Journal of Applied Sciences

ISSN 1812-5654

Journal of Applied Sciences 14 (10): 1083-1087, 2014
ISSN 1812-5654 / DOI: 10.3923/jas.2014.1083.1087

Comparison Study of Emim [Tf_2N] and Emim [CF_3SO_3] Effects on Polyethersulfone Membrane for CO_2/CH_4 Separation

Dzeti Farhah Mohshim, Hilmi Mukhtar and Zakaria Man
Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, Tronoh, 31750, Perak Darul Ridzuan, Malaysia

Abstract: Removal of CO_2 in natural gas sweetening is nowadays focusing on membrane based practice. An investigation on miscible blends of ionic liquids-polyethersulfone has been done for CO_2/CH_4 separation purpose. Different types of ionic liquids namely emim [Tf_2N] and emim[CF_3SO_3] is blended separately with polyethersulfone (PES) as the membrane casting solution. Experimental results show that both ionic liquids are miscible with PES and create dense polymeric membranes through FESEM analysis. The presence of ionic liquids in both PES membranes has considerably improved the CO_2 permeance without scarifying much on the CO_2/CH_4 ideal selectivity. At 10 barg pressure, the incorporation of emim [Tf_2N] and emim [CF_3SO_3] has also increased the CO_2/CH_4 ideal selectivity for 47 and 55% accordingly as compared to the pure PES membrane. It was noticed that blending of emim [Tf_2N] produced higher CO_2 permeance as expected and the miscible blend of emim [CF_3SO_3] has high CO_2/CH_4 selectivity as emim [CF_3SO_3] is selective towards CO_2/CH_4. It can be concluded that the imidazolium based ionic liquids are good to be used in natural gas sweeting system.

Key words: Polymeric membrane, emim [Tf_2N], emim[CF_3SO_3], CO_2 separation

INTRODUCTION

The issues on high natural gas demand have attracted ceaseless debates on undeveloped natural gas well, high carbon dioxide (CO_2) content and its removal technology. Apart from the well-implemented absorption and adsorption process (Van Der Sluijs *et al*., 1992), membrane technology has been a looking forward method because of its advantages on energy and space saving, small footprint and easy to scale up (Koros and Fleming 1993; D'Alessandro *et al*., 2010; Merkel *et al*., 2010; Strathmann, 2011; Pan *et al*., 2013). For instance, membrane technology especially polymeric membrane has already occupied about 20% of the CO_2/CH_4 separation market back in 2009 (Ebner and Ritter, 2009; Mohshim *et al*., 2012).

In addition, Room Temperature Ionic Liquid (RTIL) have pinched considerable attention in CO_2 capture since the RTIL can be tailored to possess high CO_2 affinity (Zhao, 2006). RTIL which is organic salt at room temperature are stable at high temperature, has negligible vapor pressure and non-flammable makes it suit for CO_2 separation in natural gas (Fredlake *et al*., 2004; Zhao, 2006). Recently, Universiti Teknologi PETRONAS has conducted the experiment of polymeric membrane fabrication blended with selected RTIL. Two different RTILs which are imidazolium based have been used and the performance of both RTILs is compared in this study.

MATERIALS AND METHODS

Materials and membrane preparation: Two Ionic Liquid Modidfied Polymeric Membranes (ILMPM) were prepared by blending two different ionic liquids which are 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, emim [Tf_2N] and 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate, emim [CF_3SO_3] in the solvent which is 1-Methyl-2-pyrrolidinone, NMP. Then, the polymer, polyethersulfone (PES) which is in flakes form is dissolved in the solvent-ionic liquid mixture. Pure PES membrane was also prepared with the same method without ionic liquid addition. The composition of each material is presented in Table 1.

Membrane casting and drying: Membranes were casted by using the membrane casting machine. The casting solution was poured onto glass plate and the casting

Corresponding Author: Dzeti Farhah Mohshim, Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, Tronoh, 31750, Perak Darul Ridzuan, Malaysia

knife was adjusted at 180 μm. The membranes were dried in drying oven at 90°C for overnight. The membranes were found to be fully dried as they are peeled off from the glass plate.

