Synthesis and Preparation of Asymmetric PSf/ZIF-8 Mixed Matrix Membrane for CO₂/CH₄ Separation

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Abstract

Utilizing nano-size filler into polymer matrix would overcome challenges in developing MMM by providing good dispersion in polymer matrix, high contact polymer-filler even at low filler loading. Asymmetric neat Polysulfone (PSf) and PSf/Zeolitic Imidazole Framework-8 (PSf/ZIF-8) mixed matrix membrane was prepared using dry/wet inversion method. Membrane prepared was coated with 3wt% of polydimethylsiloxane (PDMS) in n-hexane and undergoes heat treatment. The membranes was characterized using x-ray diffraction (XRD), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and gas permeation test at 4 bar. XRD pattern revealed that ZIF-8 was successfully synthesis with crystal size around 73nm. Lowered membrane Tg after embodiment of ZIF-8 suggests that additional free volume form, while thermal stability up to 350°C related to ZIF-8 stability. Neat PSf prepared shows CO₂ permeance at 4.97 GPU with CO₂/CH₄ selectivity at 7.52. Interestingly, incorporation of ZIF-8 showing improvement for both CO₂ permeance and CO₂/CH₄ selectivity up to 51% and 47% respectively. Thus, employing nano ZIF-8 as filler into PSf matrix has result promising membrane for CO₂/CH₄ separation.

Keywords: Mixed matrix membrane; PSf/ZIF-8; CO₂/CH₄ separation

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1.0 INTRODUCTION

Separation of CO₂ based on polymeric membrane emerges as potential approach to replace conventional techniques. Due to low capital cost, modest energy requirement and ease to fabricate, research on polymeric membrane has gain lots of attention in the last decades. Although polymeric membranes provide many advantages, its performance is bounded by Robeson’s trade-off limit between selectivity and permeability [1]. Incorporating inorganic filler, such as zeolite, carbon nanotube, activated carbon and carbon molecular sieve, into polymer matrices to surpass Robeson’s trade-off limit, called mixed matrix membrane (MMM).

Several guidelines have been highlighted in developing high performance MMM, most importantly is high intrinsic separation properties of both polymer and filler. Inorganic fillers such as zeolite and carbon molecular sieve, posses separation properties surpass Robeson’s trade-off limit, were among the first to be incorporated into polymer matrix. However, inorganic fillers has poor interaction with polymer matrix and often leads to defective membrane. Developing MMM defect-free membrane remain biggest challenges. Polymer-filler incompatibility defected membrane through particle agglomeration, un-selective voids formation, filler pore blockage and “sieve-in-cage” morphology leads to low separation properties. Metal organic frameworks (MOFs) emerge as potential filler due to organic linkers exist in its structure have good interaction with polymer. Besides, MOFs consist of large surface area, high adsorption capacity, ease to modifications and high affinity towards certain gas gives the edge for MOFs to be implemented as filler. Among MOFs, zeolitic imidazole framework-8 (ZIF-8) is one of the most investigated MOFs, ZIF-8 is porous crystalline structure with M-Im-M angle (M-metal) near to 145°, coincident with the Si-O-Si angle found in many zeolites. ZIF-8 show good chemical stability against polar and nonpolar solvents [2], reorientation of its structure at high pressure [3, 4] and high mechanical strength [5].

Another concern regarding MMM is the amount of filler loading. High filler loading would provide higher penetrant-filler interaction and increase MMM separation properties. However, it also likely leads to particles agglomeration. Literatures suggest that increased filler loading increase its separation performance, but eventually leads to particles to agglomerate and deteriorating its performance [6, 7]. It should be noted that high filler loading would directly reflect on membrane production cost. In contrast, incorporating small amount of filler give insignificant improvement on membrane separation properties, but highly unlikely for particles to agglomerate. Minimum filler loading with significant
improvement of membrane performance would be the ideal MMM. The study by Hashemifard et al. [8] showed that significant enhancement of membrane separation properties can be achieved even at low loading. In the study, 0.5wt% (total solid) of clay mineral (C10I50A) shows CO2 permeance and CO2/CH4 selectivity increased to 24% and 28%, respectively due to combination of polymer chain disruption and tortuous path for CH4 to permeate. In other words, layered clay minerals is exfoliated into nano layer [9] provide lower external surface area to volume ratio and ease to interact with polymer chain [10-13]. Therefore, significant improvement of membrane separation properties can be achieved using nano filler even at low filler loading.

