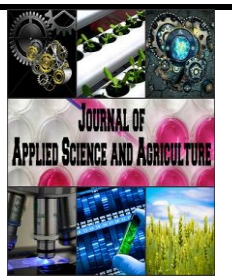
Journal of Applied Science and Agriculture, 10(5) Special 2015, Pages: 215-221

AENSI Journals

JOURNAL OF APPLIED SCIENCE AND AGRICULTURE

ISSN 1816-9112

Journal home page: www.aensiweb.com/JASA



Fabrication of SAPO-34 and Silane-modified SAPO-34/Polyimide Mixed Matrix Membranes for CO_2/CH_4 Separation

Lin Kiat Chua, Norwahyu Jusoh, Yin Fong Yeong

Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia

ARTICLE INFO

Article history:
Received 28 January 2015
Accepted 25 February 2015
Available online 6 March 2015

Keywords:
Mixed matrix membranes
SAPO-34
Polyimide
Silane modification
CO2/CH4 separation

ABSTRACT

Background: Natural gas has emerged as one of the important constituents of the world's supply of energy. Increasing demand of natural gas pushes the industry to vigorously separate impurities including CO2 in order to produce high quality of natural gas. Recently, membrane separation has become a promising technology in CO2 removal. **Objective:** In the present research, a series of mixed matrix membranes (MMMs) were fabricated. Different compositions of SAPO-34 and SAPO-34 modified with (3-aminopropyl)-triethoxysilane (APTES) were incorporated into 6FDA-durene polyimide. The synthesized SAPO-34 and silane-modified SAPO-34 were characterized by using Fourier Transform Infrared Spectroscopy (FTIR) and the resultant MMMs were characterized by using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX). The CO2/CH4 separation performances of the membranes were also tested. **Results:** The morphology of the silane-modified SAPO-34/6FDA-durene MMMs showed the improvement on the compatibility between the polymeric and inorganic phases. EDX results showed that the inorganic SAPO-34 particles were evenly distributed in the polymer matrix and no sign of agglomeration. However, all MMMs showed lower separation performance compared to pure 6FDA-durene membrane. **Conclusion:** The reduction of separation performance could be due to the rigidification of polymer matrix.

To Cite This Article: Lin Kiat Chua, Norwahyu Jusoh, Yin Fong Yeong, Fabrication of SAPO-34 and Silane-modified SAPO-34/Polyimide Mixed Matrix Membranes for CO2/CH4 Separation. ***J. Appl. Sci. & Agric.***, *10(5): 215-221, 2015*

INTRODUCTION

Carbon dioxide (CO_2) is a greenhouse gas mainly found in the combustion product of fossil fuels, natural gas stream, biogas and landfill gas. The purpose of removing CO_2 from these gas streams, especially natural gas stream is to obtain a purified fuel with enhanced energy content and to prevent corrosion problems in the gas transportation system. Membrane technology has emerged as a potential process in natural gas sweetening (CO_2/CH_4) apart from adsorption, absorption and cryogenic process due to its high energy efficiency, simple in design and construction of membrane modules, low operating cost and environmental compatibility (Zhang *et al*., 2013).

Basic separation performances of the membrane are classified into permeability and selectivity. Higher permeability decreases the amount of membrane area used, thus reduces the capital cost of membrane units, while higher selectivity will increase the purity of gas product. However, it is difficult to maintain the membrane performance and consistency in long term operation. Most membranes do not have the resilience in practical industry conditions. A high performance membrane used for CO_2 capture should possess good chemical, thermal and mechanical stability as well as high CO_2 permeability and selectivity (Freemantle, 2005).

