Enhancement of CO₂ permeation properties of polymeric membrane by incorporating metal organic framework

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Abstract. This research work focuses on the fabrication of mixed matrix membranes (MMMs) for the enhancement of CO₂ removal from CH₄. Zeolitic imidazolate framework (ZIF-8) with a framework of 0.34 nm pore size which favours CO₂ adsorption is used as filler in this work. Different loadings of ZIF-8 filler were incorporated into polysulfone (PSf) polymer matrix. From the EDX mapping, the morphology of the ZIF-8/PSf MMMs has shown compatibility between the polymer and filler phases. The MMMs demonstrated an increment of 8°C in glass transition temperature, Tg compared to the pure PSf. Based on the permeation results, MMM loaded with 1 wt% of ZIF-8 showed the highest performance with CO₂ and CH₄ permeability of 33.12 Barrer and 0.85 Barrer respectively, and CO₂/CH₄ ideal selectivity of 38.8. The development of this new type of MMM has great potential to be utilized in CO₂/CH₄ separation process.

1. Introduction

Global demand of natural gas is expected to grow tremendously at a rate of 7% annually from the year 2018 to 2020, compared to only 4% annual average growth for the past decade. A clean energy free from CO₂ contaminant is crucial to be primarily used in the petrochemical industry and electricity generation [2]. Besides, the CO₂ capture has been given much attention worldwide in order to minimize the CO₂ emission in protecting the harmful impact on climate change [3]. Up to date, CO₂ has been the largest source in contributing 60% of the global warming effects [3].

Membrane based technology has gained affluent growth and advances as this technology offers attractive features which include cost effectiveness, simple operation and good environment compatibility [4]. Early emerging of polymeric membrane technology involves lower investment costs than the competing technologies [5]. The advantages of polymeric membrane technology such as low investment costs and processing ability however been constrained to the upper performance limit [5] that indirectly shifts the attention to development of inorganic membranes. However, inorganic membranes face difficulties in large scale fabrication due to capital intensive despite having preferable properties [6]. Mixed matrix membranes (MMMs) is a likely resolution where MMM incorporates absolute properties of both polymeric membrane and inorganic materials [7]. The emergence of MMM
has been a potential prospect for the trade-off upper bound of polymeric membranes, separation performance as well as mechanical and thermal stability [8].

ZIF-8, a subclass of metal organic framework (MOF) has been used as filler in the formation of MMM as it combines desirable properties from both zeolites and MOF, such as microporosity, high surface areas and exceptional thermal and chemical stability [9]. It was found that ZIF-8 has high selective adsorption ability [10] towards CO₂, making ZIF-8 a highly appealing material for gas separation applications. On the other hand, PSf possesses attractive properties including, higher mechanical strength, higher plasticization resistance and good thermal resistance [11]. Therefore, in this work, ZIF-8/PSf mixed matrix membranes are fabricated and the performance in CO₂ removal from CH₄ is studied. By using various characterization tools, the effect of ZIF-8 loading on the gas properties including gas permeation and gas pair selectivity were evaluated.

2. Methodology

2.1. Materials

Zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, >98 wt% purity) and 2-methylimidazole (2-MeIM, 98 wt% purity) were purchased from Sigma Aldrich. Polysulfone pellets with weight-average molecular weight (Mw ~35000), methanol (99.8% purity) and chloroform (99.8% purity) were purchased from Merck. The chemicals were used as received.

2.2. Preparation of ZIF-8

Synthesis of ZIF-8 nanoparticles was adopted from our previous work [12]. Two separate solutions, 2-methylimidazole (2-MeIM) and zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) was dissolved in methanol, respectively. The prepared solutions were then mixed and stirred for 1 h. The crystals were obtained via centrifugation at 7800 rpm for a duration of 5 min. The formed crystals were then rinsed with methanol for few times and overnight drying at 85 °C in the oven. The dried ZIF-8 nanocrystals were grinded into powder form and stored in the desiccator.

2.3. Fabrication of membranes

In the current work, pure PSf flat sheet membrane was fabricated by using solution casting method as reported in the literature [13]. PSf pellets were dried in an oven at 60 °C prior to fabrication to remove moisture. After that, PSf pellets was dissolved in chloroform in a sealed glass bottle and left for 8 h, stirring at room temperature. The polymer solution formulation was set at 10% w/v. The resultant PSf solution was left for degassing overnight at room temperature. The PSf solution was subsequently casted onto a petri dish and covered with a glass plate. The PSf solution was left for 24 h to allow slow solvent evaporation at room temperature. Finally, the membrane film was peeled off from petri dish and dried at 60 °C for 8 h in vacuum oven to remove moisture and remaining solvent.

