

Composite blending of ionic liquid–poly(ether sulfone) polymeric membranes: Green materials with potential for carbon dioxide/methane separation

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ABSTRACT: The incorporation of imidazolium-based ionic liquids into a poly(ether sulfone) (PES) polymeric membrane resulted in a dense and void-free polymeric membrane. As determined through the ideal gas permeation test, the carbon dioxide (CO₂) permeation increased about 22% compared to that of the pure PES polymeric membrane whereas the methane (CH₄) permeation decreased tremendously. This made the CO₂/CH₄ ideal separation increase substantially by more than 100%. This study highlighted the utilization of imidazolium-based ionic liquids in the synthesis of ionic liquid polymeric membranes (ILPMs). Two different ionic liquids were used to compare the CO₂ separation performance through the membranes. The glass-transition temperatures (T_g s) of ILPMs were found to be lower than the T_g of the pure PES polymeric membranes; this supported the high CO₂ permeation of the ILPMs due to the increase in PES flexibility caused by ionic liquid addition. The results also draw attention to new trends of ionic liquids as a potential green candidates for future membrane synthesis. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43999.

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INTRODUCTION

Natural gas that is commercially used by end-use consumers is much different from the raw natural gas that is brought up from underground to the wellhead. The raw natural gas has impurities, such as carbon dioxide (CO₂) and hydrogen sulfide (H₂S).¹ Technological scouting has been carried out for existing CO₂-removal technologies, including absorption, adsorption, cryogenic, and membrane processes. The greatest advantage of membrane separation is its simplicity because it has almost no involvement of moving parts and the equipment can be assembled with simple construction.² However, initial acceptance of this technology was slow and was limited to smaller processes because it involves several economic risks when it is implemented in larger streams.³

Membrane processes have been proposed as a supplement to the existing conventional distillation. This is due to the fact that membrane separation processes offer more capital and energy efficiency compared to other conventional separation processes.⁴ Moreover, their simplicity, with no involvement of absorbents, make them extremely attractive for CO₂ capture; these processes can also be easily retrofitted, modularized, and scaled up for

several applications.^{2,5} Although numerous membrane materials have shown promising separation performance for CO₂ removal, there are no materials with adequate separation performance for high CO₂ contents. At this time, the main challenge in membrane application technology for the gas separation process is to obtain a material with a higher permeability and selectivity.⁶ However, for membrane materials to be viable, they need to be thermally and chemically robust, resistant to plasticization and aging effects, and cost-effective enough to the manufacturer.⁷

Conceptually, polymeric membranes are considered matured membrane types in membrane separation technology. In general, polymeric membranes are mostly nonporous; hence, gas permeation through the membrane is described by a solution–diffusion mechanism. This mechanism is based on the solubility of specific gases within the membrane and their diffusion through the dense membrane matrix. Therefore, the separation process is not only diffusion dependent, but it is also reliant on the physical–chemical interaction between the gas and the polymer, which will determine the gas quantity that accumulates in the polymeric membrane matrix.⁸ However, polymeric membranes are not perfectly effective because of their frequent

swelling and plasticization effects when they are operated under high pressure and because of high impurities in the gas inlet.

On the other hand, one research trend to fill one of the gaps in interphase morphology is the use of room-temperature ionic liquids (RTILs).⁹ In recent years, RTILs have been developed as green solvents and alternative materials for CO₂ separation in the natural gas sweetening process.¹⁰ RTILs are known as molten organic salts at ambient temperature and pressure, and they have unique physicochemical properties, such as a negligible vapor pressure,¹¹ nonflammability,¹² and a high ionic conductivity,¹³ that allow them to potentially replace conventional organic solvents in many chemical processes and purifications.¹⁴ Focus on a class of salts started when this material was verified by its higher CO₂ solubility compared to other hydrocarbon and light gases. Ionic liquids are known to have a high intrinsic physical solubility for CO₂.¹⁵ Hence, the attention of this study was on the evaluation of how imidazolium-based ionic liquids specifically affect CO₂ separation through the poly(ether sulfone) (PES) polymeric membrane.

