Abstract

The impact of controlling molar ratio of ZIF-8 precursors on Pebax 1657 and Pebax 2533 based Mixed Matrix Membranes (MMMs) on the CO\(_2\) permeability and CO\(_2\)/N\(_2\) ideal selectivity was investigated. Three types of ZIF-8 were synthesized by controlling molar ratio of 2-methylimidazole and zinc nitrate hexahydrate as 2/1, 8/1, and 32/1. The SEM images and XRD patterns of ZIF-8 showed that particle sizes and crystallinity peaks were decreased as molar ratio of ZIF-8 increased. The CO\(_2\) permeability of Pebax MMM was improved by filling with the ZIF-8 particles compared to the pure Pebax. At equivalent temperatures, the highest CO\(_2\) permeability was shown in Pebax 1657/ZIF-8 with the ZIF-8 precursors’ molar ratio of 32/1 and Pebax 2533/ZIF-8 with the molar ratio of 2/1. As molar ratio of ZIF-8 precursors increases, CO\(_2\) permeability of Pebax 1657 was increased by excessive sorption of CO\(_2\) by imidazolium ions in ZIF-8, whereas CO\(_2\) permeability of Pebax 2533 was decreased by decreasing pore size and particle size of ZIF-8. The CO\(_2\) permeability was higher in Pebax 2533/ZIF-8 compared to Pebax 1657/ZIF-8, because Pebax 2533 has more concentrations of polar groups in the polymer matrix than Pebax 1657. However, the CO\(_2\)/N\(_2\) ideal selectivity was higher in Pebax 1657/ZIF-8 compared to Pebax 2533/ZIF-8 because diffusivity of Pebax 1657 compared to Pebax 2533 is lower for nonpolar gases, such as N\(_2\), and the solubility is higher for polarizable gases like CO\(_2\). As increasing temperature, Pebax/ZIF-8 MMMs showed enhancement of CO\(_2\) and N\(_2\) permeability but decreased in CO\(_2\)/N\(_2\) ideal selectivity.

1. Introduction

The use of fossil fuels has increased the concentration of gaseous CO\(_2\) in the atmosphere, which has contributed to the greenhouse effect [1-4]. CO\(_2\) can be captured using various mixtures, such as natural gas or flue-gas, through conventional technologies like absorption with solvents and cryogenic CO\(_2\) capture [3]. However, these methods are being replaced by membrane technologies because of their low cost and energy-efficiency [1,2]. Generally, polymeric membranes have been applied to gas separation processes in industry because they consume low energy, have low cost, and are environmentally sustainable [3].

Recent studies have reported that the incorporation of a poly(ether oxide) (PEO) segment with other monomers can be used to overcome the weakness of fragile PEO segments to improve the weak mechanical strength [4,5]. Polyether block polyamide copolymers (Pebax) are widely studied for CO\(_2\) separation because they are flexible, durable, and mechanically and thermally resistant. Furthermore, they show high selectivity of CO\(_2\) over nonpolar gases, such as N\(_2\) and CH\(_4\) [6,7]. Pebax is composed of a thermoplastic polyamide (PA) segment and rubbery polyether (PE) segment [7]. PA is a rigid and hard crystalline phase that provides mechanical strength to a Pebax membrane [8,9]. PE is a flexible and soft amorphous phase that provides high CO\(_2\) permeability through its high affinity for polarizable molecules, which makes
it feasible to select polarizable gases from nonpolar gases like N₂ [10].

The Robeson upper bound represents the empirical relationship between the permeability of a specific component of a gas mixture and its separation factor, defined by Lloyd M. Robeson [11]. As the separation factor decreases, the permeability of more permeable gas components increases [11]. Therefore, there is a trade-off relationship between permeability and selectivity, which the CO₂ permeability increases for polymeric membranes such as Pebax, while the CO₂ selectivity decreases [11]. This drawback of polymeric membranes can be overcome by combining highly permeable polymers with inorganic fillers, which can increase gas selectivity while maintaining high permeability for CO₂ [12].

To improve the permeability and mitigate the loss of selectivity, inorganic fillers are dispersed in polymeric membranes to produce hybrid membranes called mixed matrix membranes (MMMs) [3,7]. The fillers include zeolites, carbon molecular sieves, and inorganic particles like silica and TiO₂. However, conventional inorganic fillers have weak adhesion with organic polymers [1]. For sustainable production of MMMS, metal organic frameworks (MOFs) have been introduced as porous materials composed of metal ions linked to organic linkers, which provide high surface area that adsorbs affinitive gas molecules [1,12].

