Fabrication of Mixed Matrix Membrane Polysulfone - Zeolite Carbon Composites (ZCC) For Gas Separation

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Abstract. Mixed matrix membrane polysulfone (PSF) - zeolite carbon composite (ZCC) was successfully fabricated in this study. The composition of ZCC as a filler in this membrane was 1%. Mixed matrix membrane PSF-ZCC 1 wt% was compared by neat polysulfone membrane. The prepared membranes were characterized using XRD to determine the membrane structure and FTIR to determine the functional groups in the membrane. The results of gas permeation for membrane permeability of O2 were 4.011 and 7.193 GPU for neat PSF and PSF-ZCC 1 wt% membrane, respectively. In addition, the permeability value of N2 was 5.603 and 7.862 GPU for neat PSF and PSF-ZCC 1 wt% membrane, respectively. Selectivities of O2/N2 for neat PSF and PSF-ZCC 1 wt% membrane were 0.715 and 0.914, respectively. The increasing permeability along with the addition of ZCC filler indicated that the membrane in this study is potentially applied for O2 and N2 separation.

1. Introduction
Membrane technology is one of the methods used for gas separation. Gas separation with membrane technology was chosen because it has several superior properties such as high efficiency, high speed and simple operational systems [1]. Polymer membranes have the advantage of economical mechanical properties and operational processes [2]. However, the gas separation performance on the polymer membrane is under Robeson upper bound line [3]. This shows that polymer membranes have high permeability with low selectivity. On the other hand, the gas separation performance with inorganic materials has good thermal and chemical stability, and high permeability compared to polymeric membranes [2]. Nevertheless, the drawback of inorganic membranes is high cost of materials and difficult fabrication processes in large production [4]. Therefore, the polymer as a matrix is combined with inorganic material into a mixed matrix membrane (MMM) to get good separation performance of gas, as well as high thermal resistance and mechanical properties.

Mixed Matrix Membrane (MMM) with dispersed inorganic fillers at the nanometer level in the polymer as a matrix is an alternative membrane. MMM has the good material to resolve problems of permeability and selectivity in polymer membranes, as well as solving fragility problems in inorganic fillers. The role of inorganic fillers is important as a molecular framework that has a selective shape and
size. Smaller molecules will diffuse more easily than larger molecules. The performance of the PSF polymer membrane on gas separation showed 5.5 for selectivity of $O_2/N_2$ with 1.58 barrers for permeability of $O_2$, while the performance of $O_2/N_2$ gas separation in MMM showed an increase with selectivity of 6.05 and $O_2$ permeability of 6.52 barrers [5].

Zeolite carbon composite is material modification for filler because it has pore regularity and microporosity, which ensures higher gas permeability and selectivity [6]. It was synthesized by furfuryl alcohol impregnation followed by propylene Chemical Vapor Deposition (CVD) method. However, there is still less information regarding to the use of zeolite carbon composite as filler in MMM. In this work, the effect of ZCC loading on the PSF membrane characteristic was investigated.

2. Material and Method

2.1. Material
The materials used for the synthesis of mixed matrix membranes were zeolite carbon composite (ZCC) from Tohoku University, Polysulfone (Udel PSF P-3500), N-methyl-2-pirrolidone (NMP, supplied from Merck), ethanol (99.9% EtOH, procured from Merck), and methanol (99.9% MeOH, procured from JT Baker). Furthermore, the materials for gas permeation test were high purity of $O_2$ (99.99% $O_2$) and high purity of $N_2$ (99.99% $N_2$).

2.2. Dope solution preparation of MMM
The dope solution of MMM consists of PSF, NMP, and ethanol with compositions of 30, 60, and 10 wt%, respectively [7]. 1 wt% ZCC as filler was added to the PSF matrix. Before the preparation of the dope solution, ZCC powder was filtered using a sieve filter (mesh 400) to obtain a uniform powder, then PSF and ZCC were dried at 60 °C for 12 hours to evaporate water perfectly [8], [9].

The preparation method for dope solution is described as follow: 1 wt% ZCC was dispersed into NMP solvents. Then, the solution was sonicated for 30 minutes to achieve homogeneous dispersion. After sonication, 10% of the total PSF was added in solution and followed by stirring for 2 hours. After that, the rest PSF was gradually added to the solution and stirred until the homogeneous solution was obtained, followed by sonication for 30 minutes to remove bubbles [9], [10]. Subsequently, the dope solution was left for 12 hours. The same preparation step was used to prepare pure dope solution as a comparison sample [11].