EXPERIMENTAL

Materials

Among available polymers, PES was chosen as the polymer basis for the synthesis of ionic liquid polymeric membranes (ILPMs). Its intrinsic properties, such as its chemical and thermal resistance and good dimensional stability, were the major advantages of using PES.¹⁶ In addition, PES is commercially available and also offers a high energy density, ease in thin film formation, and favorability toward CO₂/methane (CH₄) selectivity. This made PES a suitable candidate for membrane applications.¹⁷ The PES used in this study was a commercial PES Ultrason E 6020P purchased from BASF in flake form. Numerous reports have shown that CO₂ is very soluble in imidazolium-based RTILs.¹⁸ 1-R-3-Methyl imidazolium based RTILs become more attracted in the CO₂-removal process as their tendency is to be less viscous compared to other RTILs.¹⁹ One of the studies done by Cadena *et al.*²⁰ proved the influence of the cation structure in RTILs on CO₂ dissolution, where the methyl group had a slight impact on the imidazolium C-2 atom. Among available ionic liquids, 1-ethyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)amide (emim[Tf₂N]) and 1-ethyl-3-methyl imidazolium trifluoromethanesulfonate (emim[CF₃SO₃]) were selected in this study for the synthesis of ILPMs. As far as the selection of ionic liquid was concerned, the CO₂ solubility in the ionic liquid was a vital factor for consideration. The rate of CO₂ solubility in an ionic liquid is governed by many factors, including the operating pressure and temperature, choice of anion, and the chain presence in the anion group.²¹ The CO₂ solubility generally increases with increasing pressure and decreases with decreasing pressure. For anion selection, Pereira *et al.*²² suggested that ionic liquids that contain fluorine chains and halide ions provide a greater CO₂ solubility capacity as compared to those that contain other ions. Hence, among ionic liquids, emim[Tf₂N] and emim[CF₃SO₃] were selected in this study for the synthesis of enhanced polymeric membranes with ionic liquids so that we could compare the CO₂ solubility ability with different anions having different fluorine types.

Table I. Details of the Membrane Compositions

Membrane	Description	PES (wt/wt %)	Ionic liquid (wt/wt %)	
			emim [Tf ₂ N]	emim [CF ₃ SO ₃]
M1	Pure PES	20	—	—
M2	PES with emim[Tf ₂ N]	20	10	—
M3		20	20	—
M4	PES with emim[CF ₃ SO ₃]	20	—	10
M5		20	—	20

Between both of the selected ionic liquids, we expected to obtain a higher CO₂ permeance with emim[Tf₂N] because of its lower viscosity since a less viscous ionic liquid tends to facilitate faster gas (CO₂) diffusion.²³ Other than that, emim[Tf₂N] contains a fluoromethyl chain that could promote a greater solubility of CO₂ compared to the fluoromethane group presence in emim[CF₃SO₃]. It should be noted that only two ionic liquids were selected because the initial purpose of the study was to analyze the effects of ionic liquid blending with PES in CO₂ separation through membranes. Both ionic liquids were obtained from Sigma-Aldrich with 99.99% purity and were used without any purification. The ionic liquids used were toxic and corrosive; hence, they had to be handled with proper personal protective equipment, such as gloves, goggles, and safety jackets to prevent any related hazards.

Membrane Synthesis

There were two types of membranes synthesized in this study: the pure PES polymeric membrane and ILPMs. PES polymer flakes were first dried to remove excess moisture trapped in the polymer upon membrane synthesis. Throughout the process, the PES used was fixed at 20 wt/wt % for all of the membranes, and this percentage was based on the weight of solvent used. For the pure PES polymeric membrane, the dried PES polymer flakes were dissolved with *N*-methylpyrrolidone by 24 h of continuous stirring. For ILPM fabrication, the ionic liquid was mixed with *N*-methylpyrrolidone, and we observed that the solution was well-mixed because there was no phase separation observed. After a while, a proper amount of polymer was partially added, and stirring was also completed within 24 h. The dope solution preparation was conducted at room temperature. Through previous studies done on polymer-ionic liquid blend membranes, the polymer was optimized at 20 wt/wt %, whereas the ionic liquid used was at a maximum concentration of 20 wt/wt %, where the prepared solution was at a concentration appropriate for membrane casting. Table I shows the detailed composition of the synthesized membranes in this study. The dope solution was cast onto the clean and dust-free glass plate with a solution casting machine with a 180- μ m blade gap. The membranes were dried in a vacuum oven at 160 °C for 24 h.