Zeolitic imidazolate frameworks (ZIFs) are a subclass of MOFs, which include zinc metal cations and 2-methylimidazole anions of organic linkers that form a six-membered ring [3]. ZIFs have a special molecular sieving effect that provides strong interfacial interaction with polymers [13-16]. ZIFs are used as a membrane supplement for CO₂ capture as they have high thermal and chemical stability, and their micro-pore size of 3.4 Å is suitable for gas transport of CO₂, which has a kinetic diameter of 3.3 Å [6,17,18]. ZIF-8 particles prepared by Pecht and TiO₂ were dispersed in Pebax by forming hydrogen bonding interactions between polymer and ZIF-8 particles from the methanol solution. The deposited ZIF-8 powder was prepared by pouring methanol solution and drying at ambient temperature for 24 h [7,25].

2. Materials and methods

2.1. Synthesis of ZIF-8 particles

ZIF-8 nanoparticles were synthesized with different molar ratios of the precursors 2-methylimidazole (99%, 2-MeIM) and zinc nitrate hydrate (99%, Zn(NO₃)₂·6H₂O) (Merck, Inc.). The molar ratios of 2-MeIM/Zn(NO₃)₂·6H₂O (2-MeIM/Zn) were set as 2/1, 8/1, and 32/1 [7,25]. Furthermore, 0.55 g, 2.2 g, and 8.8 g of 2-MeIM were used with 1 g of Zn(NO₃)₂·6H₂O to obtain molar ratios of ZIF-8 particles of 2/1, 8/1, and 32/1, respectively. Each precursor was dissolved in 200 mL of methanol (99.99%, MeOH) separately. A cloudy solution was obtained after vigorous stirring for 1 h. The obtained solution was centrifuged for 1 h at 5,000 rpm to separate the synthesized ZIF-8 particles from the methanol solution. The deposited ZIF-8 powder was prepared by pouring methanol solution and drying at ambient temperature for 24 h [7,25].

2.2. Preparation of Pebax/ZIF-8 MMMS

Pebax 1657 and Pebax 2533 were provided by Arkema, Inc. Pebax 1657 and Pebax 2533 were dissolved at 3 wt.% in a solution of ethanol (99.99%, EtOH) deionized water (70 wt.%/30 wt.%) at 75°C for 2 h [6] and in 1-butanol (99.99% BuOH) at 80°C for 3 h [3], respectively. Next, 10 wt.% of each of the three different ZIF-8 powders molar ratios 2/1, 8/1, and 32/1 were added based on the ZIF-8 loading equation (Eq. (1)). Selected loading of ZIF-8 was based on the most common range of ZIF-8 loading, which are between 2 wt.% to 20 wt.%. As ZIF-8 loading increases the CO₂ permeability tends to increase, whereas the CO₂/N₂ selectivity decreases. Zheng et al. reported that as ZIF-8 loading increased from 5 wt.% to 20 wt.%, CO₂ permeability of ZIF-8/Pebax MMMS loading was increased from 99.7 to 156.2 Barrer, whereas CO₂/N₂ selectivity was decreased from 59.6 to 40.5. ZIF-8 powder was dispersed in the prepared solutions by an ultrasonic bath for 10 min. The prepared solutions of Pebax/ZIF-8 MMMS were poured in Teflon dishes and dried in a vacuum oven at 50°C for 72 h.

\[
ZIF-8\text{ loading (wt. %) = } \frac{m_{\text{ZIF-8}}}{m_{\text{Pebax}}+m_{\text{ZIF-8}}} \times 100\%
\]

(1)

Table 1 shows the abbreviations of synthesized Pebax/ZIF-8 MMMS with different 2-MeIM/Zn 10 wt.% of ZIF-8.

<table>
<thead>
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<th>Table 1.</th>
<th>ZIF-8 MMMS with different 2-MeIM/Zn 10 wt.% of ZIF-8.</th>
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</table>

2.3. Permeability test

Gas permeation tests with a single gas (CO₂ or N₂) were performed using a flat sheet module at constant volume. The single gas tests were performed at a feed pressure of 4 bar and increasing temperatures of 15, 35, 55, and 75°C. The CO₂ and N₂ permeabilities were calculated with the various temperatures of the feed gas while maintaining differences of pressure between the feed side and permeate side based on the following equation:

\[
P = \frac{V L}{A R T (P_{\text{feed}} - P_{\text{permeate}}) dt} \left(\frac{d \text{permeate}}{dt}\right)
\]

(2)

where P is the permeability of CO₂ and N₂ (Barrer, 1 Barrer = 10⁻¹⁰ cm³ (STP) cm⁻² s⁻¹ cmHg⁻¹), V is the volume of the permeate side of the membrane (cm³), L is the thickness of the membrane (cm), ṙ is the pressure of the feed, dh/ dt is the pressure of the permeate (cmHg s⁻¹), T is the varied temperature of the feed side (K), A is the membrane area (cm²), and ṙ is the ideal gas
constant (0.278 cmHg cm⁻¹ cm⁻¹ (STP) K⁻¹).