RESULTS AND DISCUSSION

Membrane characterization

- **Field emission scanning electron microscope (FESEM):** FESEM was used to analyze the influence of the ionic liquid, emim [Tf_2N] and emim [CF_3SO_3] blending with PES into the polymeric membrane fabrication. This test shows the characterization of the membrane surface morphology and the global chemical composition of the membranes and the distribution of the IL within the membranes

  Figure 1 shows examples of FESEM images of pure PES membrane and ILMPM based on emim [Tf_2N] and emim [CF_3SO_3]. It is noticed that the membranes are all dense in structure and this resembles that both ionic liquid emim [Tf_2N] and emim [CF_3SO_3] is miscible with PES and NMP as no double layer of morphology shown in the images (Rahman *et al*., 2006; Zhang *et al*., 2008)
- **Fourier transform infrared (FTIR):** In this study, FTIR test was performed in order to determine the chemical structures changes with the addition of

Table 1: Membrane composition

		Composition (wt.%)		
Membrane	Details	PES	Emim (Tf_2N)	Emim (CF_3SO_3)
Pure PES	Pure PES polymeric membrane	-	20	-
ILMPM1_10	ILPM with 10 wt.% emim (Tf_2N)	10	20	-
ILPMM2_10	ILPM with 15 wt.% emim (CF_3SO_3)	10	20	10