Membrane Characterization

The morphological structures of the synthesized flat-sheet membranes were analyzed with field emission scanning electron microscopy (FESEM). In this study, variable-pressure FESEM (Zeiss Supra 55 VP) was used to determine the qualitative structural assessment of both the surfaces and cross sections of the membranes. The dried membranes were cryogenically fractured in liquid nitrogen through their immersion for few seconds to obtain a smooth and clean cross-sectional image.^{24,25} The samples were mounted horizontally and vertically on a circular stainless steel plate holder to obtain both cross-sectional and surface view micrographs. Thermogravimetric analysis (TGA) was done to estimate the membrane thermal stability and the amount of solvent remaining in the membranes.²⁶ In this study, the membranes were thermally characterized by TGA (PerkinElmer, TGA 4000). The samples were cut into small pieces and heated from 25 to 800 °C at a 10 °C/min heating rate with inert nitrogen (N₂) flushed at 20 mL/min to prevent any interference of corrosive gas, which could cause thermal oxidative degradation. The membranes were also characterized with a TA Instruments Q20 differential scanning calorimeter to determine the glass-transition temperature (*T_g*) values of the membranes. In this study, differential scanning calorimetry (DSC) was run to determine the effect of ionic liquid blending on the membrane *T_g*. For this analysis, the membranes were cut into small pieces, weighed, and placed onto alumina DSC pans. The samples were heated from 30 to 300 °C at a rate of 10 °C/min under N₂ conditions. After they reached 250 °C, the samples were naturally cooled down to 30 °C to remove their thermal histories.²⁷ A second scan was conducted again under the same procedure. We referred to the second scan thermogram to determine the *T_g* values of the membranes.²⁸

Membrane Gas Separation Performance

The gas separation performance was analyzed with a constant volume measurement, where the upstream pressure was kept constant while we measured the flux across the membrane film.²⁶ The gas permeation experiment of the synthesized flat-sheet membranes was conducted according to previous studies,^{29,30} and the steps were carried out as follows. The synthesized membranes were tested on pure CO₂ and CH₄ gas in the pressure range of 10–30 bars to investigate the effects of the pressure, and the tests were performed at room temperature (27–29 °C). The membrane was placed on a dead-end module, and the gas flowing into the membrane cell was perpendicular to the membrane position. The gas permeation system was vacuumed for about 20 min before we started to remove all of the residual gases trapped inside. The permeating gas flow rate was measured with a bubble flow meter, and the rate was recorded every 15–20 min three to five times.^{30,31} To maintain a reliable result, the permeation rates were determined from the average of two membranes of the same composition. The individual gas permeance was calculated by the following equation:

$$\frac{P}{l} = \frac{J}{\Delta p} \quad (1)$$

where *P/l* is the permeance, which is expressed in gas permeance units [GPU; 1 GPU = 10⁻⁶ cm³ (STP)/(cm² s Hg)]; *J* is

the flux of the gas passing through the membrane (cm³/cm².s); *l* is the membrane thickness (cm); and Δp is the pressure difference across the membrane. The ideal separation performance ($\alpha_{\text{CO}_2/\text{CH}_4}$) was defined as the ratio of CO₂ permeance (*P*_{CO₂}/*l*) to the CH₄ permeance (*P*_{CH₄}/*l*) and could be expressed as follows:

$$\alpha_{\text{CO}_2/\text{CH}_4} = \frac{\left(\frac{P_{\text{CO}_2}}{l}\right)}{\left(\frac{P_{\text{CH}_4}}{l}\right)} \quad (2)$$

The gas permeation results and the ideal separation performance were analyzed with respect to the ionic liquid composition accordingly.

RESULTS AND DISCUSSION

Membrane Morphology Characterization

Representative FESEM images of the synthesized membranes are shown in Figure 1. These images show that all of the synthesized membranes were dense in structure with no void or pores observed. The addition of ionic liquid showed no significant effects on the membrane morphology where the membranes were also found to be dense for both types of ionic liquids and to have no substantial difference from the pure PES membrane [Figure 1(a)]. As reported in the literature, membranes fabricated by the dry-phase inversion method always produce membranes that are dense in structure.³² This phenomenon was also observed through this study, where the fabricated membranes had dense structures where no pores were observed at this magnification. A membrane with a dense structure is always preferable for gas and water separation functions because the presence of macrovoids in the membrane structure is undesirable because the macrovoids might have an adverse effect on the long-term membrane stability.³³ The membranes thicknesses were measured to be around 50–100 μm.