The permeation ideal selectivity of CO₂ and N₂ was calculated using the permeability ratio of the more permeable gas (CO₂) to the less permeable gas (N₂).

\[
\alpha_{\text{CO}_2/N_2} = \frac{P_{\text{CO}_2}}{P_{N_2}}
\]  

(3)

2.4. Characterization

FE-SEM (JSM-7800F Prime, JEOL Ltd, Japan) at 10-15 kV was used to characterize the size and morphology of the ZIF-8 nanoparticles and to obtain surface and cross-sectional images of Pebax 1657/ZIF-8 MMM and Pebax 2533/ZIF-8 MMM. Powder X-ray diffraction (XRD) (SmartLab, Rigaku, Japan) was performed on the ZIF-8 nanoparticles, pure Pebax, and Pebax/ZIF-8 MMM to determine the crystallinity. XRD was applied with Cu Ka radiation (40 kV-40mA) at a scan speed of 2°/min and step size of 0.02° by scanning 20 angles between 5° and 60°. A differential scanning calorimeter (DSC) (Discovery DSC, TA Instrument, USA) was used to determine the thermal properties of pure Pebax and Pebax/ZIF-8 MMM at a temperature range of -70 to 230°C at a scanning rate of 10°C/min.

Table 1

<table>
<thead>
<tr>
<th>Full name of Pebax/ZIF-8 MMM</th>
<th>Abbreviated name of MMM</th>
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<tbody>
<tr>
<td>Pebax 1657/ZIF-8 2/1M</td>
<td>P1/Z2</td>
</tr>
<tr>
<td>Pebax 1657/ZIF-8 8/1M</td>
<td>P1/Z8</td>
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<tr>
<td>Pebax 1657/ZIF-8 32/1M</td>
<td>P1/Z32</td>
</tr>
<tr>
<td>Pebax 2533/ZIF-8 2/1M</td>
<td>P2/Z2</td>
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<tr>
<td>Pebax 2533/ZIF-8 8/1M</td>
<td>P2/Z8</td>
</tr>
<tr>
<td>Pebax 2533/ZIF-8 32/1M</td>
<td>P2/Z32</td>
</tr>
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</table>

3. Results and discussion

3.1. Characterization of ZIF-8

The SEM images (Figure A1, see appendix) of ZIF-8 were analyzed to compare the sizes and shapes obtained with increasing molar ratios of 2-MeIM/Zn. As the molar ratio of 2-MeIM/Zn increased, the size of ZIF-8 particles decreased, which are in agreement with the results reported by Jomkian et al. [7,25]. Size distributions of Z2, Z8, and Z32 ranged from 295.3 nm to 712.4 nm, 220.2 nm to 531.2 nm, and 105.7 nm to 458.7 nm, respectively. The average size of Z2, Z8, and Z32 were 500.7, 363.3, and 217.1 nm, respectively.

The increase in concentration of 2-MeIM generates the large number of nuclei, which decreases the actual crystal size of ZIF-8 particle [26]. As 2-MeIM/Zn molar ratio increased, ZIF-8 particles changed from cubical to spherical shape [6] and particle aggregation was formed.

The X-ray diffraction was used to characterize the crystallinity of the ZIF-8 structures (Figure 1). As molar ratios of 2-MeIM/Zn increased, the intensity of characteristic XRD peaks decreased, and the peak became wider [6]. The decrease of XRD peaks with increasing 2-MeIM/Zn resulted from excess of MeIM [27]. The excess MeIM on the particle surface prevented particle growth, resulting in decrease of crystallinity [27]. Furthermore, the XRD pattern obtained with decreasing molar ratio of 2-MeIM/Zn showed higher and narrower peaks [6]. This means that the ZIF-8 is crystalline with decreasing 2-MeIM/Zn and is amorphous with increasing 2-MeIM/Zn [12]. This can be characterized by the Scherrer equation, in which the peak width is inversely proportional to the crystal size:

\[
B(2\theta) = \frac{k\lambda}{L \cos\theta}
\]  

(4)

where B is the peak width, K is proportionality constant called the Scherrer constant, θ is the Bragg angle, and L is the crystallite size.