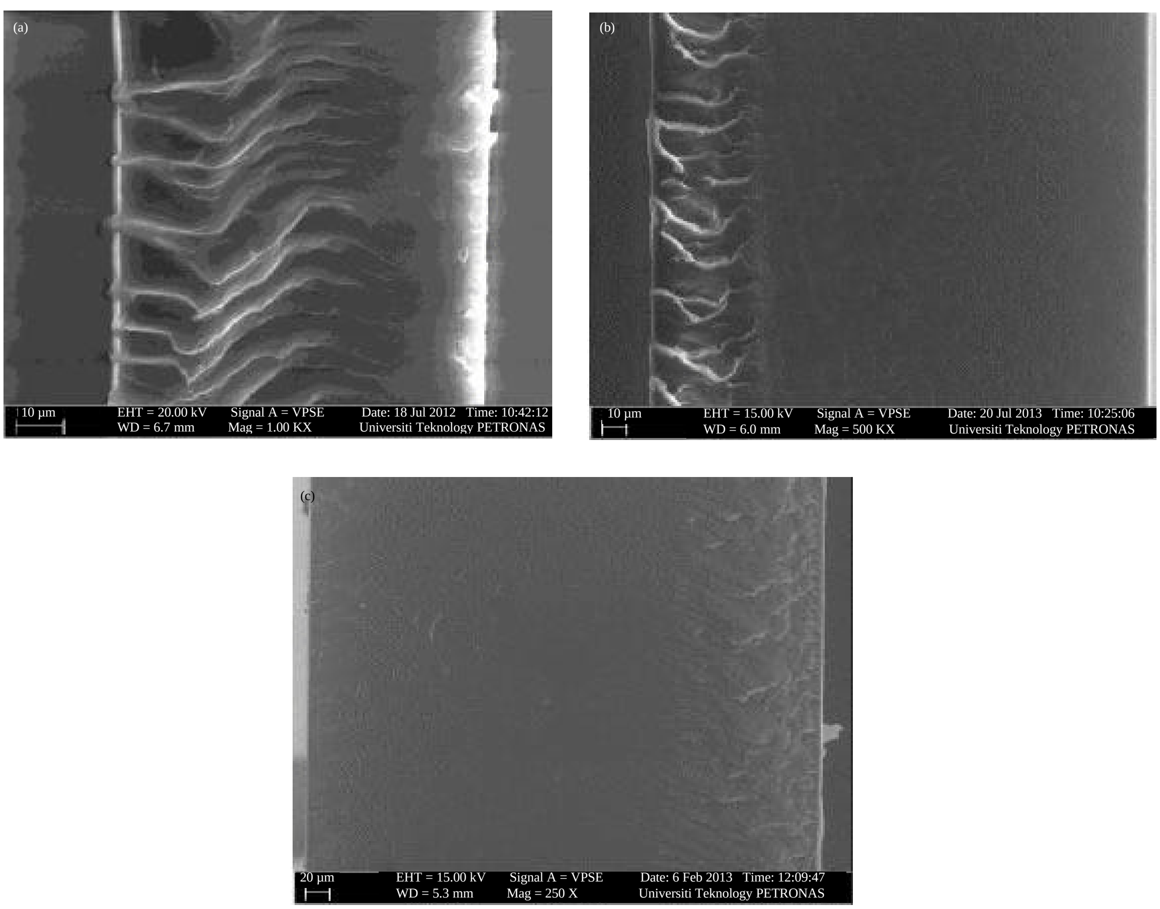


Fig. 1(a-c): FESEM images of (a) Pure PES membrane, (b) ILMPM1_10 and (c) ILMPM2_10