2.3. Fabrication of MMM in flat modul
The MMM was fabricated in flat sheet by phase inversion method. The prepared dope solution was poured over the glass plate and casted with a stainless steel roller. After that, the dope solution was left 40 seconds first in the air, then put in a coagulation bath containing deionized water until the membrane was peeled off from the plate of glass. The obtained flat sheet membrane was soaked in a distilled water for 24 hours and followed by immersing in methanol for 2 hours for post treatment. The treated membranes were dried for 3 days in room temperature [11].

2.4. Characterization of MMM
X-Ray Diffraction (XRD) was used to determine $d$-spacing of neat PSF membranes and PSF-ZCC 1 wt%. Membrane sample was cut to a size of 1 cm $\times$ 1 cm. Then, the sample was placed into the holder for testing. Furthermore, Neat PSF and PSF-ZCC 1 wt% was analyzed using Fourier Transform Infrared (FTIR) to determine differences in functional groups present between neat PSF and MMM PSF-ZCC 1 wt%. Membrane with a size of 2 cm $\times$ 4 cm was prepared to carry out the FTIR test, then the membrane was placed in a FTIR analysis pellet. The spectras were recorded in the wavenumber ranging from 400 – 4000 cm$^{-1}$. 
2.5. Gas Permeation Test
The test of gas permeation used the equipment as shown in figure 1. Membrane with a diameter of about 5.5 cm was cut and placed in a stainless steel holder. The transport properties of flat membranes were tested using pure gas (O\textsubscript{2} and N\textsubscript{2}) with a purity of 99.99%. Gas permeation test on membranes was obtained at 3 bar pressure in room temperature [10]. For accurate measurement, the membrane was tested at three replicated modules. The permeation cell was closed tightly to prevent leakage. The top of membrane was fed with gas. Then, the gas was permeated to bottom side. The permeate side was connected to soap bubble flow meter in order to get gas flow rate acrossing the membrane. The calculation of gas permeance was showed in Equation (1).

\[
P_i \frac{T}{l} = \frac{Q_i}{A \Delta P}
\]

In which, \((P_i / l)\) is gas permeability in gas permeation unit (1 GPU = 1 x 10\textsuperscript{-6} cm\textsuperscript{3} (STP)/cm\textsuperscript{2} s cm Hg), \(i\) describes gas penetrant, \(Q_i\) is gas volumetric rate (cm\textsuperscript{3}/s, STP), \(A\) is effective area of membrane (cm\textsuperscript{2}) and \(\Delta P\) is difference pressure of membrane (cmHg). The ideal selectivity of gas was obtained by taking the ratio of gas permeability component \(i\) to \(j\), as presented in Equation (2).

\[
\alpha_{i/j} = \frac{(P_i / l)}{(P_j / l)}
\]

![Image](image.png)

Figure 1. Illustration of gas permeation testing system
3. Result and Discussion

3.1 Analysis of X-Ray Diffraction

MMM PSF-ZCC 1 wt% was characterized using XRD, which aims to determine the effect of ZCC addition in the structure of the PSF membrane. Moreover, the intersegmental spacing (d-spacing) between polymer chains of the membranes observed in XRD characterization. Figure 2 showed the structure of PSF membrane with a peak at \(2\theta = 17.80^\circ\) (d-spacing = 0.484 nm) and MMM PSF-ZCC 1 wt% had peak at \(2\theta = 17.73^\circ\) (d-spacing = 0.486 nm). The addition of ZCC did not significantly alter the d-spacing of MMM PSF-ZCC 1 wt%, indicating a slight change of polymer chain mobility. Thus, it can be said that a good interaction between PSF and ZCC were occured. Furthermore, it was no significant changes from the peaks broadness and intensity after the ZCC filler was added, indicating the MMM preserved the amorphous of PSF polymer [12]. In addition, the MMM PSF-ZCC 1 wt% showed a small peak at around \(2\theta = 6.06^\circ\) and \(2\theta = 26.52^\circ\), originated from (111) and (551) plane of zeolite-Y, respectively.

![Figure 2. X-Ray diffraction pattern of (a) neat PSF and (b) MMM PSF-ZCC 1 wt%.