Membrane materials can be classified into polymeric membrane, inorganic membrane and mixed matrix membrane. Polymeric membrane is currently the dominant material for CO_2/CH_4 separation as it possesses the advantages of mechanical properties, reproducibility, flexible and having relative economic processing capability. Polymer materials such as polyimide (PI), cellulose acetate (CA), polysulfone (PSF), polyethersulfone (PES) and polycarbonates (PC) have been used to fabricate the polymeric membranes for gas separation (Zhang *et al*., 2013). Even though polymeric membranes dominate the current CO_2 separation membrane, they still suffer from either low permeability or low selectivity, which is governed by the Robeson's upper bound limit (Robeson, 2008). Besides, they also suffer from an issue of plasticization when the pressure or CO_2

Corresponding Author: Y.F. Yeong, Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia.
Tel: +605-3687649, E-mail: yinfong.yeong@petronas.com.my

concentration in the feed stream is high (Ismail and Lorna, 2002).

Inorganic membranes such as zeolite and carbon molecular sieve (CMS) are increasingly being investigated due to their attractive characteristics and advantages over the polymeric membrane for CO_2/CH_4 separation. According to (Carreon *et al*., 2008), SAPO-34 zeolite membrane on porous α-alumina supports exhibited CO_2/CH_4 selectivity ranged from 86 to 171 with CO_2 permeability of 20,000 - 40,000 Barrer. Inorganic membrane is a promising material in industrial processes due to its ability to withstand high temperature for long time and resistance to harsh operating environment. Moreover, inorganic membranes also exhibited a higher throughput and longer lifespan compared to polymeric membrane. Nevertheless, inorganic membrane is limited to the severe operating conditions due to the high manufacturing cost and low reproducibility. Besides, inorganic membrane is also facing the drawback of poor mechanical properties. It is brittle and usually with low surface-to-volume ratio (Goh *et al*., 2011). Therefore, inorganic membrane is still not a commercialized material to use in industrial applications.

Due to the limitations of polymeric and inorganic membrane, a new membrane material which is known as mixed matrix membrane (MMM) has been introduced to overcome the restrictions of the polymeric and inorganic membranes. MMM is fabricated by incorporating the inorganic fillers as dispersed phase in a continuous polymer matrix. This emerging membrane material is expected to enhance the separation performance of the existing membrane-based separation by overcoming the drawbacks in MMM fabrication including, polymer-inorganic phase separation problems and the compatibility between the polymer matrix and inorganic fillers. The choice of the polymer matrix and the inorganic particles with different loadings are the two important parameters that will affect the morphology and performance of the MMM. The gas transport mechanism and the gas component transport through the membrane should take into consideration in order to choose the most suitable continuous polymer phase and dispersed inorganic phase in the MMM fabrication (Chung *et al*., 2007).

In this research, SAPO-34 crystals and 6FDA-durene were used as the inorganic fillers and polymer matrix, respectively. SAPO-34 particles were incorporated into 6FDA-durene polymer for the fabrication of MMM. 6FDA-durene is a type of aromatic Polyimide (PI) materials. According to (Liu, *et al*., 2003), 6FDA-durene showed the highest CO_2 permeability, which is 458 Barrer. 6FDA-durene becomes an ideal polymer phase in MMM fabrication due to its excellent thermal and mechanical properties. It shows a good intrinsic gas separation performance as compared to other 6FDA-based polyimides.

SAPO-34 zeolite is a silicoaluminophosphate molecular sieve with the composition $(Si_xAl_yP_z)O_2$, where x = 0.01-0.98, y = 0.01-0.60 and z = 0.01-0.52. (Li *et al*., 2006) reported that SAPO-34 molecular sieve has a 0.38 nm framework pore diameter; which is similar in size to CH_4 but larger than CO_2. SAPO-34 has high CO_2/CH_4 selectivity due to its remarkable characteristic such as molecular sieving effect, CO_2 diffusivity and adsorption properties (Venna and Carreon, 2011).Besides, (Li *et al*., 2006) reported that SAPO-34 membrane showed separation selectivity as high as 95 and CO_2 permeability of 1433 Barrer.