3.2. Characterization of Pebax/ZIF-8 MMMs

The XRD patterns of Pebax 1657/ZIF-8 MMMs and Pebax 2533/ZIF-8 MMMs show the crystallinity of both Pebax and ZIF-8 (Figures 2 and 3). In Figure 2, P1 shows a broad peak in the range of 16.8 to 22.7° and a sharp peak at 24°, which represents the amorphous PEO segment and crystalline PA segment, respectively [12,28]. Distinct peaks of ZIF-8 in MMMs at 7.3°, 10.4°, 14.7°, and 26.7° were observed in the XRD pattern of Pebax 1657/ZIF-8, which are in good agreement with other studies [12,13,29]. From the peak range of the PEO segment (between 16.8° and 22.7°), P1/Z32 showed the most similar pattern to P1, as Z32 has more amorphous structure than Z8 or Z2 (Figure 1). From the peak of the PA segment at 24°, P1/Z2 showed more obvious and distinct PA peaks than P1/Z8 and P1/Z32 because Z2 has more crystalline structure than Z8 or Z32 (Figure 1). As molar ratio of ZIF-8 precursors increases, the crystal growth decreases as concentration of unreacted 2-MeIM increases; whereas concentration of Zn stays constant, resulting in less crystalline structure [27].

In Figure 3, P2 showed a peak at 20° for the crystalline PA segment, which agrees with previous work by Kim et al. [30]. Distinct peaks of ZIF-8 at 7.3°, 10.4°, and 14.7° were also observed in the pattern of Pebax 2533/ZIF-8 XRD pattern. P2/Z2 showed the highest peak compared to P2/Z8 and P2/Z32, as in the XRD patterns of Pebax 1657/ZIF-8 MMM.
The DSC curves (Figures A2-A9, see appendix) were analyzed to determine the glass transition temperatures of PE and PA in the Pebax and Pebax/ZIF-8 MMMs. The polymer crystallinity can be determined by measuring the enthalpy of fusion of the polymer \([12,31]\) (Eq. (5)).

\[
X_c = \frac{\Delta H_m}{\Delta H_m^0}
\]  

(5)

where \(\Delta H_m\) is the melting enthalpy of a semi-crystalline polymer and \(\Delta H_m^0\) is the melting enthalpy of the pure crystalline of PE and PA. The melting enthalpy of PEO, PTMEO, and PA were 166.4 J/g, 200 J/g, and 230 J/g, respectively, which were obtained from literature \([12,31,32]\). The membrane crystallinities of PE and PA segments of Pebax/ZIF-8 MMMs were calculated (Table 2). The crystallinity in Pebax 1657 MMMs was lowest in P1/Z32. On the other hand, the crystallinity in Pebax 2533 MMMs was lowest in P2/Z2. Both DSC results of Pebax/ZIF-8 MMMs were in good agreement with XRD results.

<table>
<thead>
<tr>
<th></th>
<th>(\Delta H_m) (PE) (J/g)</th>
<th>(\Delta H_m) (PA) (J/g)</th>
<th>XPE (%)</th>
<th>XPA (%)</th>
<th>Xc</th>
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<td>P1/Z32</td>
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<td>7.7</td>
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<td>15.68</td>
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<td>2.28</td>
<td>11.9</td>
</tr>
<tr>
<td>P2/Z32</td>
<td>29.94</td>
<td>6.58</td>
<td>14.97</td>
<td>2.86</td>
<td>12.5</td>
</tr>
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</table>

3.3. The effect of controlling molar ratio of ZIF-8 on gas permeability of Pebax/ZIF-8 MMMs

Figures 4 and 5 showed that the CO\(_2\) permeability of Pebax 2533 MMMs was much higher than that of Pebax 1657 MMMs at the same temperature. The different CO\(_2\) permeabilities can be explained by the chemical structure and affinity with CO\(_2\) gas molecules. The effect of increasing molar ratios of 2-MeIM/Zn on the CO\(_2\) permeability of Pebax/ZIF-8 MMMs (Figures 4 and 5) was investigated. At a temperature of 15°C, Pebax 1657/ZIF-8 MMM showed the highest CO\(_2\) permeability with P1/Z32, followed by P1/Z8 and P1/Z2. At the same temperature, Pebax 2533/ZIF-8 MMM showed the highest CO\(_2\) permeability for P2/Z2, followed by P2/Z8 and P2/Z32.