3.2 Analysis of FTIR

Figure 3 showed FTIR spectras from PSF membrane and MMM PSF-ZCC 1 wt%. The PSF membrane showed peaks in the region: 1149 and 1168 cm\(^{-1}\) (symmetric vibration stretching of Ar-SO\(_2\)-Ar); 1243 cm\(^{-1}\) (vibration stretching Ar-O-Ar, C-O stretching); 1325 cm\(^{-1}\) (symmetric stretching vibration S = O); 1380 cm\(^{-1}\) (asymmetric–CH\(_3\)) and 1583 cm\(^{-1}\) (vibration stretching C = C aromatic). The similar peaks of neat PSF were observed in other study reported by Kiadehi et al. [13]. On the other hand, the spectra of MMM PSF-ZCC 1 wt% appeared new absorption peak in 3187 cm\(^{-1}\) (vibration stretching O-H) cm\(^{-1}\) from the ZCC surface. In addition, no change in the wavenumber shift was observed in MMM PSF-ZCC 1 wt%, indicating no chemical interaction occured during the fabrication of membrane [14].
3.3 Permeation Gas Test

The performance of MMM PSF-ZCC was tested using single gas N$_2$ and O$_2$. Gas separation performance on membranes was determined from the value of permeability and selectivity. The result of permeability and selectivity in this work was shown in Table 1. Compared to PSF membrane, the MMM permeability of O$_2$ and N$_2$ increased up to 79.33% and 40.34%, respectively, along with the O$_2$/N$_2$ selectivity increment of 27.83%. It indicated that the addition of 1 wt% ZCC enhanced the permeability along with the selectivity of O$_2$/N$_2$ due to the ZCC dispersion on the polymer matrix. The enhanced O$_2$ and N$_2$ permeability and selectivity were also observed in Kiadehi et al. study by incorporating carbon nano fiber (CNF) inside PSF matrix. However, the improved permeability in this study was higher compared to these literature [13].

Table 1. Gas performance of membrane.

| Membrane      | Condition | P (bar) | T (°C) | Permeability O$_2$ (GPU) | Permeability N$_2$ (GPU) | Selectivity O$_2$/N$_2$ | Reference |
|---------------|-----------|---------|--------|--------------------------|--------------------------|------------------------|-----------|
| Neat PSF      | 3         | RT      | 4.011  | 1.36                     | 5.603                    | 1.90                   | This work |
| PSF-ZCC 1 wt% | 3         | RT      | 7.193  | 2.44                     | 7.862                    | 2.67                   | This work |
| PSF           | 4         | RT      | -      | 0.31                     | -                        | 0.19                   | [13]      |
| PSF-CNF 1 wt% | 4         | RT      | -      | 2.24                     | -                        | 0.58                   | 3.86      | [13]      |

Gas transport mechanism in membrane might be referred with the Knudsen diffusion. The selectivity for O$_2$/N$_2$ in Knudsen diffusion is 0.94 [15]. Moreover, the selectivity values of O$_2$/N$_2$ in this work for PSF-ZCC 1 wt% membrane was 0.914. This result was close to the O$_2$/N$_2$ selectivity value of Knudsen Diffusion, thus gas transport mechanism in this study can be described with Knudsen Diffusion mechanism. It indicated that the membrane possessed some interfacial void between PSF and ZCC [16].

The performance of gas separation O$_2$/N$_2$ in the MMM PSF-ZCC 1 wt% as well as the neat PSF membranes was compared with upper bound of Robeson as shown in Figure 4. The point of neat PSF and MMM PSF-ZCC 1 wt% was located under the Robesons’s trade off for O$_2$/N$_2$ gas separation. It showed that the gas separation worked with low performance. Moreover, the performance of gas
Separation of MMM PSF-ZCC can be improved by surface coating to reduce the membrane voids and it is still under investigation.

4. Conclusion
Mixed matrix membrane (MMM) consisting of PSF and ZCC filler in this study was successfully fabricated by phase inversion method. The addition of ZCC can preserve the structure and improve gas separation performance at MMM PSF-ZCC. In this study, the permeability of O\textsubscript{2} was 4.011 and 7.193 GPU for PSF and PSF-ZCC 1 wt% membrane, respectively. In addition, the permeability value of N\textsubscript{2} was 5.603 and 7.862 GPU for PSF and PSF-ZCC 1% membrane, respectively. Selectivity of O\textsubscript{2}/N\textsubscript{2} for PSF and PSF-ZCC 1 wt% membrane were 0.715 and 0.914, respectively. The Knudsen Diffusion was appropriate in the gas transport mechanism of this research.

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Figure 4. The separation performance of O\textsubscript{2}/N\textsubscript{2} gas.
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