

# Synthesis, Characterization and Performance Study of Newly Developed Amine Polymeric Membrane (APM) for Carbon Dioxide (CO<sub>2</sub>) Removal

Rizwan Nasir, Hilmi Mukhtar, Zakaria Man, and Dzeti Farhah Mohshim

**Abstract**—Carbon dioxide has been well associated with greenhouse effect, and due to its corrosive nature it is an undesirable compound. A variety of physical-chemical processes are available for the removal of carbon dioxide. Previous attempts in this field have established alkanolamine group has the capability to remove carbon dioxide. So, this study combined the polymeric membrane and alkanolamine solutions to fabricate the amine polymeric membrane (APM) to remove carbon dioxide (CO<sub>2</sub>). This study entails the effect of three types of amines, monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA). The effect of each alkanolamine group on the morphology and performance of polyether sulfone (PES) polymeric membranes was studied. Flat sheet membranes were fabricated by solvent evaporation method by adding polymer and different alkanolamine solutions in the N-Methyl-2-pyrrolidone (NMP) solvent. The final membranes were characterized by using Field Emission Electron Microscope (FESEM), Fourier Transform Infrared (FTIR), and Thermo-Gravimetric Analysis (TGA). The membrane separation performance was studied. The PES-DEA and PES-MDEA membrane has good ability to remove carbon dioxide.

**Keywords**—Amine Polymeric membrane, Alkanolamine solution, CO<sub>2</sub> Removal, Characterization.

## I. INTRODUCTION

GAS separation through membrane technology has been attracting great attention [1]. Since this attention is mainly due to some desirable characteristics of membrane technology such as higher reliability, energy efficiency and lower capital cost compared to other conventional processes [2], [3]. Polymeric membrane has some advantages as compared to inorganic membranes due to ease of processing and appropriate robustness [4].

Due to the vulnerability of polymeric membranes towards chemical degradation and thermal instability, their applications have been limited to separation processes where hot reactive gases are not encountered [5]-[7]. These membranes show low throughput as compared to porous materials. Solution-diffusion transport mechanism presented trade off limitation between permeability and selectivity for polymeric membranes [8], [9].

There are some alkanolamine solutions like monoethanolamine (MEA), diethanolamine (DEA) [10],

methyldiethanolamine (MDEA) etc., which has been used for carbon dioxide removal [11]. The amine based absorption process has been used for 60 years for the removal of CO<sub>2</sub> from natural gas and flue streams due to old process this technology is well matured [12]. Though it has extensive commercial use, this technique has some limitations like low CO<sub>2</sub> loading capacity, high corrosion rate, high energy consumption [12], high solution circulation rate and solution degradation [13].

These days' researchers are working on the facilitated transport membrane (FTM). In this type the polymeric membranes carry a liquid to enhance the separation ability of the polymeric membrane [14].

In this study a new amine polymeric membrane (APM) has been fabricated by the addition of different amines solution with fixed weight ratio in the polymeric membrane. This membrane has the properties of polymeric material and amine solutions.

## II. METHODOLOGY

### A. Materials

Polyethersulfone PES (ULTRASON E 6020P) was purchased from BASF Germany, (molecular weight 50,000g/mol). Polyethersulfone was the main polymer for the fabrication of polymeric membranes. N - Methyl - 2 - Pyrrolidone (NMP) was obtained from Merck Germany. NMP was used as solvent for the preparation of polymeric solution. Ethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) were purchased from Merck Germany. These amines were used for the synthesis of amine supported polymeric membrane.

### B. Synthesis of Flat Sheet Amine Polymeric Membrane

The polymer (PES) was added in the solvent (NMP) step by step with the weight ratio of 20 wt%. The addition of polymer in the solvent was carried out at room temperature with continuous stirring. After the complete addition of polymer different amines with fixed weight ratio of 10 wt% was added, and the solution was stirred for 24 hours. A viscous dope solution was obtained after 24 hours. The solution was kept for another 24 hour at room temperature for stabilization.

Then this dope solution on the casting machine by adjusting the knife angle to 180 microns. After the casting put the membrane in oven at 90°C for next 24 hours.