In order to develop high performance MMM at low filler loading, nano filler with good polymer-filler interaction is necessary. Thus, this study aims to develop nano-size ZIF-8 using aqueous system method[14] with base-type. Addition of triethylamine (TEA) as base-type additive during synthesis step show nano-size ZIF-8 can be produce due to deprotonated ligands. The influence of nano ZIF-8 dispersed in polymer matrix is investigated. Up to this date, the development of MMM-MOF mainly focused on dense membrane [15-18]. This study also provides the preparation of asymmetric MMM using dry/wet inversion method for CO2/CH4 separation.

2.0 EXPERIMENTAL

2.1 Materials

Zinc nitrate hexahydrate (Zn(NO3)2·6H2O), 2-methylimidazole (H-MeIM) and triethylamine (TEA) was purchased from Sigma Aldrich. Polysulfone (PSUdel® P-3500) was purchased from Solvay Plastic. N,N-methylypyrrolidone (NMP), tetrahydrofuran (THF) and ethanol was purchased from Merk. For coating solution, polydimethylsiloxane (PDMS) was purchased from Sigma Aldrich and n-hexane was purchased from Merk. All chemicals were used without further purification.

2.2 ZIF-8 Synthesis

ZIF-8 was prepared using aqueous system method [14] with base-type. Briefly, Zinc nitrate (10g) was dissolved into deionized water (100g) while H-MeIM (16.56g) was dissolve into TEA (10ml) in 400g of deionized water. Zinc nitrate solution was added to the H-MeIM solution and cloudy solution formed upon mixing the solutions. The solution was stirred continuously for 30 minutes. The solution was centrifuge to remove separate the mixture and washed with deionized water several times to remove reactants. The solution was dried in oven at 60°C overnight. The powder formed was collected and weighted to calculate mass yield

2.3 Membrane Preparation

Asymmetric flat sheet neat membranes was prepared by casting solution consisted of polysulfone (30 wt%), NMP (35 wt%), THF (30 wt%), EtOH (5 wt%) and ZIF-8 (1 wt% from total solid). Approximately 10% of polymer solution was then added to the MOFs suspension to priming the MOFs particles. Remaining polymer was added until dissolved. The solution was left at ambient to check solution homogeneity. Casting process was performed by hand-casting at ambient atmosphere. Then, membrane was left for free standing at atmosphere for a certain period before immersion in an aqueous bath and remained there for 1 day. Finally, the washed membrane was solvent-exchanged with methanol for 2 h, followed by n-hexane for 2 h and then air-dried for 1 day. MMM with 1wt% of ZIF-8 is marked as MMM-1.

Membranes were dip-coated for 10 minutes in 3wt% PDMS in n-hexane to seal possible pinhole on membrane surface. Then, membrane undergoes “curing” at 60°C overnight.

2.1 Characterization

Differential scanning calorimeter (DSC) is used to determine the glass transition temperature (Tg) of prepared membranes using Mettler Toledo DSC 822e. The membrane sample was cut into small pieces, weighed and placed into pre-weighed aluminum crucible. Then, the sample was heated from 50 to 400°C at a heating rate of 10°C min⁻¹ in the first cycle to remove the thermal history. The sample was cooled from 400 to 30°C at the rate of 10°C min⁻¹. The same heating protocol was repeated in the next heating cycle. Tg of the sample was determined as the midpoint temperature of the transition region in the second heating cycle.