Similar casting method was used to fabricate ZIF-8/PSf membranes [13]. An appropriate amount of PSf was dissolved in chloroform in a sealed glass bottle. The polymer solution was left stirring for 8 h at room temperature. In the meantime, different amount of ZIF-8 was dissolved into chloroform solvent in different sealed glass bottles. The filler suspension was alternately stirred and sonicated for 1 h to disperse the particle. Subsequently, priming method was adapted where 10% of the PSf solution was added into the filler-solvent suspension, followed by alternate stirring and sonication for 1 h. The step was repeated by adding the remaining 90% of the PSf solution into filler-solvent suspension. The final mixture solutions were vigorously stirred for 1 h before casted onto the petri dish. The mixture solutions were left at room temperature for 24 h to allow solvent evaporation. Table 1 summarized the membranes fabricated in this present work.
Table 1. Membranes fabricated in this work.

| Membrane   | ZIF-8 wt% |
|------------|-----------|
| PSf        | 0         |
| ZIF 8-0.5/PSf | 0.5      |
| ZIF 8-1.0/PSf | 1.0      |
| ZIF 8-1.5/PSf | 1.5      |
| ZIF 8-2.0/PSf | 2.0      |

2.4. Characterization of ZIF-8 filler and resultant membranes

X-ray diffraction (XRD) was performed to obtain the crystalline structure at 2θ from 5° ≤ 2θ ≤ 30° with CuKα radiation of 1.54059 Å wavelength (X’Pert3 Powder, PANalytical). Field emission scanning electron microscope (FESEM) was conducted to observe the morphology and determine the size of the filler (SUPRA 55VP, Varl Zeiss Inc). Differential scanning calorimetry (DSC) was performed to obtain the glass transition temperature (Tg) of the resultant membranes (Thermal Analysis (TA) instruments DSC Q2000). The distribution of the filler in the polymer matrix was investigated by energy dispersion X-ray (EDX) mapping (Oxford Instrument Inca).

2.5. Gas Permeation Performance

The single gas permeation for CO₂ and CH₄ was conducted for the resultant membranes using a custom-built permeation test rig operated at 5 bar and 25°C [14]. The permeability for single gas is calculated using equation (1) as follows [15]:

\[ P = \frac{Q}{A\Delta p} \]  

(1)

where \( P \) refers to the membrane permeability (Barrer), \( Q \) refers to the volumetric flow rate of permeate (cm³(STP)/s), \( l \) is the thickness of membrane (cm), \( A \) refers to the membrane area (cm²) and \( \Delta p \) is the differential pressure across the membrane (cmHg). The CO₂/CH₄ selectivity is calculated using equation (2) as follows [15]:

\[ \alpha_{CO_2/CH_4} = \frac{P_{CO_2}}{P_{CH_4}} \]  

(2)

where \( \alpha \) represents the ideal selectivity of membrane.

3. Results and Discussion

3.1. Characterization of particles and membranes

The characterization results of the ZIF-8 nanoparticles by using FESEM and XRD were shown in figure 1 and 2, respectively. From figure 1, the ZIF-8 particles possess the rhombic dodecahedron shaped, which is coherent with the results reported in the literature [9, 15]. An average ZIF-8 particle size of ≈50 nm is obtained in this work. Meanwhile, figure 2 shows the crystallinity of the ZIF-8 particles at 20 range from 5° to 30° using XRD. The intensive peaks are clearly observed at 20 = 7.56°, 10.58°, 12.94° and 18.27°. The XRD pattern of ZIF-8 is in close agreement with the reported literatures [10, 16]. Thus, it can be concluded that ZIF-8 nanoparticles with high crystallinity was successfully synthesized in this work.
Figure 1. Morphological feature of ZIF-8.

Figure 2. X-ray pattern of ZIF-8 particles obtained in this work.

Figure 3 shows the EDX mapping of the fabricated MMMs. Referring to figure 3, it can be seen that Zn element is well distributed throughout the polymer matrix, reflecting that the filler particles are uniformly dispersed within the membrane. Besides, it can be observed from figure 3 that the concentration of Zn element in MMMs increase with the loading of ZIF-8 particles in the continuous phase. However, at higher ZIF-8 loading of 1.5 and 2.0 wt%, minor aggregations of ZIF-8 particles are found in figure 2 (c) and (d). This results could be due to the nano-ZIF-8 particles formed bigger cluster in the PSf polymer matrix during membrane formation.
Figure 3. EDX mapping of Zn element in the resultant MMMs (a) ZIF 8-0.5/PSf (b) ZIF 8-1.0/PSf (c) ZIF 8-1.5/PSf (d) ZIF 8-2.0/PSf.

