Ionic Liquid Blend Thin Film Composite Membrane for Carbon Dioxide Separation

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Abstract

To utilize the superior properties of ionic liquid (IL), this work developed thin film composite (TFC) membrane incorporated with [EMIM][Tf2N] prepared via interfacial polymerization (IP). The effect of IL on membrane properties and CO2/CH4 separation performance were studied. The IL loading was varied from 1-5wt%. The fabricated membranes were characterized and the gas separation performance of the membranes was evaluated in term of CO2 permeability and CO2/CH4 selectivity. Analysis from Fourier-transform Infrared Spectroscopy (FTIR) shows the presence of [EMIM][Tf2N] functional groups proving the successful attachment of the IL in the membrane. Furthermore, it is noted that with increasing IL loading up to 3vol%, the surface morphology became rougher and the membrane became more rigid based on the Differential Scanning Calorimeter (DSC) thermogram and Atomic Force Microscopy(AFM) analysis, accordingly. Based on the gas permeation test at 1 bar feed pressure, membrane with 5wt% of IL showed CO2 permeability of 3424.44 GPU and CO2/CH4 selectivity of 32.15. Compared to pure TFC membrane, TFC/IL membranes showed as much as 103 times and 32 times improvement for CO2 permeability and CO2/CH4 selectivity, accordingly. The improved gas separation performance shows promising results of incorporating IL in TFC membrane for CO2 separation.

Keywords: Thin film composite membrane; interfacial polymerization; [EMIM][Tf2N]; CO2 separation
1.0 Introduction

As the increase in carbon dioxide (CO$_2$) emission to the environment has become global concern, the development of CO$_2$ removal has been widely conducted including adsorption, absorption, cryogenic and membrane separation [1-3]. In the past decade, interest have been shifting on the improvement of the performance of polymeric membrane for gas separation due to the trade-off limit between permeability and selectivity [4] including the fabrication of thin film composite membrane (TFC) [5, 6]. TFC consists of ultrathin polyamide (PA) selective layer constructed on porous substrate layer. The ultrathin selective layer (less than 0.2 $\mu$m) provide minimal mass transport resistance compared to dense membrane which contribute to the effective gas permeability and selectivity.

Numerous methods for TFC preparation have been studied including dip-coating [7, 8], phase inversion [9, 10] and interfacial polymerization (IP) method [11, 12]. In dip-coating process, the porous substrate is dipped in into the polymer (PA) solution at fixed speed. For phase inversion method, the selective layer is casted on the membrane support and the solvent removal process can be conducted either via dry, wet or dry-wet phase inversion step. In IP, the ultrathin selective layer is fabricated by the reaction of monomers on top of the porous substrate [13]. While TFC preparation via IP has shown permeation improvement for water separation compared to other methods of preparation, there is not enough studies has been conducted for gas separation thus come the propose of this paper.

Furthermore, various methods have been developed to enhance the gas separation performance including by introducing CO$_2$-philic materials during the fabrication such as IL and amine solvents. Recent studies have shown the significant improvement with the incorporation of ionic liquid (IL) [14-16]. IL is a salt which contains an organic cation and inorganic and organic anion where it possesses high CO$_2$ solubility, high selectivity, negligible volatility and highly tunable according to unique application [1, 17]. However, there are still limited works on incorporating IL into TFC membrane, especially for TFC fabricated via interfacial polymerization (IP). While it is evident that IL can improved membrane separation performances [18], the IL presence during IP could alters the polymerization reaction thus affect selective layer formation where it occurs at the interface between two phases.

Therefore, this project aims to fabricate TFC membrane incorporated with [EMIM][TF$_2$N] via IP and investigate the effect of [EMIM][TF$_2$N] on membrane properties and gas separation performance. With the presence of [EMIM][TF$_2$N] which is known to have high CO$_2$ affinity, the
gas separation performance of TFC-IL is expected to be improved compared to that of TFC membrane.