Membrane Thermal Characterization

TGA was basically used to quantify the weight loss of the materials across temperatures. When a material is heated uniformly across a range of temperatures, a continuous plot of weight loss against temperature can be obtained. Figure 2 shows the TGA curves for the synthesized membranes. For M1, which was the base PES membrane, there were two weight losses observed, where the first weight loss occurred around 210 °C. The weight loss continued until 270 °C, and this was due to the remaining solvent after the membrane was dried. The calculated weight loss was only 2–3%, and it stayed nearly constant up to 470 °C. Another observed weight loss started at 470 °C and ended at 590 °C; this indicated a total of 42% weight loss. The weight loss at this temperature range was attributed to polymer decomposition because PES was reported to start decomposing at 450 °C onward.³⁴ Furthermore, the residual amount of membrane left was about 20%.

On the other hand, all of the synthesized polymeric ionic liquid membranes (M2–M5) seemed to be free from moisture, as there no weight loss was observed up to 100 °C.³⁰ However, the membrane decomposition temperatures were lower compared to that of the pure PES polymeric membrane. Membranes with emim[Tf₂N] started to decompose at 410 °C, whereas the

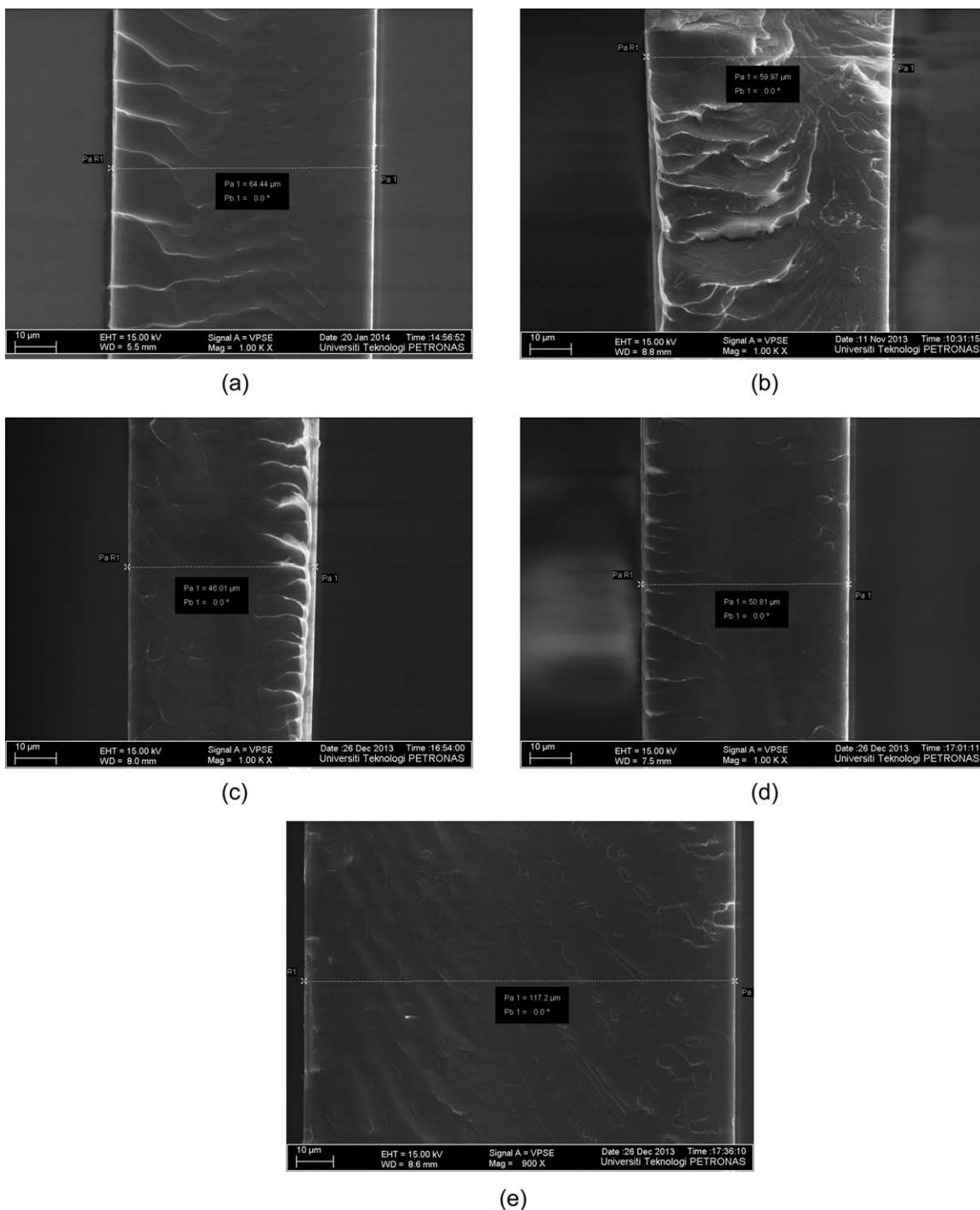


Figure 1. Cross-sectional images of the fabricated membranes: (a) M1, (b) M2, (c) M3, (d) M4, and (e) M5. Pa 1, Pb 1, Pa and R1 is the annotation of a distance in FESEM for the thickness measurement.

membrane with $\text{emim}[\text{CF}_3\text{SO}_3]$ started to decompose at 395 °C. This quantified that the addition of ionic liquid lowered the polymer degradation temperature; this meant that the imidazolium-based ionic liquid decreased the thermal stability of the PES membrane. Membranes with imidazolium-based ionic liquid tended to decompose earlier with the ionic liquid addition, and this caused by the ether bond break in PES.²⁶ Other than that, the incorporation of ionic liquid decreased