R. Nasir, H. Mukhtar, Zakaria Man, and D. F. Mohshim are with Universiti Teknologi PETRONAS, Bandar Seri Iskandar 31750 Tronoh Perak Malaysia (e-mail: rizwan.raai@gmail.com, hilmi\_mukhtar@petronas.com.my, zakaman@petronas.com.my, dzetifarhah@gmail.com).

### C. Characterization of Amine Polymeric Membrane

The characterization of newly developed membrane was carried out in order to identify the functional groups, determine the membrane morphology, and weight loss. FTIR, FESEM, and TGA were the equipment used for characterization of membranes.

### D. Gas Permeability Study

The APM membranes were tested for a pure carbon dioxide ( $\text{CO}_2$ ) and methane ( $\text{CH}_4$ ) gases using variable pressure of 2, 4, 6, 8, 10 bars. The permeance was measured after the steady state was reached, which took about 10-15min.

## III. RESULTS AND DISCUSSION

### A. Thermo Gravimetric Analysis

The thermal decomposition behavior of the pure polyethersulfone (PES), PES-MEA, PES-DEA, and PES-MDEA polymeric membrane was studied by TGA. Fig. 1 shows the weight loss of these membranes as a function of temperature. The heating range of sample was  $30^\circ\text{C}$  to  $800^\circ\text{C}$  at the rate of  $10^\circ\text{C}/\text{min}$ . The curves showed two stages of decomposition between  $150^\circ\text{C}$  to  $299^\circ\text{C}$  and  $450^\circ\text{C}$  to  $630^\circ\text{C}$ . The first stage indicated that the amines were decomposing, and second stage shown the decomposition process of PES. All curves shown almost 3-4% weight loss between  $30^\circ\text{C}$  to  $200^\circ\text{C}$ , which may be due to loss of water absorbed [15]. Almost 10% weight loss has been observed in all curves between  $200^\circ\text{C}$  to  $300^\circ\text{C}$  which indicated the decomposition of amines. In the range of  $450^\circ\text{C}$  to  $630^\circ\text{C}$  there is almost 46% weight loss has been observed decomposition of polymer.

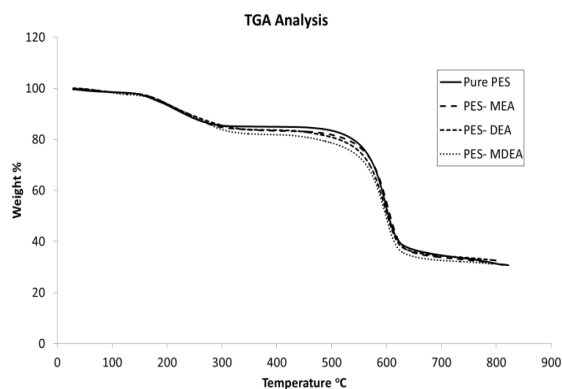


Fig. 1 TGA analysis

### B. FTIR Spectroscopy

FTIR spectroscopy of pure PES membrane, PES – MEA membrane, PES – DEA membrane, and PES – MDEA membrane was employed to identify interactions between the different components of with same compositions at the molecular level. During the preparation of dope solution it found that PES and amines were miscible with each other at room temperature. According to Han et al., the sulfone group ( $\text{SO}_2$ ) of PES shown at  $1141$  and  $1280\text{cm}^{-1}$ , for symmetrical and asymmetrical vibrations, respectively. The peak at  $1241$

$\text{cm}^{-1}$  belonged to aromatic ether ( $-\text{C}-\text{O}-\text{C}-$ ) linkages. The absorption bands at  $1481$  and  $1581\text{cm}^{-1}$  are assigned to aromatic benzene rings [16]. By the addition of 10% of MEA, DEA, and MDEA  $\text{SO}_2$  wave number shifted to  $1147\text{cm}^{-1}$ ,  $1145\text{cm}^{-1}$ , and  $1145\text{cm}^{-1}$  respectively. The wave number of aromatic ether C-O-C also shifted to  $1297$ ,  $1295$ ,  $1295\text{cm}^{-1}$  respectively. In the presence of MEA and DEA the wave number of aromatic benzene was found also same but different intensity, but in the presence of MDEA it shifted to  $1479\text{cm}^{-1}$  due to formation of hydrogen bond.