2.0 Experimental

2.1 Materials
Polysulfone (PSF, Merck), poly (vinyl pyrrolidone) (PVP, Sigma-Aldrich), N-M ethyl-2-pyrrolidone (NMP, Sigma-Aldrich), Trimesoyl chloride(TMC) (98%, Sigma-Aldrich), diethylene glycol bis(3-aminopropyl) ether (DGBAmE, 98%, Sigma-Aldrich), 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TF$_2$N], 99.9%, Sigma-Aldrich), distilled water (prepared in lab).

2.2 PSF Support Fabrication
PSF support is prepared by mixing 15wt% PSF pallet with 3wt% PVP and 82wt% of NMP. The mixture is let to stir for 24 hours before casting. The membrane support is casted using glass rod with thickness of approximately 200 µm. The membrane is immersed in water bath for removal of residual solvent for overnight. The membrane is stored in distilled water before use.
2.3 Interfacial Polymerization (IP)
The TFC membranes were prepared via interfacial polymerization (IP) process. 0.28% w/v of TMC was mixed with heptane as solvent as the organic phase while 0.35% w/v of DGBAmE was mixed with water for the aqueous phase. The PSF membrane support was sandwiched between a glass plate and Viton rubber frame. Organic phase was first poured onto the membrane for at least 10 minutes. The excess solution was poured before pouring aqueous phase solution. The IP process was allowed to take place for 5 minutes before the membrane is let dried overnight in ambient condition. The TFN membrane was prepared by mixing 1vol% - 5vol% of [EMIM][Tf2N] into the aqueous phase as shown in table 1. For characterization purposes, PA layer for all membrane is prepared without PSF support.

| Sample   | [EMIM][Tf2N] loading in vol% (based on the total weight of monomer) |
|----------|---------------------------------------------------------------|
| Pure PA  | 0                                                             |
| PA-IL1   | 1                                                             |
| PA-IL2   | 2                                                             |
| PA-IL3   | 3                                                             |
| PA-IL4   | 4                                                             |
| PA-IL5   | 5                                                             |

2.4 Characterization
Fourier Transform Infrared Spectrometer (FTIR) analysis was done to determine the functional group changes with the incorporation of [EMIM][Tf2N]. The analysis was done using Perkin-Elmer Spectrum 1 Fourier transform Infrared spectrometer and the spectra were analyzed by the Spectra One Software.

Differential scanning calorimetry (DSC) was used to analyze the effect IL in TFC membranes from the glass transition temperature ($T_g$) data. Firstly, small cuts and cleaned membranes were placed on the DSC pans. The samples were heated from 30 °C to 800 °C at a rate of 10 °C/min. After reaching 250 °C, the samples were naturally cooled to remove the thermal history. Under the same procedure, the second scan was conducted again. To get the $T_g$ value of the TFCs, the second scan values were referred.

Lastly, Atomic Force Microscopy (AFM) analysis was conducted to study the membrane surface topology and surface roughness using Universal Scanning Probe Microscopy (USPM-AFM, Nano Navi, SII). The scanning probe was conducted on the top surface of the TFC membranes with scan surface of area 25 μm x 25 μm.
2.5 Gas separation performance testing

The membranes undergo CO₂ and CH₄ single gas permeation test at 1 bar feed pressure. The permeability is calculated by using following equation:

\[
\frac{P}{I} = \frac{Q_{STP}}{A \times \Delta P}
\]

(1)

where \( P/I \) is the permeance \([\text{cm}^3(\text{STP})/(\text{sec cm}^2 \text{ cmHg})]\), \( A \) is the effective surface area \([\text{cm}^2]\), \( \Delta P \) is pressure gradient across feed and permeate \([\text{cmHg}]\), \( Q_{STP} \) is the permeance flow rate at standard temperature and pressure \([\text{cm}^3(\text{STP})/\text{sec}]\). Permeability is expressed in gas permeation units, GPU as 1 GPU = \( 1 \times 10^{-6} \) \( \text{cm}^3 \) (STP) \( \text{cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1} \).