the thermal stability of the PES polymer; this was due to the reduction in the intermolecular forces between the ionic liquid and the polymer, and at the same time, the segmental motion of the polymer network was enhanced.³⁵ In addition, the polymer degradation weight loss increased up to 60% of the total polymer as compared to only 42% of the polymer weight loss observed in the pure PES membrane. This indicated the presence of ionic liquid in the polymeric membrane. The

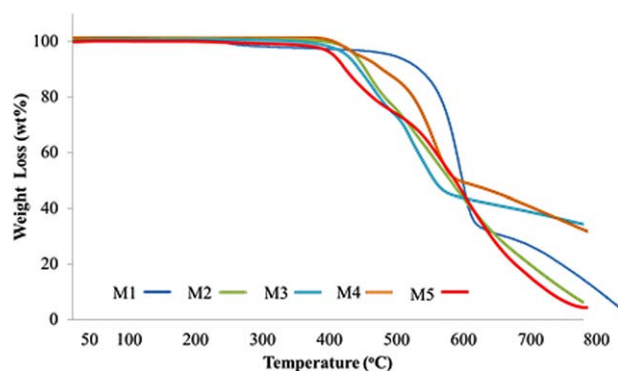


Figure 2. TGA curves of the fabricated membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

observation was deliberated more as the increase in the ionic liquid concentration increased the membrane residual weight. However, in this case, no components were volatile as there was no weight loss when the membranes were heated up to 350 °C. These findings confirm that the thermal stability of these membranes for natural gas purification application would be safe.

T_g

DSC is another membrane thermal characterization tool that is widely used to study the phase transition across a range of temperatures. Typically, the T_g values of membranes will change when there is an alteration made to the membrane. Table II shows the T_g values for the synthesized membranes determined from DSC analysis.

As shown in Table II, T_g of the fabricated PES was found similar to the value reported in the literature, which was 220 °C.³⁶ The effects of the ionic liquid incorporated into the PES membranes were also analyzed by the DSC experiment. We found that T_g was lower than the base PES membrane T_g , and T_g also decreased as the ionic liquid concentration was increased. This observation was similar to that in the literature, where the addition of low-molecular-weight additives decreased the T_g values of pure polymeric membranes.³⁷ The addition of a low-molecular-weight additive with a very low T_g diluted the polymer matrix and, thus, decreased T_g .³⁸ The polymer phase transitions were directly related to their chain flexibility. So, it is important to study T_g because it marks the polymer transition phase between brittle properties to more flexible properties at higher temperatures. Thus, with the addition of ionic liquid, the PES flexibility increased, and this resulted in a decreased in T_g . These findings also showed that the PES–ionic liquid membranes had a less crystalline and amorphous structure compared