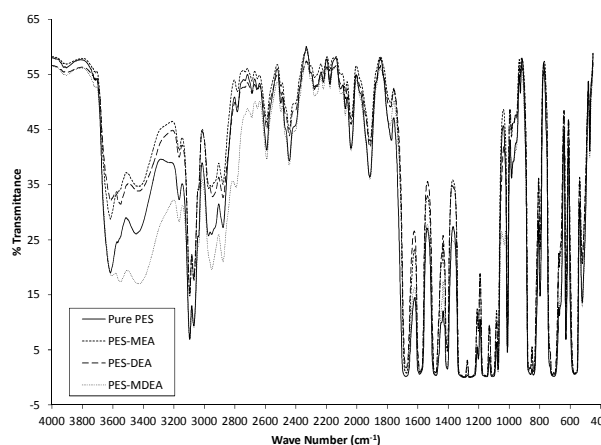


Fig. 2 FTIR Analysis

### C. FESEM Analysis

Membrane structure is strongly related to the composition of the casting solution. The type and concentration of components play important role for modification of membrane properties. The effect of amine addition on membrane morphology was investigated by FESEM. The variations in cross sectional morphology were shown by FESEM. Fig. 3 shows the cross section of (a) pure PES membrane, (b) PES – MEA membrane, (c) PES – DEA membrane, and (d) PES – MDEA membrane. All membranes were found dense and non-porous. In the presence of MEA two layers were found one was smooth and other is wavy. By the addition of DEA complex structure was found, due to high viscosity of DEA than MEA and MDEA. The addition of MDEA also gave layer on the surface of membrane. The bottom part of PES-MDEA membrane is smooth and dense as shown in the Fig. 3 (d). It also observed some channel like structure which is due to the polymer elongation during the sample preparation.

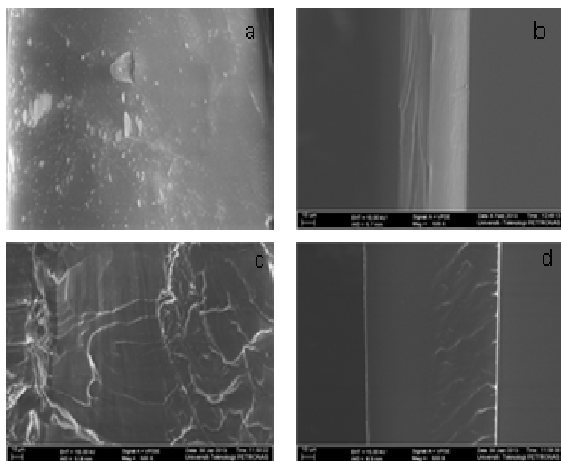


Fig. 3 (a) Pure PES, (b) PES - MEA, (c) PES – DEA, (d) PES - MDEA (Magnification 500x)

#### D. Gas Permeability Study

The gas permeability study has been carried out for carbon dioxide ( $\text{CO}_2$ ) and methane ( $\text{CH}_4$ ). Table I showed the performance of the amine polymeric membrane (APM) in term of permeability and selectivity.

TABLE I  
PERMEANCE AND SELECTIVITY OF AMINE POLYMERIC MEMBRANE

Membrane	Pressure (Bars)	$\text{CO}_2$ Permeance (GPU)	$\text{CH}_4$ Permeance (GPU)	Selectivity
Pure PES	2	7.03	6.48	1.08
	4	6.42	5.82	1.10
	6	6.40	4.05	1.58
	8	6.34	4.00	1.59
	10	5.63	3.50	1.61
PES-MEA	2	7.32	1.97	3.72
	4	7.07	2.08	3.40
	6	7.00	2.40	2.91
	8	5.98	2.76	2.17
	10	5.24	2.73	1.92
PES-DEA	2	28.79	11.77	2.45
	4	24.72	11.73	2.11
	6	22.89	11.17	2.05
	8	21.30	13.14	1.62
	10	29.51	12.51	2.36
PES-MDEA	2	107.14	12.85	8.33
	4	44.89	16.05	2.80
	6	37.78	17.11	2.21
	8	29.63	20.56	1.44
	10	40.81	21.69	1.88