Table 2 summarizes the T_g values of the resultant membranes. Based on table 1, the glass transition temperature, T_g of pure PSf is 181.05°C. This T_g value is comparable with the value reported in the literature [17]. Meanwhile, all the resultant MMMs exhibited T_g value from 187.34°C to 189.95°C. These results imply that the addition of ZIF-8 increased the rigidity of the polymer chain. This is mainly attributed from the shifted polymer arrangement and difference in structure of the membrane [18]. Besides, the increase in T_g signify that the interactions between the ZIF-8 particles and polymer has caused the polymer chains in the membrane to be more rigid, thus increasing the crystallinity of the membrane [19].

| Membrane     | T_g (°C) |
|--------------|----------|
| PSf          | 181.05   |
| ZIF 8-0.5/PSf| 187.34   |
| ZIF 8-1.0/PSf| 188.37   |
| ZIF 8-1.5/PSf| 189.40   |
| ZIF 8-2.0/PSf| 189.95   |

3.2. Gas Permeation Performance
The PSf and ZIF-8/PSf MMMs were tested for gas permeation performance in single gases CO_2 and CH_4. Figure 4 shows addition of different filler loadings on the performance of single gas permeability of the membranes. From figure 4, the permeability of CO_2 and CH_4 increases in the resultant MMMs in comparison to PSf membrane. The MMMs exhibits CO_2 permeability (Barrer) of 11.86, 33.12, 34.11, and 25.07, for ZIF 8-0.5/PSf, ZIF 8-1.0/PSf, ZIF 8-1.5/PSf, ZIF 8-2.0/PSf, respectively. Meanwhile, PSf membrane exhibits CO_2 permeability of 6.28 Barrer. The gas permeability value obtained for pure PSf membrane is in comparison with the value reported in the literature [13]. The increase in permeation values for MMMs was contributed by the presence of ZIF-8 particles where the large mesopores of ZIF-
8 allow an easy diffusion route for the transport of gases through the membranes [20]. Furthermore, the electrostatic field of ZIF-8 with quadrupole moment of CO$_2$ eased the permeation of gases [21]. The increase in $T_g$ value of the MMMs further supported the improvement of the gas permeation performance of the membranes.

![Figure 4](image1.png)

**Figure 4.** (a) CO$_2$ and (b) CH$_4$ permeability of the resultant membranes.

Figure 5 demonstrates higher CO$_2$/CH$_4$ selectivity in ZIF-8-0.5/PSf and ZIF-8-1.0/PSf MMMs in comparison to PSf membrane, with selectivity of 35.2 and 38.8, respectively. The increase in CO$_2$ permeability and CO$_2$/CH$_4$ ideal selectivity of ZIF-8-0.5/PSf and ZIF-8-1.0/PSf was validated by the EDX-mapping in figure 3 (a) and (b). A uniform dispersion of filler particles was observed within the membranes which in return increased the gas permeation performance. On the other hand, as shown in figure 5, ZIF-8-1.5/PSf and ZIF-8-2.0/PSf MMMs exhibit lower CO$_2$/CH$_4$ selectivity compared to PSf membrane, with values of 15.4 and 13.2, respectively. The decrease in ideal gas selectivity maybe due the intervention of the packing of polymer chains resulting in unselective highly permeable voids within the membranes [22]. The results obtained further supports the EDX-mapping distribution of particles in figure 3 (c) and (d) where agglomeration of particles were found in the membrane. It can be inferred that the loading of filler and its distribution within the membrane greatly influence the separation performance.

![Figure 5](image2.png)

**Figure 5.** Selectivity of CO$_2$/CH$_4$ of the resultant membranes.
4. Conclusion
In this present work, MMMs incorporated with different loadings of ZIF-8 were fabricated. The successful formation of ZIF-8 filler was confirmed by XRD pattern and FESEM image. From the EDX mapping results, MMMs demonstrated a good dispersion of particles at low loadings and agglomeration of particles occurred when higher filler loadings were embedded in the polymer matrix. Besides, the MMMs exhibited an increment of glass transition temperature, $T_g$ from the DSC characterization. The good distribution of ZIF-8 within PSf polymer has caused increase in both CO$_2$ and CH$_4$ permeability and ideal selectivity of CO$_2$/CH$_4$ to 40% in comparison to PSf membrane. Thus, the MMMs fabricated in this study can be exploited for further enhancement study in terms of its properties.

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