Table II. T_g Values of the Fabricated Membranes

Membrane	T_g (°C)
M1	220
M2	142
M3	126
M4	160
M5	100

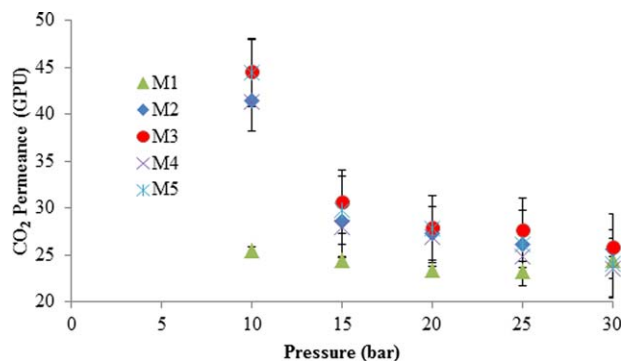


Figure 3. CO₂ permeance of the fabricated membranes across pressure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

to the pure PES membrane. Chaurasia *et al.*³⁵ also found the same decreasing trend for T_g when they incorporated 1-butyl-3-methylimidazolium tetrafluoroborate into poly(vinylidene fluoride) membranes. They also mentioned that the incorporation of ionic liquid, which acted as a plasticizer, was expected to decrease the degree of crystallinity; it reduced the intermolecular forces between the ionic liquid and polymer and eventually reduced T_g . Other than that, the team also found similar findings in earlier research, where the incorporation of ionic liquid decreased T_g . They claimed that ionic liquid not only provided the mobile ion but also led to enhancements in the amorphicity and decreased crystallinity.³⁹ The decreasing trend in T_g was observed for both types of ionic liquids; this indicated that both imidazolium-based ionic liquids increased the flexibility of the PES matrix.²⁶ In parallel to the gas permeation results, membranes with ionic liquid addition had a higher ideal separation factor.⁴⁰ The increase in the ionic liquid content in the membrane further reduced T_g . In addition, the increasing loading of emim[CF₃SO₃] reduced T_g more than emim[Tf₂N]. This might have been due to the higher viscosity of emim[CF₃SO₃], which caused the membrane to be more amorphous and, thus, lowered the T_g values of the membranes containing emim[CF₃SO₃].

Ideal Gas Separation Performance

The gas permeation results observed were the average values of at least two membranes for all compositions. Instead, two parts were tested for all membranes from the same sheet. Other than that, the permeance of CO₂ passing through the membrane was measured a minimum of two times, and each measurement was an average of five readings. Therefore, the reproducibility and repeatability of the gas permeation separation performance could be maintained. The gas permeation rates of CO₂, and CH₄ and the ideal CO₂/CH₄ selectivity across pressure are presented in Figures (3 and 4), and 5, respectively. It should be noted that all of the synthesized membranes were in good condition without any damage or breakage, even after testing at 30 bar of pressure.

Effects of the Ionic Liquid Concentration. As mentioned earlier, both of the selected ionic liquids were imidazolium based because this cation exhibits good absorption of CO₂, as reported in the literature.⁴¹ The comparison study was done between the trifluoromethanesulfonyl amide [Tf₂N] and

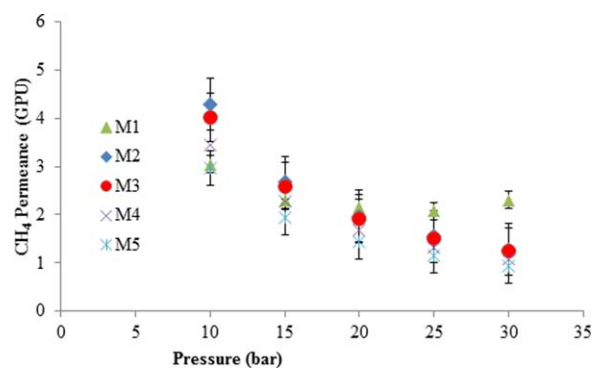


Figure 4. CH₄ permeance of the fabricated membranes across pressure. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

trifluoromethanesulfonate [CF₃SO₃] anions as the CO₂ absorbents in separation performance. As shown in Figure 3, the CO₂ permeation results of both types of ionic liquids increased with increasing concentration of ionic liquid. However, the CO₂ permeation of the PES membrane containing emim[TF₂N] was higher than the CO₂ permeation of the PES membrane containing emim[CF₃SO₃].