Besides, the selectivity of membrane, \( a_{CO_2/CH_4} \) can be determined by ratio of higher permeable gas \( i \) to lesser permeable gas \( j \). The equation for selectivity is shown in equation below

\[
a_{CO_2/CH_4} = \frac{P/I_{CO_2}}{P/I_{CH_4}} = \frac{P_{CO_2}}{P_{CH_4}}
\]

(2)
3.0 Results and discussion

3.1 Membrane characterization

![FTIR Spectrum](image)

Figure 1: FTIR Spectrum for fabricated pure PA and PA-IL5. and FTIR spectra for [EMIM][TF2N] spectra is adapted from [19]

The fabricated TFC membranes were analyzed using FTIR to determine the change in functional group in PA membrane with the incorporation of [EMIM][TF2N] as presented in Figure 1. For comparison, only PA and PA-IL5 were included while the FTIR spectra for [EMIM][TF2N] is adopted from [19]. For PA membrane, it is noticeable that characteristic peaks of PA which include N-H group at wavelength of 1646 cm\(^{-1}\), C-H group at wavelength of 1451 cm\(^{-1}\) and O-H group 1087 cm\(^{-1}\). Thus, this proving that the PA layer was successfully fabricated.

Upon incorporation of [EMIM][TF2N], the presence of additional broad bands, can be observed at wavelength of 789 cm\(^{-1}\)which represents the C-H bond, S=O group at wavelength of 1184 cm\(^{-1}\), C-O group presents at wavelength of 1134 cm\(^{-1}\) and S=O present at wavelength of 1355 cm\(^{-1}\). The presence of [EMIM][TF2N] characteristic peaks indicates an additional interaction between [EMIM][TF2N] and PA which confirms that the IL is successfully embedded in the PA-IL5 TFC membrane. Hence, based on these results it confirms that there is a successful attachment of the IL bonds onto the PA membrane.
Table 2: Glass transition temperature

| Sample   | Glass Transition Temperature, $T_g$ $(^\circ C)$ |
|----------|-----------------------------------------------|
| PA       | 130.16                                        |
| PA-IL1   | 131.01                                        |
| PA-IL2   | 133.06                                        |
| PA-IL3   | 133.42                                        |
| PA-IL4   | 128.83                                        |
| PA-IL5   | 128.13                                        |

For DSC, the effective thin layer of PA (without PSF support) was sent for analysis to determine the glass transition temperature ($T_g$) of PA layer of the membranes and the effect of the presence of IL on $T_g$. The $T_g$ of the membranes are tabulated on Table 2. The $T_g$ of PA is recorded at 130.16 $^\circ$C. The $T_g$ increases with the incorporation of IL from PA till PA-IL3. As the loading increase, the interaction between the [EMIM][TF$_2$N] and polymer increased. The presence of IL increases the $T_g$ of the membrane which indicates the increase in polymer chain rigidity [20]. This is due to possible increase in interaction between PA and [EMIM][TF$_2$N] with increasing loading up to 3vol%.

However, it can be seen that the glass transition decreases at IL loading of PA-IL4 and PA-IL5. It is postulated that at higher loading (more than 3vol%) of the ionic liquid act as plasticizer which causes the polymer to relax and results in decrease in rigidity[21] and the gas separation performance (subsection 3.2). The presence of higher percentage of IL loading in the membrane decreases the $T_g$ value of the membrane which indicates the increase in polymer chain flexibility [20].
Figure 2: Cross-sectional membrane morphology at 10000x magnification at different IL loading

The surface morphologies for the prepared samples were determined by using Atomic Force Microscopy (AFM) as presented in Figure 2. The color intensity stipulates the vertical profile of the membrane surface where the pores and regions are on the dark regions and the peak points are on the bright regions. It can be observed that the membranes developed possess nodules-like-leaf form of roughness feature. The formation of the features is caused by the release of nanobubbles in the organic monomer solution during the IP process [22]. Based on the Figure 2, it can be observed that the roughness of the surface decreases with increasing [EMIM][TF3N] loadings. Pure PA possesses the roughest surface while PA-IL5 possess the smoothest surface.
Table 3: Membrane surface roughness for all PA-ILTFC membranes

| Sample   | Average roughness, $R_a$ (nm) |
|----------|-------------------------------|
| PA       | 22.49                         |
| PA-IL1   | 18.79                         |
| PA-IL2   | 30.19                         |
| PA-IL3   | 50.56                         |
| PA-IL4   | 43.73                         |
| PA-IL5   | 34.58                         |