Differential scanning calorimetric analysis (DSC) uses to study the glass transition temperature of prepared samples. TGA records the weight changes of sample when heated continuously. The samples were heated from 50 to 900°C at the heating rate of 10°C min⁻¹ under nitrogen atmosphere with a nitrogen flow rate of 20 mL min⁻¹.

XRD analysis used to confirm the phase of ZIF-8 similar with literature. X-Ray Diffraction (XRD) analysis using Siemens D5000 Diffractometer is non-destructive analysis to measuring wavelength of samples and identifies its structure. The XRD will emit x-rays to the sample and the x-rays diffracted at different angles and intensity by using CuKα radiation with a wavelength (λ) = 1.54Å at room temperature. Particle size estimation was calculated using Williamson-Hall equation [19, 20].

Gas permeation tests were performed with a permeation cell by using pure methane (CH4) and carbon dioxide (CO2), respectively. Circular membrane discs with an effective permeation area of 13.5 cm² were used. Feed pressure was controlled at 4 bar while permeate side was opened to atmosphere. Experiments were carried out at ambient temperature. Permeance are calculated using Equation (1)

$$P_i = \frac{1}{A \Delta P} \int_{t_i}^{t} \frac{dV_i}{dt}$$  
(1)

where i represents the gas penetrant i, V is the volume of gas permeated through the membrane (cm³, STP), A the effective membrane area (cm²), t the permeation time (s) and ΔP is the transmembrane pressure drop (cmHg). Permeances is expressed in gas permeation units, GPU, where

1 GPU = 1×10⁻⁶ cm³ (STP) cm⁻² s⁻¹ cmHg⁻¹.

Selectivity was obtained using Equation (2):

$$\alpha_{ij} = \frac{(P_i/P_j)}{(P_i/P_j)}$$  
(2)
3.0 RESULTS AND DISCUSSION

3.1 Characterization

The synthesized ZIF-8 was first characterized by XRD to identify phase purity and crystal structure. XRD pattern of synthesized ZIF-8 was shown in Figure 1 and the prepared ZIF-8 shows high crystalline structure. Compared to the Basolite Z1200, the intensity of the as-synthesized peak, especially on 20 = 7.25, are significantly lower. The differences can be related to guest molecule occupying ZIF-8 pores caused pattern destructive and retarded gas uptake capacity [21, 22]. Besides, the BET surface area of prepared ZIF-8 is 413.97 m²/g, significantly lower than Basolite Z1200 (1223.19 m²/g) are also related to the occupied ZIF-8 pore. Particle size of synthesized ZIF-8 is estimated around 73 nm using Williamson-Hall plot. ZIF-8 crystal then further confirmed by FTIR, indicate no foreign chemical bond exist in the molecule to cause the destructive pattern of XRD (Figure 1b).

The gas permeation was conducted to evaluate ideal separation properties of both membranes are presented in Table 1. The gas permeation of MMM-1 shows better in both CO₂ permeance and CO₂/CH₄ selectivity. Increased in CO₂ permeance with incorporated ZIF-8 create more free volume among polymer chain [28, 29] as supported by lowered membrane Tg. Thus, increase flux for both tested gases are evident. Significant increment in CO₂/CH₄ selectivity suggest that CO₂ preferred to access filler’s pore rather than bypassing it due to interaction between quadrupole moment of CO₂ and unsaturated metal sites in ZIF-8 [30, 31]. Table 2 shows relative comparison between this work to literature data using different polymer-filler combination. Although small amount of filler incorporated in polymer matrix was implement in this study, significant improvement of both CO₂ permeance and CO₂/CH₄ selectivity somehow comparable with literature data. It is expected since synthesized ZIF-8 in nano-scale provide lower external surface area to volume ratio and ease to interact with polymer chain [10-13]. Significant improvement of MMM performances using nano-sized ZIF-8 also suggest that better dispersion of filler into polymer matrix ease interaction between filler-penetrant.