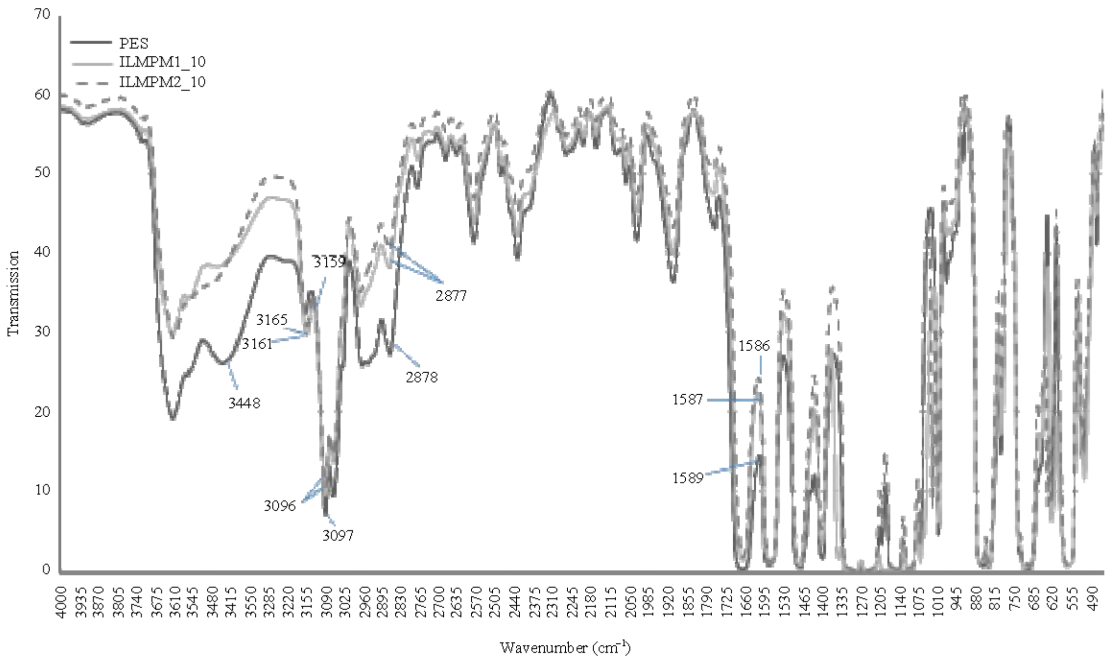


Fig. 2: FTIR spectra for all fabricated membranes

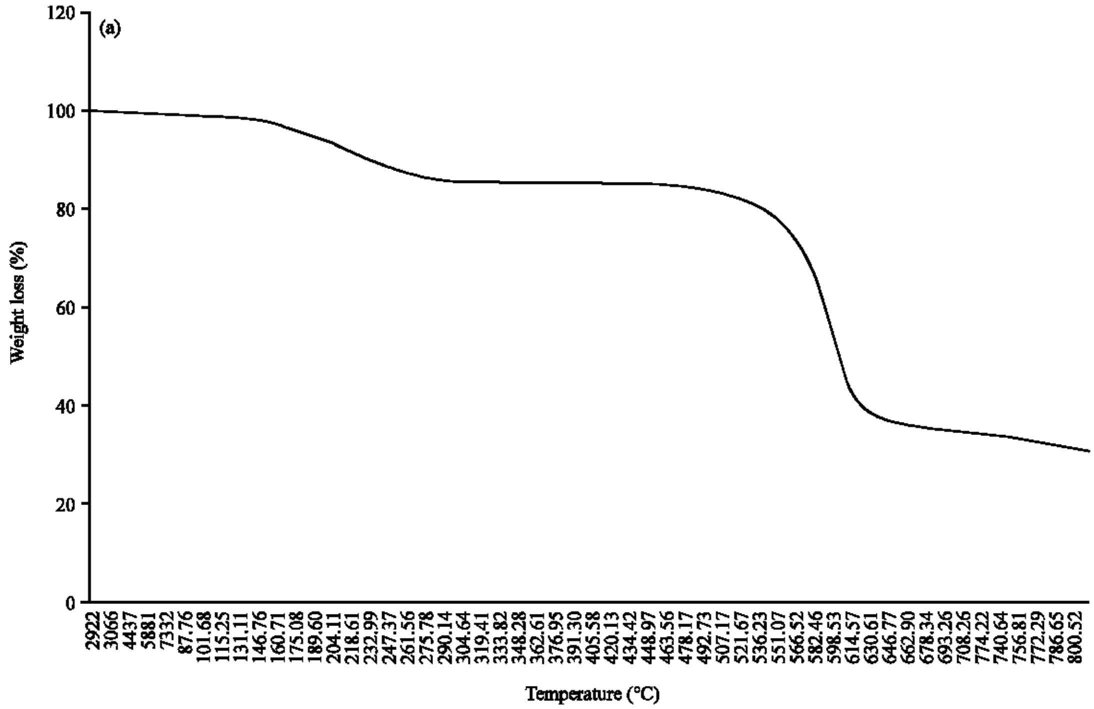
emim [CF_3SO_3]. All samples were mounted at the sample position with outer skin surface facing the IR beam and IR absorption spectra were obtained at room temperature from 4000-450 cm^{-1} and average of 16 scans

From Fig. 2, we can see some pronounced peaks at about 3097, 1590, 2880 and 3160 cm^{-1}. The peaks at 3097 and 1590 cm^{-1} are attributed to the stretching vibration of C-H and aromatic ring accordingly in PES group. For a membrane consists of miscible blends, frequency shifts usually indicate specific interactions between the characteristic group of the mixture. The wavenumber of pronounced peaks are mostly shifted from 3097-3096 cm^{-1} and from 1589-1587 and 1586 cm^{-1} in membranes containing ionic liquid. This shifting indicates that the membranes are performing new O-H bond with the addition of ionic liquid (Rahman *et al*., 2006). On the other hand, the peaks at 2880 and 3160 cm^{-1} represent the CH_3 group and C-H stretching in ionic liquids. In addition, the peak of 3448 cm^{-1} in pure PES membrane is missing in both ILMPM which indicate some other bonding are formed

- **Thermogravimetric analysis (TGA):** TGA was performed to measure the weight loss of each sample as a function of temperature. Figure 3 shows the TGA result for pure PES membrane and ILMPM1_10 and ILMPM2_10. Both analysis shows samples are still containing solvent which presents the weight loss occurred at 202°C, at the boiling point of NMP. However, there is a slight different of weight loss at high temperature. In Fig. 3a, a massive weight loss at temperature above 500°C while in Fig. 3b, the massive weight loss occurred at temperature around 400°C. This weight loss is due to the degradation of polymer PES containing ionic liquid which degrades at lower temperature as compared to pure PES membrane

Membrane separation performance: Membrane gas permeation test was performed to check the membrane separation performance. The test was conducted using pure CO_2 and pure CH_4 gases and CO_2 permeance and CO_2/CH_4 ideal selectivity were calculated from the results. Figure 4 shows the CO_2 permeance and CO_2/CH_4 ideal selectivity across the pressure.