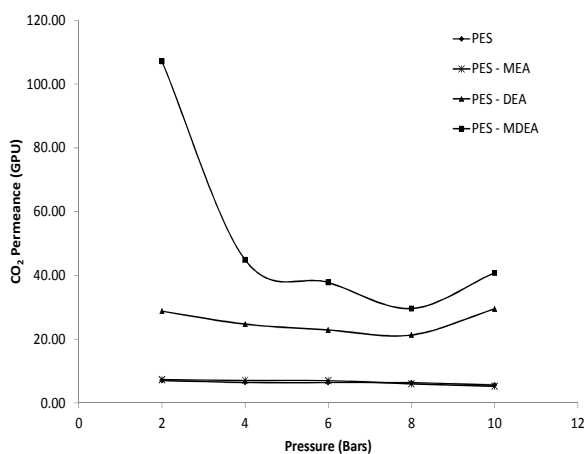


Fig. 4  $\text{CO}_2$  permeance

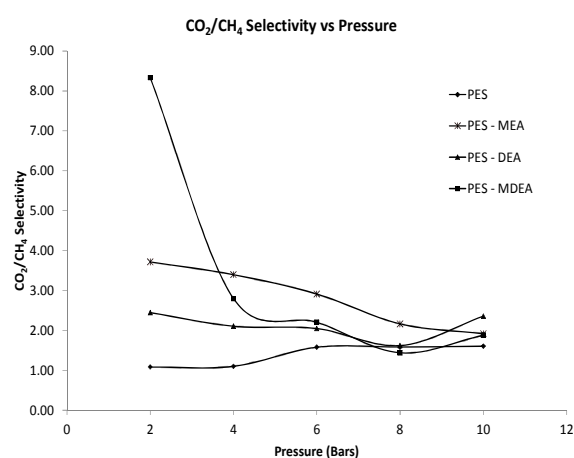


Fig. 5  $\text{CH}_4$  permeance

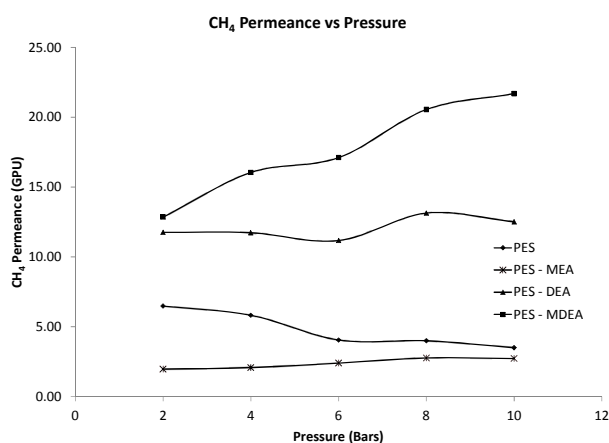


Fig. 6  $\text{CO}_2/\text{CH}_4$  selectivity

The performance of amine polymeric membrane has been investigated by plotting the permeance of  $\text{CO}_2$ ,  $\text{CH}_4$  and ideal selectivity for  $\text{CO}_2/\text{CH}_4$  of each amine polymeric membrane against the feed pressure. Fig. 4 indicated that by the addition

of amine the permeance of CO<sub>2</sub> has been increased, especially for PES-DEA membrane and PES-MDEA membrane than pure PES membrane. The PES – MEA membrane did not show any remarkable increase in the permeance of CO<sub>2</sub>, because MEA has higher vapor pressure than DEA and MDEA. So it can be evaporate from the membrane upon drying. According to Fig. 5 the permeance of CH<sub>4</sub> has been increased with increase in pressure for PES –MDEA membrane. Another study concluded that the presence of solvent in the final membrane may cause the increase of permeance and decrease of selectivity [17]. That study concluded that in Fig. 5 the CH<sub>4</sub> permeance through the PES – DEA membrane has been shown the decreasing and increasing trend due to its complex structure. In Fig. 6 the selectivity increased as compared to polymeric membrane. It also has been showed the behavior of glassy polymer that the CO<sub>2</sub>/CH<sub>4</sub> ideal selectivity has been decrease with the increase in pressure. Some studies has been highlight this property of glassy polymer [18], [19].

