases tested compared to Matrimid®. 271% for CH₄ from 0.24 to 0.89 Barrers, 239% for N₂ from 0.31 to 1.05 Barrers, 170% for O₂ from 2.18 to 5.88 Barrers, 158% for CO₂ from 9.52 to 24.55 Barrers, 147% for H₂ from 28.88 to 71.22 Barrers, and 53% for C₃H₈ from 0.34 to 0.52 Barrers. This increase in permeability is in contrast to results reported by Moore et al. [29] for hybrid membrane materials in which a decrease in permeability was observed with increased additive loading. For our system, the increase in permeability up to 40% (w/w) suggests that the addition of ZIF-8 nanoparticles to Matrimid® increases the distance between polymer chains creating more polymer free volume. It has been reported that nanoparticles disrupt chain packing in other glassy polymers leading to increases in polymer free volume and permeability [65-67]. For example, Merkel et al. incorporated fumed silica nanoparticles into poly(4-methyl-2-pentene) resulting in an increase in polymer free volume and a significant enhancement in permeability [65]. Similarly, Ahn et al. discovered that the addition of silica nanoparticles to polysulfone significantly enhanced gas permeability [66]. In addition, at high loadings, gas penetrants of an appropriate diameter diffuse through the pores of the additive. The 3.4 Å pore aperture of the ZIF-8 structure selectively transports small gas molecules, such as H₂ and CO₂, resulting in their relatively higher permeability values at this loading.

At the 50% (w/w) ZIF-8 loading, the permeabilities of all gases decreased significantly relative to the 40% (w/w) loading. For CH₄, the permeability decreased by 94% from 0.89 to 0.05 Barrer approaching the detection limit of our instrument at these experimental conditions as reflected by the large standard deviation in the measurement. Decreases of 81% were observed from 0.52 to 0.10 Barrer for C₃H₈, from 24.55 to 4.72 Barrer for CO₂, and from 5.88 to 1.13 Barrer for O₂. N₂ decreased by 83% from 1.05 to 0.18 Barrer, and H₂ decreased by 75% from 71.22 to 18.07 Barrer. In this case, the higher percentage of ZIF-8 nanoparticles in the MMM reduced the amount of polymer available for gas transport, increased the diffusion pathlength for the gas penetrants as they were forced to take a more tortuous path around the ZIF-8 nanoparticles [68-70], and likely increased the density of the remaining polymer chains thereby reducing free volume in the membrane [71]. Sadeghi et al. showed that the presence of silica nanoparticles at loadings up to 20 wt% in polybenzimidazole decreased gas permeability by impeding the diffusion of gases through the polymer matrix due to an increase in tortuosity [70]. The similar magnitudes of the decrease in permeabilities for all gases tested suggest that permeability was primarily governed by gas diffusion through the polymer matrix at this 50% (w/w) ZIF-8 loading. Specifically, increased tortuosity and polymer density overwhelmed any preferential access to the ZIF-8 pores by the smaller gas molecules. These results suggest that there is an upper limit to the amount of additive that can enhance the permeability properties of a given polymer.

Compared to the 50% (w/w) ZIF-8 loading, there was an apparent increase in permeability for all gases at the 60% loading. This increase could only be due to the beginning formation of non-separative voids between aggregated ZIF-8 nanocrystals as the particle loading continued to increase. Süer et al. incorporated zeolite 4Å particles into polyethersulfone and found that, at higher loadings, agglomeration of the zeolite crystals created void spaces that resulted in an increase in gas permeability [71].

Figs. 10 and 11 show the graphical representations of the ideal selectivity values, which are given in Table 2 in the Supplementary Information section. For the majority of gas pairs (O₂/N₂, CH₄/N₂, H₂/O₂, H₂/CO₂, H₂/N₂), there is no significant change in the ideal selectivity up to 40% (w/w) ZIF-8 loading. This result is expected because an increase in polymer free volume does not contribute to gas transport selectivity [72]. However, the ZIF-8 nanocrystal could alter the polymer chain packing at loadings up to 40% (w/w), which could result in defects that do not greatly alter selectivities [73]. At 50% (w/w) ZIF-8 loading, an increase in selectivity is observed specifically for gas pairs such as CO₂/CH₄ and H₂/CH₄ that contain small gas molecules. Compared to Matrimid®, the selectivity increased 213% for CO₂/CH₄ from 40 to 124, and 290% for H₂/CH₄ from 121 to 472. These values only estimate the upper limit of ideal selectivities for these gas pairs because the CH₄ permeabilities at this loading are low and challenge our measurement capabilities. Nevertheless, these high selectivities are attributed to a molecular sieving effect of the small pore aperture of ZIF-8.
Table 2
Separation of gas mixtures with Matrimid® and ZIF-8/Matrimid® MMMs.

<table>
<thead>
<tr>
<th>ZIF-8 loading (w/w)</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ideal H₂/CO₂</td>
</tr>
<tr>
<td>Matrimid®</td>
<td>2.96 ± 0.11</td>
</tr>
<tr>
<td>50%</td>
<td>3.82 ± 0.11</td>
</tr>
<tr>
<td>60%</td>
<td>4.43 ± 0.10</td>
</tr>
</tbody>
</table>

* Standard deviation is large due to low CH₄ permeability at 50% (Table 1 Suppl.), which is at measurement limit of permeameter.