From Fig. 4a, it shows that the membranes exhibit the glassy polymeric membrane behaviour as the CO_2 permeance is decreasing when the pressure increased. Overall, the addition of ionic liquid has also improved the CO_2 permeance as compared to pure PES membrane. It is also noticed that, the CO_2 permeance of ILMPM1 is slightly higher than ILMPM2. In contrast, the CO_2/CH_4 ideal selectivity of all membranes is increasing with increasing of pressure which indicates the generic glassy polymeric membrane behaviour. At 10 barg pressure, the incorporation of emim [Tf_2N] and emim [CF_3SO_3]



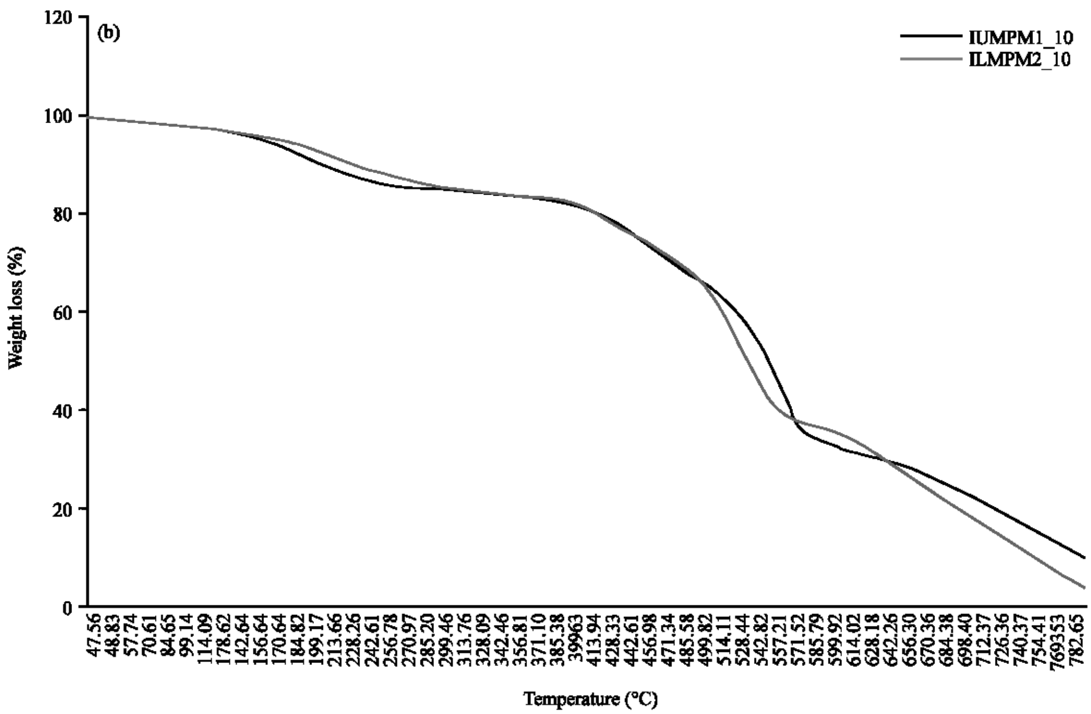


Fig. 3(a-b): TGA for (a) Pure PES membrane and (b) ILMPM1_10 and ILMPM2_10

has also increased the CO_2/CH_4 ideal selectivity for 47 and 55% accordingly as compared to the pure PES membrane. However, the ILMPM2 is having higher CO_2/CH_4 ideal selectivity as compared to ILMPM1 as emim $[CF_3SO_3]$ is more selective towards CO_2/CH_4.