#### IV. CONCLUSION

The amine polymeric membranes were fabricated by using different amines of same concentration to check the effect of amine on separation performance of pure PES membrane. It has been found that PES – DEA and PES –MDEA membranes has the ability to separate more carbon dioxide with some modification in the membrane. Although there is an increase in permeance and selectivity in small numbers it can be increased by increasing the concentration of amines.

#### ACKNOWLEDGMENT

The authors gratefully acknowledge the financial support provided by Universiti Teknologi PETRONAS for this study.

#### REFERENCES

- [1] X.-G. Li and M.-R. Huang, "Water-casting ultrathin-film composite membranes for air separation," *Separation Science and Technology*, vol. 31, pp. 579-603, 1996.
- [2] D. R. Paul and Y. P. Yampol'skii, *Polymeric gas separation membranes*. Boca Raton: CRC, 1993.
- [3] S. Alexander Stern, "Polymers for gas separations: the next decade," *Journal of Membrane Science*, vol. 94, pp. 1-65, 1994.
- [4] L. M. Robeson, "Correlation of separation factor versus permeability for polymeric membranes," *Journal of Membrane Science*, vol. 62, pp. 165-185, 1991.
- [5] N. Widjojo and T. S. Chung, "Thickness and air gap dependence of macrovoid evolution in phase-inversion asymmetric hollow fiber membranes," *Industrial & engineering chemistry research*, vol. 45, pp. 7618-7626, 2006.
- [6] Y. Li, H. Zhou, G. Zhu, J. Liu, and W. Yang, "Hydrothermal stability of LTA zeolite membranes in pervaporation," *Journal of Membrane Science*, vol. 297, pp. 10-15, 2007.
- [7] K. Li, *Ceramic membranes for separation and reaction*: Wiley, 2007.
- [8] A. Ebadi Amooghin, H. Sanaeepur, A. Kargari, and A. Moghadassi, "Direct determination of concentration-dependent diffusion coefficient in polymeric membranes based on the Frisch method," *Separation and Purification Technology*, vol. 82, pp. 102-113, 2011.
- [9] H. Sanaeepur, A. E. Amooghin, A. Moghadassi, and A. Kargari, "Preparation and characterization of acrylonitrile-butadiene-styrene/poly (vinyl acetate) membrane for CO<sub>2</sub> removal," *Separation and Purification Technology*, vol. 80, pp. 499-508, 2011.
- [10] B. Guo and A. Ghalambor, *Natural gas engineering handbook* vol. 22: Gulf publishing company Houston, TX, 2005.
- [11] J. G. Speight, *Natural Gas: A Basic Handbook*: Gulf Publishing Company, 2007.
- [12] A. A. Olajire, "CO<sub>2</sub> capture and separation technologies for end-of-pipe applications – A review," *Energy*, vol. 35, pp. 2610-2628, 2010.
- [13] K. Liu, C. Song, and V. Subramani, *Hydrogen and syngas production and purification technologies*: Wiley Online Library, 2010.
- [14] E. Cussler, R. Aris, and A. Bhowan, "On the limits of facilitated diffusion," *Journal of Membrane Science*, vol. 43, pp. 149-164, 1989.
- [15] P. Qu, H. Tang, Y. Gao, L. Zhang, and S. Wang, "Polyethersulfone composite membrane blended with cellulose fibrils," *BioResources*, vol. 5, pp. 2323-2336, 2010.
- [16] J. Han, W. Lee, J. M. Choi, R. Patel, and B.-R. Min, "Characterization of polyethersulfone/polyimide blend membranes prepared by a dry/wet phase inversion: Precipitation kinetics, morphology and gas separation," *Journal of Membrane Science*, vol. 351, pp. 141-148, 2010.
- [17] K. C. Khulbe, T. Matsuura, G. Lamarche, and H. J. Kim, "The morphology characterisation and performance of dense PPO membranes for gas separation," *Journal of Membrane Science*, vol. 135, pp. 211-223, 1997.
- [18] J. Petropoulos, "Quantitative analysis of gaseous diffusion in glassy polymers," *Journal of Polymer Science B Polymer Physics*, vol. 8, pp. 1797-1801, 1970.
- [19] W. Koros, R. Chern, V. Stannett, and H. Hopfenberg, "A model for permeation of mixed gases and vapors in glassy polymers," *Journal of Polymer Science B Polymer Physics*, vol. 19, pp. 1513-1530, 1981.