However, the incorporation of SAPO-34 fillers in the polymer phase may cause the poor compatibility between these two phases. There are some methods that can improve the interfacial strength between these two phases in order to enhance their membrane performance. One of them is the silane (chemical) modification of the surface of SAPO-34 zeolite with silane coupling agent, such as (3-Aminopropyl)-triethoxysilane (APTES). Silane coupling agent is a silicon-based chemical which contains two types of reactive groups, namely organic and inorganic groups in the same molecule (Junaidi *et al*., 2014). By introducing the silane coupling agent, it may modify the surface properties of SAPO-34 zeolite from hydrophilic to hydrophobic, and increase SAPO-34 affinity to the functional groups of the polymer matrix (Li *et al*., 2006). In the present research, SAPO-34/6FDA-durene and silane-modified SAPO-34/6FDA-durene MMMs were fabricated and their performances towards the CO_2/CH_4 gas separation were compared.

Experimental:

Materials:

4, 4'- (Hexafluoroisopropylidene) diphthalic anhydride (6FDA, 99% purity, Sigma-Aldrich) monomers were purified by vacuum sublimation prior to use. 2, 3, 5, 6-Tetramethyl-p-phenylenediamine (durene-diamine, 99% trace metals basis, Sigma-Aldrich) monomers were purified by re-crystallization in methanol. N-methyl-2-pyrolidone (NMP) was purified by using a rotary evaporator. Propionic anhydride (PA, ≥ 98% purity, Merck) and triethylamine (TEA, ≥ 99% purity, Merck) were used as received. Methanol (≥99.9% purity, Merck) and dichloromethane (DCM, ≥ 99.8% purity, Sigma-Aldrich) solvent were used as received. Phosphoric acid (H_3PO_4, 85% aqueous solution), aluminium isopropoxide ($C_9H_{21}AlO_3$, ≥ 98% purity) and tetraethyl-orthosilicate (TEOS, ≥ 99% purity) were purchased from Merck. Tetraethylammonium hydroxide (TEAOH, ~40% aqueous solution) template solution and toluene (99.8% purity) were supplied by Sigma Aldrich. The silane coupling agent, (3-Aminopropyl)-triethoxysilane (APTES, ≥ 98% purity, Sigma-Aldrich) was used without further purification.

Synthesis of 6FDA-durene polymer:

The synthesis of 6FDA-durene polymer was carried out using chemical imidization method reported by (Wijenayake, *et al*., 2013) and (Liu *et al*., 2001). Equal mole of durene-diamine and 6FDA monomers were dissolved in purified NMP. The mixture was stirred for 24 h under nitrogen purge to obtain polyamic acid (PAA) solution. Propionic anhydride (PA) and triethylamine (TEA) were added slowly to the PAA solution for chemical imidization, with the mole ratio of PA/TEA to 6FDA of 4:1. The polyimides were precipitated in methanol and then washed with methanol before dried at 150°C in vacuum oven for 24 h.

Synthesis of SAPO-34 particles:

Synthesis of SAPO-34 particles was carried out by hydrothermal synthesis method reported by (Askari and R.Halladj, 2012). A gel with molar composition of Al_2O_3: P_2O_5: 0.6 SiO_2: 2 TEAOH: 70 H_2O was prepared by mixing aluminium isopropoxide, $C_9H_{21}AlO_3$, TEAOH and deionized water. Silica source (TEOS) and H_3PO_4 were added to the solution and stirred for 1 h. The gel solution was then transferred into the Teflon-lined synthesis reactor for hydrothermal growth at 200^{o}C for 24 h. After synthesis, the solid products were recovered by centrifuging and dried in oven at 110^{o}C overnight. As-synthesized crystals were then calcined in furnace at 550^{o}C for 6 h.

Preparation of silane-modified SAPO-34 particles:

The procedure for the preparation of silane-modified SAPO-34 particles was derived from (Li *et al*., 2006) method. A mixture of toluene, APTES and SAPO-34 particles were stirred for 24 hours at room temperature under nitrogen purge. SAPO-34 crystals were filtered with toluene and then washed with methanol before dried in oven at 110^{o}C overnight.