Bondar et al. [24] and Kim et al. [30] explained the difference in permeability of the two types of Pebax in terms of chemical structure, diffusivity, polarity, and solubility of Pebax. The chemical structure of Pebax 2533 has a higher content of rubbery PTMEO, which is a gas-transport-dominating phase, so it has higher permeability than Pebax 1657 [24]. The diffusivity of Pebax 2533 is lower than that of Pebax 2533 because it has more concentrations of polar groups in polymer matrix, which lowers gas diffusion coefficient [24]. However, the CO\(_2\)/N\(_2\) selectivity of Pebax 1657 may be higher than that of Pebax 2533 because the diffusivity of Pebax 1657 is lower for nonpolar gases, such as N\(_2\), and the solubility is higher for polarizable gases like CO\(_2\) [30,33].

![Fig. 3 XRD graphs of P2, P2/Z2, P2/Z8, and P2/Z32.](image)

![Fig. 4 CO\(_2\) permeability of P1, P1/Z2, P1/Z8, and P1/Z32.](image)

![Fig. 5 CO\(_2\) permeability of P2, P2/Z2, P2/Z8, and P2/Z32.](image)

There are several important factors in the opposite trends of CO\(_2\) permeability for Pebax 1657/ZIF-8 and Pebax 2533/ZIF-8 based on different molar ratios of ZIF-8 precursors (Figures 4 and 5): (1) particle size, numbers of pore, and pore size of ZIF-8 with increasing molar ratio of 2-MeIM/Zn, (2) the polarity of Pebax, (3) the affinity for CO\(_2\) gas molecules, and (4) the crystallinity change of Pebax MMMs in terms of ZIF-8 molar ratio.

For Pebax 1657 MMMs, as the molar ratio 2-MeIM/Zn of ZIF-8 precursors increased, the CO\(_2\) permeability at a fixed temperature of 15°C increased (Figure 4). Jomekian et al. [7] reported on the trend of increasing permeability of Pebax 1657/ZIF-8 corresponding to increasing molar ratios of 2-MeIM/Zn. The increasing molar ratio of 2-MeIM/Zn increases the CO\(_2\) permeability by higher gas sorption capacity [7]. Increasing the molar ratio of 2-MeIM/Zn showed higher numbers of nanoparticles, which are related to high sorption capacity [7]. As the sizes of nanoparticles decrease, the surface areas become larger and create interfacial regions in the organic polymers.
Furthermore, the gas adsorption is enhanced as the numbers of pores in ZIF-8 particles are increased [7,33]. The polarity of Pebax is another important factor of the permeability increase of Pebax 1657 MMMs with increasing molar ratio 2-MeIM/Zn of ZIF-8. Pebax 1657 has a high concentration of polar groups in PEO chain segments, which have a high affinity for CO2 [24]. Imidazolium ions and PEO segments in the Pebax 1657 result in excessive adsorption of CO2 molecules [7]. Excessive sorption of CO2 by imidazolium ions causes plasticization of Pebax 1657, which enhances the polymer chain mobility [7,34]. The result of highest permeability of Pebax 1657 with increasing 2-MeIM/Zn can be also explained by the crystallinity change with incorporation of ZIF-8 with increasing 2-MeIM/Zn. As described in subsection 3.2, P1/Z2 showed the lowest crystallinity in DSC results (Table 2), which also showed the highest CO2 permeability.

However, for Pebax 2533 MMMs, increasing the molar ratio of ZIF-8 resulted in lower CO2 permeability at 15°C (Figure 5). When the molar ratio of 2-MeIM/Zn increases, the shape of ZIF-8 particles changes from cubical to spherical (Figure 1A), and as a result, the fillers aggregate and tend to fill the interstitial regions of the polymer, which could prevent access to the polymer matrix [35]. The diffusivity may be decreased by the smaller pore size and particle size of ZIF-8 with increasing molar ratio of 2-MeIM/Zn. According to Jomékian et al. [7,25], increasing the ZIF-8 molar ratio decreases the particle size and pore volume of ZIF-8 particles. As molar ratio of ZIF-8 increase, the permeation of ZIF-8 decreases along with the pore size [7,25]. This implies that particles aggregate more and may reduce space in the polymer matrix for penetrants to diffuse.

Compared to Pebax 1657, the polarity of Pebax 2533 is lower in the PTMEO segment, which has a low affinity for CO2 [24]. When the molar ratio of 2-MeIM/Zn increases, the concentration of polar imidazolium ions in ZIF-8 increases. However, less polar PTMEO in Pebax 2533 may not be enough to interact with imidazolium to adsorb CO2 and enhance the polymer chain mobility. It suggests that increasing the molar ratio of ZIF-8 can prevent the interstitial volume from accessing the polymer segment and decrease the free volume and diffusivity. Although the loading ZIF-8 of any molar ratio in Pebax 2533 enhanced the permeability of CO2 molecules compared to pure Pebax 2533, increasing the molar ratio was not effective for Pebax 2533 to enhance the CO2 permeability. The result of highest CO2 permeability of Pebax 2533 with decreasing 2-MeIM/Zn can be also explained by the lowest crystallinity of P2/Z2 in DSC results (Table 2).