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Fig. 10. Ideal selectivity plots of ZIF-8/Matrimid® MMMs for O₂/N₂, CH₄/N₂, H₂/O₂, H₂/CO₂, and H₂/C₃H₈ at 0%, 20%, 30%, 40%, 50%, and 60% (w/w) ZIF-8 loadings.

that cannot accommodate larger gas molecules like CH₄. Venna and Carreon reported that the small pore aperture of ZIF-8 favors the diffusion of small gas molecules such as CO₂ [74]. This sieving effect is also evident for H₂/C₃H₈ and CO₂/C₃H₈ gas pairs where there is a continuous increase in selectivity as the ZIF-8 loading is increased. This result is consistent with H₂ and CO₂ fitting inside the ZIF-8 pore, while the larger propane molecule is excluded. For the 50% (w/w) ZIF-8/Matrimid® membrane, there appears to be a transition from a polymer driven to a ZIF-8 controlled gas transport process because the gas penetrants are forced to diffuse through the pores of ZIF-8. As-synthesized, non-activated, pore-filled ZIF-8 was used as a control to demonstrate the sieving effect of the pores for the transport of small gases. In this case, the ZIF-8 pores were filled with the synthesis solvent DMF. The permeabilities for the 50% (w/w) filled ZIF-8/Matrimid® MMM were significantly higher than for Matrimid® and for the MMM made with activated ZIF-8 at the same loading. The optimum control experiment would be to use solid-filled ZIF-8 additives in Matrimid® as the synthesis solvent could potentially affect gas transport leading to increased permeability. However, the selectivities for the control MMM were comparable to Matrimid® suggesting that when the pores of ZIF-8 are blocked, gas permeability is governed by the polymer. The enhanced CO₂/CH₄ selectivity performance of the ZIF-8/Matrimid® MMMs at higher loadings are comparable to a class of thermally modified polymers that have molecular sieving properties [17].

The diffusivity values calculated from the time-lag in the plots of downstream pressure versus time (data not shown) increased for the smaller gas molecules, such as CO₂, O₂, and N₂, up to 40% (w/w) ZIF-8 loading, and then decreased at higher loadings. In contrast, the diffusivity of CH₄ and C₃H₈ decreased continuously with increased ZIF-8 content indicating that the larger gas molecules could not easily diffuse through either the ZIF-8 pores or the rigidified polymer. This result illustrates the role that ZIF-8 has on gas transport through the membrane. The relative magnitudes of diffusivity also correlate with the kinetic diameters of the gases, wherein the smaller molecules diffused faster through the membrane.

Gas mixtures of H₂/CO₂ (50:50 mol%) and CO₂/CH₄ (10:90 mol%) were used to test 50% and 60% (w/w) ZIF-8/Matrimid® MMMs using a minimum of 4 membranes per loading. The selectivities obtained for both gas mixtures at both ZIF-8 loadings were comparable to the obtained ideal selectivities considering their respective standard deviations (Table 2). Some variation in selectivity between pure gas and mixed gas measurements has always been observed and is believed to arise from the effects of penetrant competition, gas phase non-ideality, plasticization of the polymer, and gas polarization [75,76]. The selectivities for 50/50 H₂/CO₂ are consistent with the observation that both small gas molecules can readily diffuse through the aperture and into the pores of ZIF-8. This result also suggests that there is no competitive adsorption for the H₂/CO₂ gas blend. In contrast, an increase in selectivity was expected for the 10/90 CO₂/CH₄ gas mixture, as compared to the pure gases (i.e., ideal selectivity), due to the faster diffusion of the smaller CO₂ gas molecule. However, this result was not observed suggesting that a competition existed between the gas penetrants in which the larger CH₄ molecule, which was present at a much higher concentration than CO₂, could have blocked the pore aperture. Also, studies have shown that CH₄ can slowly pass through the 3.4 Å pore aperture of ZIF-8, indicating that the framework structure is flexible rather than static in nature [77].

4. Conclusions

ZIF-8/Matrimid® MMMs with loadings up to 60% (w/w) ZIF-8 were fabricated and tested. Higher loadings resulted in less flexible MMMs that were difficult to handle. This observation was supported by a measured decrease in tensile strength as the loading of ZIF-8 increased. The permeability values obtained for all gases tested increased as the ZIF-8 loading increased up to 40% (w/w).
However, at higher loadings of 50% and 60% (w/w), the permeability decreased for all gases. This result suggests a transition from a polymer-driven to a ZIF-8-controlled gas transport process, where at higher loadings the sieving effect of the ZIF-8 nanocrystals is more evident. Increases in ideal selectivities were obtained at the higher ZIF-8 loadings for gas pairs containing small gas molecules, such as H₂/CH₄, CO₂/CH₄, H₂/C₃H₈, and CO₂/C₃H₈, suggesting that the ZIF-8 may act as a molecular sieve for smaller gas molecules. This ability of the ZIF-8 material to selectively transport smaller gas molecules, such as H₂ and CO₂, combined with its stability at high temperatures, makes it a promising material for gas separations at higher pressures and higher temperatures, at which most industrial gas separation processes are conducted.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.memsci.2010.06.017.

References


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