Preparation of pure 6FDA-durene film:

6FDA-durene dense film was prepared by following the method as reported by (Wijenayake *et al*., 2013). A 3% w/v solution of polymer in DCM was prepared and then cast on a Petri dish using a syringe through 1 µm filter. The cast film was dried in an oven at 60°C for 24 h followed by another 24 h under vacuum. The oven temperature was increased from 60 to 250°C at a heating rate of 25°C/h before annealed at 250°C for 24 h.

Preparation of SAPO-34/6FDA-durene and silane-modified SAPO-34/6FDA-Durene MMM:

MMM with inorganic fillers loadings was prepared by following the procedure as described by (Wijenayake *et al*., 2013). SAPO-34 crystals of 5, 10, 15 and 20 wt% were added to the DCM, stirred and sonicated for 2 h (alternating 30 min stirring followed by 30 min sonication) to disperse SAPO-34 in DCM. 6FDA-durene polymer was added to the DCM and stirred for 1 hour to produce polymer solution. 10% of the polymer solution was primed to the SAPO-34 dispersion followed by 2 h of stirring and sonicating. The remaining polymer solution was added and the mixture was further stirred and sonicated for 2 hours and finally stirred for 2 hours. The mixture was then casted on a Petri dish. Silane-modified SAPO-34/6FDA-durene MMMs were fabricated by using the same procedure for the preparation of SAPO-34/6FDA-durene MMM. The amounts of silane-modified SAPO-34 crystals loaded into 6FDA-durene were 5, 10, 15 and 20 wt% as well.

Characterization of SAPO-34 and MMM:

The morphology of SAPO-34 was verified by Scanning Electron Microscopy (SEM). The possible functional groups and silane- group present in SAPO-34 and silane-modified SAPO-34 was determined by using the Fourier Transform Infrared Spectroscopy (FTIR). The morphology of MMM was studied by using the Scanning Electron Microscopy (SEM), while the dispersion of fillers in MMM was studied by using the Energy Dispersive X-ray (EDX). The performances of the resulting MMMs on CO_2/CH_4 separation were tested by using the CO_2 membrane permeation test rig. The operating temperature and feed pressure were maintained at 5 bar and 25^{o}C. The permeability of the membrane was calculated as below (Mohammadi *et al*., 2008):

$$P_A = \frac{V_p t}{A_m (f_h - f_l)} \quad (1)$$

Where P_A is the permeability of membrane, V_p is the permeate flow rate, t is the thickness of membrane, A_m is the membrane area , f_h and f_l are the fugacity in feed side and permeate side respectively, and A is CO_2 or CH_4.

The ideal selectivity of the membrane can be obtained by dividing the permeability of CO_2 over permeability of CH_4 as follows:

$$\alpha_{CO_2/CH_4} = \left(\frac{P_{CO_2}}{P_{CH_4}} \right) \quad (2)$$

Where α is the ideal selectivity.

RESULTS AND DISCUSSIONS

SAPO-34 particles:

Figure 1 illustrates the SEM image of SAPO-34 crystals. The particles have a smooth external surfaces and displaying cubic shape morphology, which is typical of SAPO-34 crystals (Askari and R.Halladj, 2012). The crystals have an average size of ~2 µm.

Figure 2 shows the FTIR spectra of SAPO-34 and silane-modified SAPO-34 crystals. The significant band between the wavenumber of 900-1350 cm^{-1} in the FTIR spectra for both samples indicates the asymmetric vibration modes of Si-O and Al-O group in the SAPO-34 crystals. A band of N-H at around 1450-1550 cm^{-1} was observed in the

Journal of Applied Science and Agriculture, 10(5) Special 2015, Pages: 215-221

spectra of silane-modified SAPO-34. This result shows that the silane group was successfully grafted onto the SAPO-34 structure (Junaidi *et al*., 2014).