The incorporation of ZIF-8 in Pebax MMMs enhanced the CO2 permeability for both Pebax 1657 and 2533 by increasing CO2 diffusivity and solubility. The hydrogen bonds between ZIF-8 and PA segment stabilized the structure of MMMs and disrupted PEO segment, which enhanced free volume, decreased the crystallinity of PEO, and increased the CO2 permeability of Pebax MMMs. Pebax 1657 MMM showed highest CO2 permeability with increasing molar ratio of ZIF-8, which agrees with the lowest crystallinity of P1/Z2 in the DSC results. Pebax 2533 MMM showed highest CO2 permeability with decreasing molar ratio of ZIF-8, which agrees with the lowest crystallinity of P2/Z2 in the DSC results. Therefore, Pebax 1657 was more effective for the permeation of CO2 with Z2, whereas Pebax 2533 was more effective for the permeation of CO2 with Z2. The ZIF-8 filler increased the CO2 solubility of Pebax 1657 more than that of Pebax 2533 through CO2 sorption of the polar groups in organic ligand of 2-MeIM [12].

Even though the permeation tests for pure Pebax and Pebax/ZIF-8 MMMs were performed at different temperatures due to the limitation related to experimental setup, the permeability of pure Pebax 1657 was 83.7 Barrer at 25°C and 130 Barrer at 40°C, whereas the lowest permeability of P1/Z2 was 212 Barrer at 15°C (Figure 4). The permeability of pure Pebax 2533 was 272 Barrer at 25°C and 370 Barrer at 40°C, whereas the lowest permeability of P2/Z2 was 399 Barrer at 15°C (Figure 5). Therefore, the CO2 permeability of Pebax/ZIF-8 MMM was higher than those of both Pebax 1657 and Pebax 2533 alone, even at lower temperature.

The higher CO2 permeability of Pebax with the incorporation of ZIF-8 particles can be achieved by high CO2 solubility and diffusivity of ZIF-8 [1,12]. CO2 adsorption capacity in ZIF-8 is high because polar organic ligands of 2-MeIM in ZIF-8 adsorb polarizable CO2 molecule selectively, which can improve CO2 solubility [1,12]. Flexible porous structures of ZIF-8 increase free volume in Pebax matrix, which can improve diffusion of gas molecules with large kinetic diameters [13].

The enhancement of the free volume is a mechanism for increasing diffusion, which is described by the Cohen and Turnbull equation (Eq. (6)) [36]:

$$D = A \exp \left( \frac{-\Delta T}{T^2} \right)$$  \hspace{1cm} (6)

where $D$ is the diffusion coefficient, $A$ is the pre-exponential factor, $\gamma$ is an overlap factor to avoid the double-counting of free volume elements, $V$ is the minimum free volume element size that a penetrant can pass, and $V_o$ is the average free volume in the polymer that is available for a penetrant to be transported through [37]. Therefore, incorporation of ZIF-8 on Pebax increases both diffusivity and solubility, which can improve the permeability based on the solution-diffusion mechanism in Eq. (7):

$$P = P_i D_i S_i$$  \hspace{1cm} (7)

where $P$ is the permeability of gas $i$, $D_i$ is the average effective diffusion coefficient, and $S_i$ is the solubility coefficient.

Furthermore, at the interfacial region between ZIF-8 and Pebax, ZIF-8 particles form hydrogen bonding with PA in Pebax, which occur between (1) the aldehyde groups in the PA segment and methyl groups in the 2-methylimidazole in the ZIF-8, as well as (2) N-H groups in the PA and N atoms of the imidazole ring [19,20]. ZIF-8 particles not only enhance structural stability by forming hydrogen bonds with PA [12], but also disrupt chain packing of PEO segment in Pebax [12]. As the chain packing is disrupted, the PEO chain interaction is decreased, resulting in increasing free volume for penetrants to diffuse [12]. Also, the disrupted PEO chain packing results in decrease of the crystallinity of PEO segment [35]. Kim et al. [30] reported that the crystallinity region in a Pebax polymeric matrix decreases the permeability of the Pebax because the crystalline phase forms uniform and rigid chains that lack sorption sites and the mobility of chains for the permeation of penetrants.