Table 3 shows the roughness of membrane surface with maximum height and maximum valley at different [EMIM][TF$_2$N] loading. Based on the table, it can be observed that average roughness of the membrane decreases from PA (22.49 nm) to PA-IL1 (18.79 nm) and then increases from PA-IL1 to PA-IL3. Moreover, it can be observed that the average roughness of membrane decreases from PA-IL4 to PA-IL5, albeit still higher than PA TFC membrane. It is postulated that the decrease in surface roughness is related to the reduction in $T_g$ (Table 2). At higher loading (more that 3vol%), the polymer relaxes due to the lesser interaction between IL and PA resulting in decreasing surface roughness. Overall, it can be analyzed that PA-IL3 possess highest value of average roughness which is at 50.56 nm while PA-IL1 possess lowest value of the average roughness which is at 18.79 nm.

From the result, it can be postulated that the surface roughness increases with the increasing IL loading (except for PA-IL1) when compared to PA TFC membrane. The increase in roughness may be due to the increase in PA-IL interaction at the polymer surface (Table 2) and the fluctuation of the PA-IL interface interaction [23], resulting in bigger gap on the maximum and minimum height of the valley-like roughness features, thus the increase in the average surface roughness.
3.2 Gas permeation test

The fabricated TFC membranes were successfully tested for CO₂ permeability and CO₂/CH₄ selectivity under different loading at 1 bar feed pressure. The gas separation performance is shown in Figure 3. Overall, with increasing [EMIM][TF₂N] loading, the CO₂ permeability increases. Pure PA membrane shows CO₂ permeability of 33.43 GPU. With 1vol% -3vol% of [EMIM][TF₂N], the CO₂ permeability increases slightly for about less than 2% increment. Meanwhile, the CO₂ permeability increases significantly with 4vol% and 5vol% of [EMIM][TF₂N] with increment of as much as 103 times for incorporation of 5vol% of IL. It is postulated that at higher [EMIM][TF₂N] loading (more than 3 vol%), the presence of IL relaxes the polymer matrix (Table 2) thus resulting in the outstanding increase in CO₂ permeability.

Meanwhile, for CO₂/CH₄ selectivity, the trend follows that of CO₂ permeability. The CO₂/CH₄ selectivity starts at 1.78 for pure PA TFC membrane. With the incorporation of 1vol% of IL, the CO₂/CH₄ selectivity increases 4 times while with the highest [EMIM][TF₂N] loading of 5vol%, the CO₂/CH₄ selectivity increases by 17 times compared to pure PA TFC membrane. The increase in the CO₂/CH₄ selectivity is due to the higher interaction between [EMIM][TF₂N] and CO₂ compared CH₄ thus resulting in high CO₂/CH₄ selectivity. As the gas solubility in IL is highly dependent on anion, the fluorine group (CO₂philic group) in [EMIM][TF₂N] played a major role in enhancing the CO₂ permeability and therefore increasing the CO₂/CH₄ selectivity.

Figure 3: CO₂ permeability and CO₂/CH₄ selectivity for all PA-ILTFC membrane tested at 1 bar feed pressure
4.0 Conclusion

The PA-IL membrane were successfully fabricated and the effects on membrane properties and gas separation performance were discussed. FTIR analysis confirmed the successful fabrication of all TFC membranes with the presence of characteristic peaks of [EMIM][TF₂N]. The top surface morphologies show that [EMIM][TF₂N] reduces the membrane roughness. Thermal analysis also confirm that TFC/IL membrane become rigid until 3vol% and become more flexible with loading more than 4vol%. Based on the gas permeation test, it can be observed that PA-IL5 gives the highest gas separation performance at 1 bar feed pressure. CO₂ permeability increases from 33 to 3200 GPU while CO₂/CH₄ selectivity increases from 1.78 to 34 compared to that of pure PA TFC membrane. This shows that PA-IL TFC membrane has the opportunity to be further explored in fabricating composite membrane for gas separation application.

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