Mixed Matrix Membranes (MMMs):

Figure 3 depicts the cross-section view of SEM images of pure 6FDA-durene dense film and MMMs. The thickness of all membranes was between 35-45 μm.

The purpose of introducing the silane coupling agent on the surface of SAPO-34 is to improve the compatibility between the polymeric and inorganic phases. From the SEM images as shown in Figure 3, the interfacial void between the polymeric and inorganic phases was improved for silane-modified SAPO-34/6FDA-durene MMMs as compared to the SAPO-34/6FDA-durene MMMs. Energy Dispersive X-ray (EDX) was carried out to study the dispersion of SAPO-34 fillers in the MMM. Figure 4 displays the EDX mapping for SAPO-34/6FDA-durene MMM loaded with 15 wt% SAPO-34, while Figure 5 displays the mapping for silane-modified SAPO-34/6FDA-durene MMM loaded with 15 wt% silane-modified SAPO-34. The images in both figures showed that SAPO-34 particles were uniformly dispersed in 6FDA-durene polymer matrix.

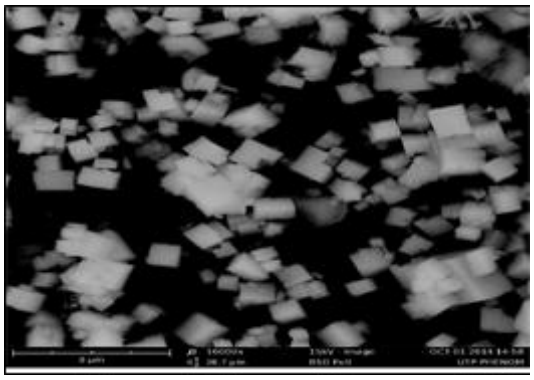


Fig. 1: SEM image of SAPO-34 crystals.

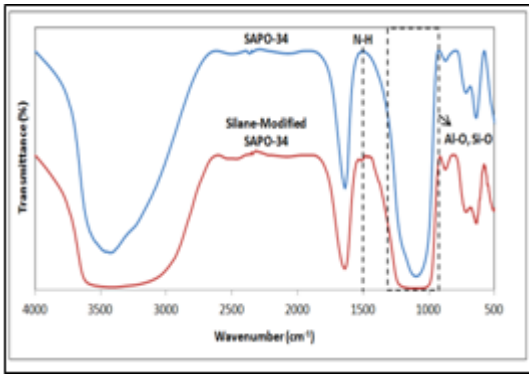


Fig. 2: FTIR spectra of SAPO-34 and silane-modified SAPO-34 crystals.