3.4. The effect of temperature on gas permeability of Pebax/ZIF-8 MMMs with different molar ratio of ZIF-8

To confirm the effect of the permeating temperature on Pebax MMMs, the MMMs with the highest permeabilities were tested with CO2 gas and N2 gas at increasing temperature. Pebax 1657/ZIF-8 MMM with a molar ratio of 32/1 and Pebax 2533/ZIF-8 with molar ratio of 2/1 were used at a constant feed pressure of 4 bar and temperatures of 15, 35, 55, and 75°C. As the temperature increased, the CO2 permeability obtained with both P1/Z32 and P2/Z2 increased.

The temperature dependency of the permeability was calculated using the van’t Hoff-Arrhenius equation (Eq. (8)):

$$P = P_o \exp \left( \frac{-E_a}{RT} \right), \ E_a = E_d + \Delta H_s$$  \hspace{1cm} (8)

where $P$ is the permeability coefficient, $P_o$ is a pre-exponential factor, and $E_o$ is the activation energy of permeation, which is the sum of the activation energy for diffusion, $E_d$, and the enthalpy of sorption, $\Delta H_s$ [30,37]. $R$ is the gas constant, and $T$ is the operating temperature [38]. Based on this equation, if either the activation energy for diffusion or the enthalpy of sorption decreases, the permeability increases.

A logarithmic function was applied to the van’t Hoff-Arrhenius equation (Eq. (9)) to calculate the pre-exponential factor $P_o$ and activation energy of permeation, $E_o$ (Figures 6 and 7):

$$\log P = -\frac{E_a}{R} \frac{1}{T} + \log P_o$$  \hspace{1cm} (9)

The activation energy of permeation can be calculated from the slope of the log of permeability, $-\frac{E_a}{R}$. Before filling the Pebax polymer with ZIF-8, the activation energy of permeation of Pebax 2533 (16.7 kJ/mol) is lower than that of Pebax 1657 (18.6 kJ/mol) (Table 3) [39].

However, from the calculation of $P_o$ and $E_o$ of P1/Z32 and P2/Z2 (Table 3), the activation energy of diffusion of P1/Z32 (5.2 kJ/mol) is lower than that of P2/Z2 (9.7 kJ/mol). The polar PEO chains of Pebax 1657 interact with highly polar imidazolium ions in ZIF-8 nanoparticles and both of them have high affinity for CO2. Therefore, CO2 molecules are excessively adsorbed, which results in plasticization [7,12,40]. This decreases the enthalpy of sorption, resulting in lower activation energy of permeation [30].

From Eq. (9), the pre-exponential factor $P_o$ can be calculated by 10 to the power of the y-intercept. The pre-exponential factor and activation energy of permeation are high when penetrants are not significantly affected by the temperature change [41]. According to Table 3, both the activation energy of permeation and pre-exponential factor of Pebax 1657 were lower than those of Pebax 2533, which means that Pebax 1657 MMM is more sensitive to temperature changes, and the permeability was increased more significantly.
[41], even though the increase of temperature increases the permeability for both Pebax 1657 MMM and Pebax 2533 MMM. When the temperature increased, the interaction between more polar PEO groups in Pebax 1657 and polar imidazolium ion in ZIF-8 may have increased the permeability of penetrants. The reason is that the enthalpy of sorption is decreased by the CO2 sorption of more polar groups in Pebax 1657 and 2-MeIM in ZIF-8 [12,30]. On the other hand, less polar PTMEO groups in Pebax 2533 are less polar to adsorb CO2, which may result in less of a decrease in the enthalpy of sorption than that of Pebax 1657 MMM. Increasing the permeating temperature increased the permeabilities of both Pebax 1657/ZIF-8 and Pebax 2533/ZIF-8. However, the permeability of Pebax 1657/ZIF-8 MMM was more dependent on the temperature, which was proven by the low activation energy of permeation.

As the permeating temperature increased, the ideal selectivity of CO2/N2 decreased for both P1/Z32 and P2/Z2 (Figures 8 and 9). This phenomenon occurred for both Pebax/ZIF-8 and pure Pebax. Kim et al. [30] reported that the CO2/N2 selectivity of Pebax 1657 decreased. As the temperature increases, the polymer loses its chemical nature of favoring particular gases because segmental motion of the gas molecules increases regardless of the penetrants [41]. Also, the flexible structure of ZIF-8 in Pebax MMMs creates a pore that increases micro-void for diffusion of all gas molecules [12,13].