The thermal stability of membranes are illustrated in Figure 2. At temperature 130°C-350°C, weight loss is evident in both membrane, with neat PSf at 1.23 % while MMM-1at 2.43 %. The weight loss are attribute to residual solvent evaporation. MMM-1 showed greater weight loss compared to neat PSf results from residual solvent trapped in ZIF-8’s [23]. At temperature above 350°C, the second weight loss occurred in regards to degradation of polymer matrix. MMM-1 shows greater weight loss than neat PSf due to the oxidation of ZIF-8 and turn to ZnO [24]. The change in membrane Tg is evident at low ZIF-8 loading, where Tg of MMM-1 is 155°C while neat PSf is 165°C. The decrease in membrane Tg indicate that Disruption of polymer chain, creating flexible intermediate phase between polymer and nano ZIF-8 [16, 23].

### Table 1 CO₂ and CH₄ permeation for neat PSf and PSf/ZIF-8

<table>
<thead>
<tr>
<th>Membrane</th>
<th>P₄₅₆₈ (GPU)</th>
<th>P₄₅₆₈ (GPU)</th>
<th>α CO₂/CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PSf</td>
<td>0.66 ± 0.30</td>
<td>4.97 ± 0.12</td>
<td>7.52</td>
</tr>
<tr>
<td>MMM-1</td>
<td>0.68 ± 0.06</td>
<td>7.50 ± 1.81</td>
<td>11.03</td>
</tr>
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</table>

*the gas permeation was conducted at 4 bar, 27°C

### Table 2 Comparison between literatures

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Filler</th>
<th>Loading (%)</th>
<th>Δ</th>
<th>P₄₅₆₈ (GPU)</th>
<th>Δ</th>
<th>α CO₂/CH₄</th>
<th>Reference</th>
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<tbody>
<tr>
<td>PPEES</td>
<td>ZIF-8</td>
<td>10</td>
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<td>1.393</td>
<td>1.29</td>
<td></td>
<td>[15, 16]</td>
</tr>
<tr>
<td>PSf</td>
<td>MIL-53(AI)</td>
<td>25</td>
<td>1</td>
<td>1.2</td>
<td>1.84</td>
<td></td>
<td>[13]</td>
</tr>
<tr>
<td>PVAc</td>
<td>Zeolite 4A</td>
<td>56</td>
<td>1</td>
<td>1.009</td>
<td>1.624</td>
<td></td>
<td>[25]</td>
</tr>
<tr>
<td>PI</td>
<td>Zeolite FAU/FMT</td>
<td>25</td>
<td>2.497</td>
<td>0.861</td>
<td></td>
<td>[26]</td>
<td></td>
</tr>
<tr>
<td>PSf/PI</td>
<td>Silica Sol</td>
<td>13</td>
<td>1</td>
<td>2.58</td>
<td>2.027</td>
<td></td>
<td>[27]</td>
</tr>
<tr>
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<td>ZIF-8</td>
<td>1</td>
<td>1</td>
<td>1.51</td>
<td>1.467</td>
<td>This work</td>
<td></td>
</tr>
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</table>

Figure 1 a) XRD pattern of as-synthesized ZIF-8 (solid line) and compared with Basolite Z1200 (dashed line), b) comparison between FTIR transmittance of synthesized ZIF-8 and literature [14]
CONCLUSION

Nano-size ZIF-8 has been successfully synthesized and incorporated into PSi matrix. The membrane was characterized via TGA and DSC has shown that ZIF-8 altered PSi membrane properties. Besides, improvement in both CO2 permeance and CO2/CH4 selectivity are show due to good interaction between quadrupole moment of CO2, molecular sieving effect and unsaturated metal sites in ZIF-8. Besides, nano-ZIF-8 use in this study provide better dispersion through polymer phase, which evident through significant increase separation properties. Thus, the MMM prepared with nano-filler show great potential to be further improvement and commercialized.

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