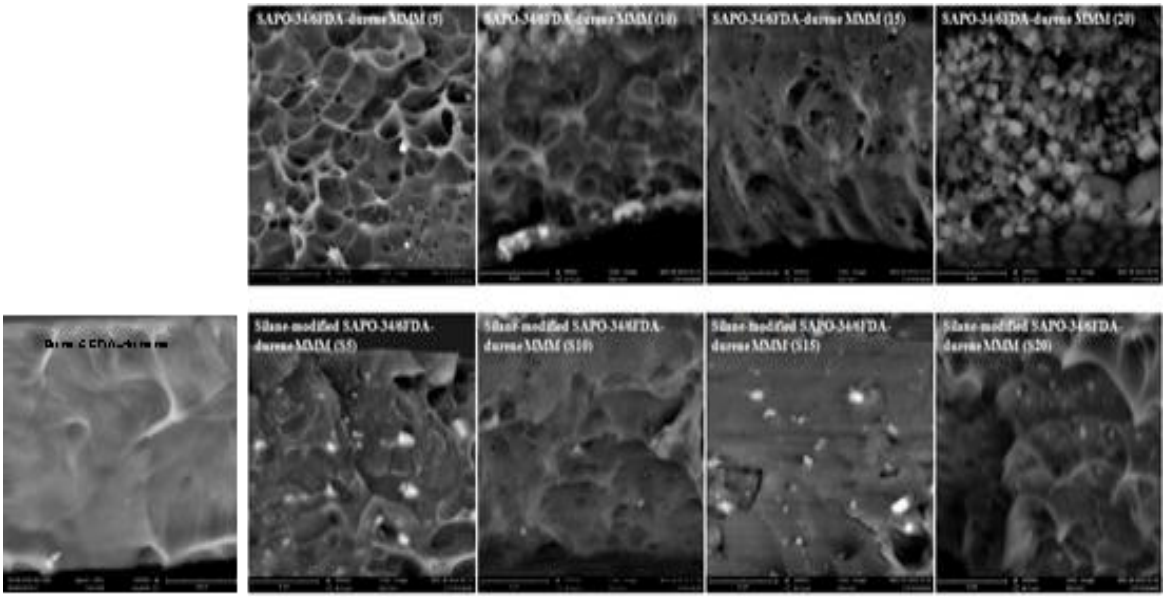


Fig. 3: Comparison of cross-section SEM images of pure 6FDA-durene membrane, SAPO-34/6FDA-durene and silane-modified SAPO-34/6FDA-durene MMMs. (5, 10, 15 and 20) and (S5, S10, S15 and S20) represent the loadings of SAPO-34 and silane-modified SAPO-34 in wt%, respectively.

Journal of Applied Science and Agriculture, 10(5) Special 2015, Pages: 215-221

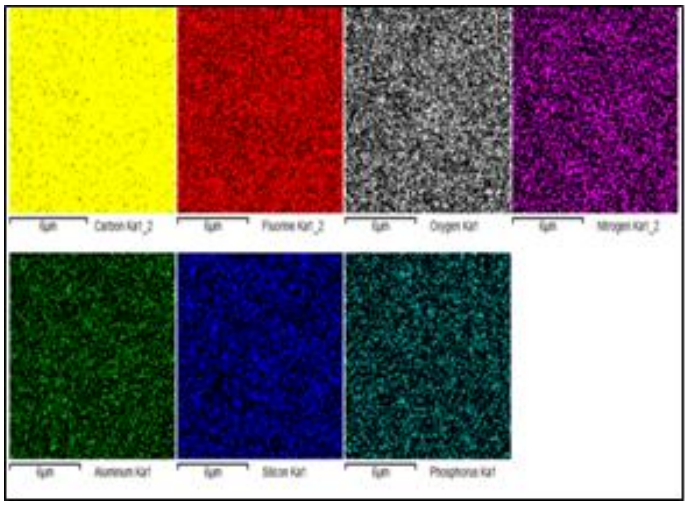


Fig. 4: EDX mapping of SAPO-34/6FDA-durene MMM loaded with 15 wt% SAPO-34.

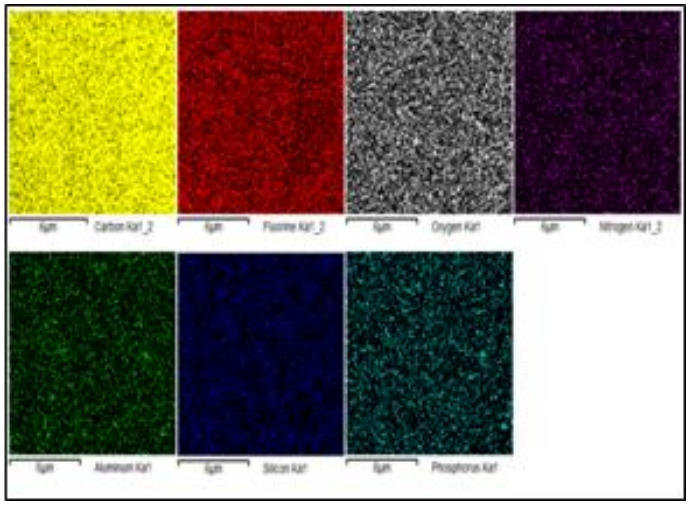


Fig. 5: EDX mapping of silane-modified SAPO-34/6FDA-durene MMM loaded with 15 wt% silane-modified SAPO-34.