Figure 3 shows that the CO₂ permeance of the PES–emim[CF₃SO₃] membrane only increased about 5% compared to that of the PES–emim[TF₂N] membrane, which increased by 15%. This might have been due to the higher viscosity of emim[CF₃SO₃], as it was reported that a high-viscous ionic liquid decreased the CO₂ permeation.¹⁴ As reported in the material safety datasheets of both ionic liquids, the viscosity of [CF₃SO₃] (51.7 cP) was almost double that of emim[TF₂N] (28 cP). The membrane with the [TF₂N] anion was known to have a higher CO₂ affinity compared to that with the [CF₃SO₃] anion. Another explanation for the different gas permeation performance might simply have been the larger size of [TF₂N] anion, which was preferable for CO₂ diffusion through the membrane.⁴²

The same trend was observed for CH₄ permeation, where the [TF₂N] anion exhibited a higher CH₄ permeation than the [CF₃SO₃] anion, as shown in Figure 4. However, with increasing concentration of emim[CF₃SO₃], the CH₄ permeation in this membrane seemed to show no significant difference. Even experimental studies of CH₄ solubility in emim[CF₃SO₃] are scarce. This finding shows that emim[CF₃SO₃] had a very low affinity toward CH₄, where the addition of this ionic liquid did not much affect the CH₄ permeation. This could have been due to the lower size of the [CF₃SO₃] anion, which did not allow the CH₄ to pass through it and resulted in a stagnant effect of CH₄ permeation at any loading.⁴² Because of these reasons, the membrane containing emim[CF₃SO₃] had a higher CO₂/CH₄ selectivity than emim[TF₂N], as plotted in Figure 5.

Effects of Pressure. As shown in Figures 3 and 4, it was observed that all of the fabricated membranes had similar decreasing CO₂ and CH₄ permeance trends with increasing pressure. These trends clearly showed the typical behavior of PES as a glassy polymer, where the gas permeance was inversely proportional to the pressure. Instead, the CO₂ permeance was

higher than the CH₄ permeance for all of membranes because of the ability of CO₂ gas to be more soluble in PES-based glassy polymers. In addition, CO₂ was more condensable compared to CH₄. Furthermore, the larger gas molecular size restricted the interaction with the polymer chain and, thus, decreased the diffusion coefficient compared to the smaller gas molecules.⁴³ As a result, a smaller kinetic diameter of a molecule like CO₂ (0.33 μm) is always favorable for pass through over larger molecules such as CH₄ (0.38 μm).⁴⁴

However, at 30 bar of pressure, we observed an increasing value in the PES membrane permeance and a decreasing trend in the CO₂/CH₄ selectivity. The interference in the membrane packing density and the chain mobility during the plasticization effects led to an opposite phenomenon, where the gas permeance increased, and the selectivity decreased. This was caused by the sorption of CO₂ into the excess free volume of the PES glassy polymer. Generally, glassy polymer membranes exhibit an increase in the CO₂/CH₄ selectivity and a decrease in the CO₂ permeance with increasing feed pressure. However, the gas permeance only started to increase as the feed pressure reached higher than a specific value; this is known as a plasticization effect.⁴⁵ Remarkably, because of ionic liquid addition, the membrane still behaved accordingly up to 30 bar of pressure. This showed that ionic liquid addition increased the plasticization pressure of the membrane. Unlike conventional plasticizers, the ionic liquid did not destroy the mechanical integrity of the polymeric membranes; even the ionic liquid reduced *T_g*. Chaurasia³⁵ claimed that this property was due to the negligible vapor pressure of the ionic liquid to make it a better plasticizer. In addition, Bachman *et al.*⁴⁶ also stated that the increased in the membrane stability was expected to increase the membrane plasticization resistance. Moreover, the addition of the ionic liquid also enhanced the condensable gas, including CO₂, and made it condense and soluble in the PES matrix because the alkyl and fluoroalkyl chain in imidazolium-based ionic liquids attracted CO₂ and made it more soluble.