<table>
<thead>
<tr>
<th>MMMs</th>
<th>Penetrant Gas</th>
<th>$E_p$ (k/mol)</th>
<th>$P_w$ (Barrer)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1/Z32</td>
<td>CO2</td>
<td>5.2</td>
<td>3.88 x $10^4$</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>N2</td>
<td>13</td>
<td>8.06 x $10^3$</td>
<td>This work</td>
</tr>
<tr>
<td>Pebax 1657</td>
<td>CO2</td>
<td>18.6</td>
<td></td>
<td>[39]</td>
</tr>
<tr>
<td></td>
<td>N2</td>
<td>35.8</td>
<td>1.98 x $10^4$</td>
<td>This work</td>
</tr>
<tr>
<td>Pebax 2533</td>
<td>CO2</td>
<td>16.7</td>
<td></td>
<td>[39]</td>
</tr>
</tbody>
</table>

The performance of Pebax 1657/ZIF-8 MMMs and Pebax 2533/ZIF-8 MMMs synthesized with three different types of ZIF-8 at 35°C is presented with Robeson upper bound line on Figure 10. Based on Robeson graph [11], P1/Z32 at temperature 35°C showed the most ideal performance satisfying both high CO2 permeability and CO2/N2 ideal selectivity. P2/Z2 showed higher CO2 permeability compared to P1/Z32 at 35°C, but CO2/N2 ideal selectivity values are far beneath the Robeson upper bound. As observed in Figures 8 and 9, Pebax/ZIF-8 MMMs showed that as temperature increases, the CO2 permeability increases but the ideal selectivity is decreased. The result of Pebax 2533/ZIF-8 MMMs are far beneath the Robeson upper bound, which indicating very low CO2/N2 ideal selectivities.
4. Conclusions

In this study, the effect of molar ratio of ZIF-8 precursors on the performance of CO$_2$ and N$_2$ permeation of Pebax 1657 and Pebax 2533 MMMs was investigated. Studies of CO$_2$ permeability of Pebax 1657/ZIF-8 MMMs with controlling molar ratio was investigated in this work, which was explained by the important relationship between ZIF-8 and Pebax based on their chemical structures and morphological characteristics that determine the CO$_2$ permeability. ZIF-8 with a higher molar ratio of 2-MeIM/Zn had a smaller size and showed weaker and wider peaks in XRD spectra than that of ZIF-8 with a lower molar ratio of ZIF-8 precursors (2-MeIM/Zn), which represents the chemical nature of an amorphous material.

The CO$_2$ and N$_2$ permeability were higher in Pebax/ZIF-8 MMMs than in pure Pebax. In terms of different molar ratio of ZIF-8, the CO$_2$ and N$_2$ permeability were highest for Pebax 1657 MMM with ZIF-8 molar ratio of 32/1 and for Pebax 2533 MMM with ZIF-8 molar ratio of 2/1. Compared to pure Pebax 2533, P2/Z2 showed increment of permeability by 158%, whereas compared to pure Pebax 1657, P1/Z32 showed increment of permeability by 216%. Because Pebax 1657 has a polar PE segment (60% of PEO), higher sorption capacity of ZIF-8 molar ratio of 32/1 enhanced CO$_2$ sorption, which resulted in improvement of CO$_2$ ideal selectivity over N$_2$. On the other hand, because Pebax 2533 has higher PE content (80% of PTMEO), but has a lower polarity that provides higher gas transport, fewer aggregating ZIF-8 particles with molar ratio of 2/1 enhanced free volume of Pebax 2533, which resulted in increase of CO$_2$ permeability.

The effect of temperature on the CO$_2$ and N$_2$ permeability was investigated as well. As the temperature increased, the permeabilities increased for both Pebax 1657/ZIF-8 and Pebax 2533/ZIF-8 MMMs. As the temperature increases, the diffusivity of polymer increased for all gas molecules, so the CO$_2$/N$_2$ ideal selectivity decreased for both Pebax 1657 and 2533. Also, the porous structure of ZIF-8 increased the micro-void in Pebax matrix, which increased the free volume for diffusion of all gas molecules.

In summary, Pebax 1657/ZIF-8 with a molar ratio of 32/1 and Pebax 2533/ZIF-8 with a molar ratio of 2/1 had the best performance for CO$_2$ permeation. This means that better permeability and compatibility between the polymer and particles can be achieved by controlling the molar ratio of ZIF-8 precursors and selecting the right Pebax polymer based on chemical nature and interfacial interactions.

Appendix

Figure A1. SEM images of ZIF-8 particles with different 2-MeIM/Zn (A) Z2, (B) Z8, and (C) Z32.
Figure A2. DSC curve of P1.

Figure A3. DSC curve of P1/Z2.

Figure A4. DSC curve of P1/Z8.
Figure A5. DSC curve of P1/Z32.

Figure A6. DSC curve of P2.

Figure A7. DSC curve of P2/Z2.
Acknowledgement

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References