Gas separation performance:

The separation performance of the resultant membranes were summarized in Table 1.For the pure 6FDA-durene membrane, the gas permeability and CO_2/CH_4 ideal selectivity are comparable to the results reported in literature (Liu *et al*., 2003). However, it was found that the permeability of CO_2 and CO_2/CH_4 ideal selectivity of the resulting MMMs decrease significantly as compared to the pure 6FDA-durene membrane.

Formation of rigidified polymer layer at SAPO-34/6FDA-durene interphase (matrix rigidification) could be the major contribution towards the decrement of the separation performance. Rigidified polymer might form in the resulting MMM and caused the immobilization of polymer chains between SAPO-34/6FDA-durene interphase, which has caused the reduction of the gas permeation (Manson and Chiu, 1973). In addition, rigidified polymer might seal the SAPO-34 pores and caused the pores blockage, which is known as "plugged sieves" (Rezakazemi *et al*., 2014). Thus, the gas permeability and selectivity are seriously affected in the current case.

Besides, there was no significant improvement on the permeability and selectivity of the resulting MMMs after introducing the silane coupling agent (APTES) in the inorganic phase. Theoretically, the application of silane group should improve the interfacial strength between the polymeric and inorganic phases, and thus enhance the membrane selectivity. Therefore in the current work, APTES might not be the suitable silane coupling agent and its effect towards the separation performance of MMM is not significant.

Journal of Applied Science and Agriculture, 10(5) Special 2015, Pages: 215-221

Table 1: Permeability and CO_2/CH_4 selectivity of resultant membrane at 25°C and 5 bar.

Mixed Matrix Membrane (MMM)	Permeability		CO_2/CH_4 Ideal Selectivity
	Carbon Dioxide, CO_2 (Barrer)	Methane, CH_4 (Barrer)	
6FDA-durene	408.23	18.71	21.82
5 wt% SAPO-34 in 6FDA-durene	239.50	23.28	10.29
10 wt% SAPO-34 in 6FDA-durene	206.97	21.49	9.63
15 wt% SAPO-34 in 6FDA-durene	251.32	26.10	9.63
20 wt% SAPO-34 in 6FDA-durene	217.72	24.95	8.73
5 wt% silane-modified SAPO-34 in 6FDA-durene	183.61	16.39	11.20
10 wt% silane-modified SAPO-34 in 6FDA-durene	166.32	15.35	10.84
15 wt% silane-modified SAPO-34 in 6FDA-durene	243.93	24.39	10.00
20 wt% silane-modified SAPO-34 in 6FDA-durene	235.87	24.95	9.45

Conclusion:

In the present research, 6FDA-durene polymer, SAPO-34 and silane-modified SAPO-34 crystals were successfully synthesized prior to the fabrication of MMM. 6FDA-durene polymer was synthesized by chemical imidization method while SAPO-34 crystals were synthesized by hydrothermal synthesis method. SAPO-34/6FDA-durene and silane-modified SAPO-34/6FDA-durene MMMs were successfully fabricated by incorporating different loadings (5, 10, 15 and 20 wt%) of inorganic fillers in polymer matrix. The formation of SAPO-34 phase was verified by the SEM. The FTIR spectra showed that silane group was successfully grafted onto the SAPO-34 structure. The cross-section SEM morphology of the fabricated MMMs generally showed the improvement on the compatibility between the polymeric and inorganic phases. EDX results showed that inorganic SAPO-34 was well distributed in the polymer matrix. No agglomeration was found in the EDX mapping for both SAPO-34/6FDA-durene and silane-modified SAPO-34/6FDA-durene MMMs.. However, the permeability of CO_2 and CO_2/CH_4 ideal selectivity of the resulting MMMs decreased significantly compared to the pure 6FDA-durene membrane. This was mainly due to polymer matrix rigidification of the resulting MMM. In overall, modifications of the membrane fabrication procedure as well as selection of suitable silane-coupling agent are needed in later works in order to improve the performances of MMM in CO_2/CH_4 separation.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial and technical supports provided by CO_2 Management (MOR) research group, Universiti Teknologi PETRONAS and Ministry of Education (Higher Education Department) under MyRA Incentive Grant for CO_2 Rich Natural Gas Value Chain Program.