Comparison with Literature Data. The membranes developed through this study were also compared with other supported ionic liquid membranes reported in the literature, as tabulated in Figure 6.⁹ The main comparisons of these studies were on

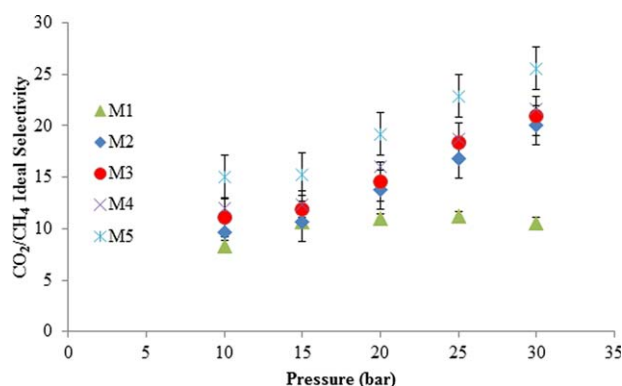


Figure 5. CO₂/CH₄ ideal selectivity of the fabricated membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

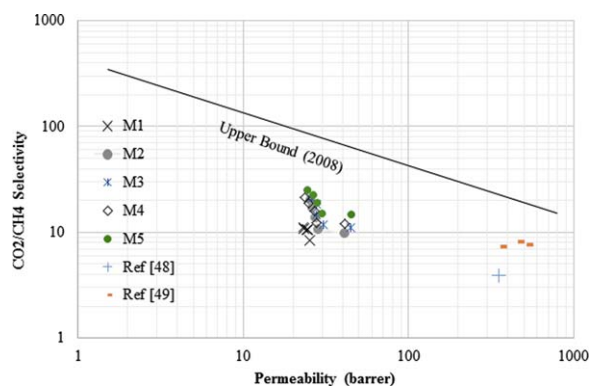


Figure 6. Comparison with literature data. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the tested pressure and the synthesized method. The referred literature was mostly on supported ionic liquid membranes, where the membranes were coated with ionic liquid. However, in this study, we used the blending method of an ionic liquid and polymer during the membrane synthesis process. Apart from that, the maximum operating pressure for the referred literatures was at 20 bar, whereas the membranes in this studies was tested up to 30 bar of pressure. However, the comparison was done at a pressure of about 20 bar for a reasonable comparison. It should be noted that the unit of the permeance was converted from GPU to $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ with the following equation⁴⁷:

$$3000 \text{ GPU} = 10^{-6} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1} \quad (3)$$

As shown in Figure 6, the permeance obtained in this study was comparable to that in the supported ionic liquid membranes. Even the supported ionic liquid membranes showed higher CO_2 permeabilities, and the reported CO_2/CH_4 selectivity for the referred literatures was below 10.^{48,49} However, through this novel approach, the CO_2/CH_4 ideal selectivity reached about 40, which is approaching the Robeson upper bound. It was obvious that the separation factor increased with the ionic liquid blending with the polymer. This was due to the fact that the ionic liquid mixed homogeneously with the polymer, and this eventually enhanced the CO_2 affinity in the membranes. On the other hand, the increase in the CO_2 permeation depicted was due to the presence of the fluorine chain in the ionic liquid. The fluorine chain was believed to increase the CO_2 solubility in the membranes and restrict the permeation of CH_4 ; hence, it increased the overall CO_2/CH_4 selectivity⁴². Other than that, the incorporation of ionic liquid decreased the chain rigidity of the polymer. The decrease in the chain rigidity of the gas increased the free volume in the membranes, and this increased the penetrant mobility within the membrane and eventually led to a higher permeability.⁵⁰

The improved CO_2 permeance and CO_2/CH_4 ideal selectivity showed that these imidazolium-based ionic liquids adsorbed CO_2 faster than CH_4 . The role of the ionic liquid was not only to increase the separation performance but also to act as a wetting agent within the polymer matrix for better CO_2 affinity.

CONCLUSIONS

PES polymeric membranes with different imidazolium-based ionic liquids were fabricated with a dry-phase inversion method.

FESEM cross-sectional analysis showed that the ionic liquid was homogeneously mixed in the polymer matrix, as the synthesized membranes were defect free and dense in structure with no phase separation. The newly ILPMs were compared with the base PES polymeric membrane, and the separation performance was also compared on the basis of the type of ionic liquid. Both innovative types of membranes showed significant improvements in the CO_2 permeation and ideal CO_2/CH_4 selectivity. However, membranes with emim[Tf_2N] addition gave higher CO_2 permeation values, whereas membranes with emim[CF_3SO_3] gave higher ideal CO_2/CH_4 selectivity values. This was due to the fact that emim[Tf_2N] increased both CO_2 and CH_4 permeation, whereas emim[CF_3SO_3] only significantly increased the CO_2 permeation. These results demonstrate that the imidazolium-based ionic liquids were fast CO_2 adsorbents, and this method could be used as a preliminary study for the advancement of materials in membrane fabrication.

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