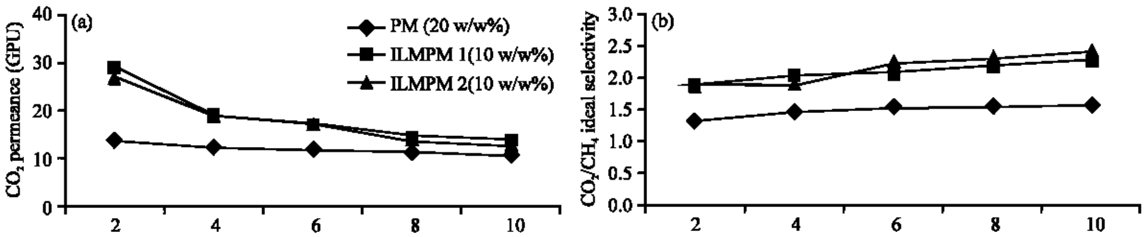


Fig. 4(a-b): (a) CO_2 permeance and (b) CO_2/CH_4 ideal selectivity across pressure

CONCLUSION

The properties of PES membranes containing ionic liquid imidazolium based give good contact between the polymer and the ionic liquid. Pure CO_2 and CH_4 gas permeation data showed a substantial improvement for both blending. The CO_2 permeation for eminTf$_2$N-PES blending has been improved as expected while the CO_2/CH_4 ideal selectivity is improved with emim CF_3SO_3-PES blending as compared to the pure PES membrane separation performance.

ACKNOWLEDGMENTS

We would like to thank to the Universiti Teknologi PETRONAS for the facilities provided and to the ERGS Grant No. ERGS/1/2011/TK/UTP/02/46 for financial support.

REFERENCES

D'Alessandro, D.M., B. Smit and J.R. Long, 2010. Carbon dioxide capture: Prospects for new materials. Angewandte Chem. Int. Edn., 49: 6058-6082.

Ebner, A.D. and J.A. Ritter, 2009. State-of-the-art adsorption and membrane separation processes for carbon dioxide production from carbon dioxide emitting industries. Sep. Sci. Technol., 44: 1273-1421.

Fredlake, C.P., J.M. Crosthwaite, D.G. Hert, S.N.V.K. Aki and J.F. Brennecke, 2004. Thermophysical properties of imidazolium-based ionic liquids. J. Chem. Eng. Data, 49: 954-964.

Koros, W.J. and G.K. Fleming, 1993. Membrane-based gas separation. J. Membr. Sci., 83: 1-80.

Merkel, T.C., H. Lin, X. Wei and R. Baker, 2010. Power plant post-combustion carbon dioxide capture: An opportunity for membranes. J. Membr. Sci., 359: 126-139.

Mohshim, D.F., H.B. Mukhtar, Z. Man and R. Nasir, 2012. Latest development on membrane fabrication for natural gas purification: A review. J. Eng., 10.1155/2013/101746

Pan, X., D. Clodic and J. Toubassy, 2013. CO_2 capture by antisublimation process and its technical economic analysis. Greenhouse Gases: Sci. Technol., 3: 8-20.

Rahman, W.A., W. Aizan and A.F. Ismail, 2006. Formation and characterization of mixed matrix composite materials for efficient energy gas separation. http://eprints.utm.my/2830/1/75126.pdf.

Strathmann, H., 2011. Introduction to Membrane Science and Technology. John Wiley and Sons, New York, ISBN-13: 9783527324514, Pages: 473.

Van Der Sluijs, J.P., C.A. Hendriks and K. Blok, 1992. Feasibility of polymer membranes for carbon dioxide recovery from flue gases. Energy Convers. Manage., 33: 429-436.

Zhang, Y., K.J. Balkus Jr., I.H. Musselman and J.P. Ferraris, 2008. Mixed-matrix membranes composed of Matrimid® and mesoporous ZSM-5 nanoparticles. J. Membr. Sci., 325: 28-39.

Zhao, H., 2006. Innovative applications of ionic liquids as green engineering liquids. Chem. Eng. Commun., 193: 1660-1677.