REFERENCES

Askari, S. and R. Halladj, 2012. "Ultrasonic pretreatment for hydrothermal synthesis of SAPO-34 nanocrystals." Ultrasonics Sonochemistry, 19(3): 554-559.

Carreon, M.A., S.Li.J.L. Falconer and R.D. Noble, 2008. "Alumina-Supported SAPO-34 Membranes for CO2/CH4 Separation." Journal of the American Chemical Society, 130(16): 5412-5413.

Chung, T.S., L.Y. Jiang, Y.L. Li and S. Kulprathipanja, 2007. "Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation." Progress in Polymer Science, 32(4): 483-507

Goh, P.S., A.F. Ismail, S.M Sanip, B.C. Ng and M. Aziz, 2011. "Recent advances of inorganic fillers in mixed matrix membrane for gas separation." Separation and Purification Technology, 81: 243-264.

Ismail, A.F. and W. Lorna, 2002. "Penetrant-induced plasticization phenomenon in glassy polymers for gas separation membrane." Separation and Purification Technology, 27(3): 173-194.

Junaidi, M.U.M., C.P. Khoo, C.P. Leo and A.L. Ahmad, 2014. "The effects of solvents on the modification of SAPO-34 zeolite using 3-aminopropyl trimethoxy silane for the preparation of asymmetric polysulfone mixed matrix membrane in the application of CO2 separation." Microporous and Mesoporous Materials, 192: 52-59.

Mohammadi, T., M.T. Moghadam, M. Saeidi, M. Mahdyarfar, 2008. " Acid Gas Permeation Behavior Through Poly(Ester Urethane Urea) Membrane." Industrial Engineering Chemistry Research, 47: 7361-7367.

Liu, S.L., R. Wang, Y. Liu, M.L. Ching and T.S. Chung, 2001. "The physical and gas permeation properties of 6FDA-durene/2, 6-diaminotoluene copolyimides." Polymer, 42(21): 8847-8855.

Li, Y., H.M. Guan, T.S. Chung and S. Kulprathipanja, 2006. "Effects of novel silane modification of zeolite surface on polymer chain

rigidification and partial pore blockage in polyethersulfone (PES)-zeolite A mixed matrix membranes." Journal of Membrane Science, 275(1-2): 17-28.

Freemantle, M., 2005. "Membranes for gas separation." Chemical & Engineering News, 83: 49-57.

Manson, J.A. and E.H. Chiu, 1973. "Permeation of Liquid Water in a Filled Epoxy Resin. ." Journal of Polymer Science: Polymer Symposia, 41(1): 95-108.

Rezakazemi, M., A.E. Amooghin, M.M.M. Rahmati, A.F. Ismail and T. Matsuura, 2014. "State-of-the-art membrane based CO2 separation using mixed matrix membranes (MMMs): An overview on current status and future directions. ." Progress in Polymer Science, 29(5): 817-861.

Robeson, L.M., 2008. "The upper bound revisited." Journal of Membrane Science, 320(1-2): 390-400.

Li, S., J.L. Falconer, 2006. "Improved SAPO-34 Membranes for CO2/CH4 Separations." Advanced Materials, 18: 2601-2603.

Venna, S.R. and M.A. Carreon, 2011. "Amino-Functionalized SAPO-34 Membranes for CO2/CH4 and CO2/N2 Separation." Langmuir, 27(6).

Wijenayake, S.N., N.P. Panapitiya, S.H. Versteeg, C.N. Nguyen, S. Goel, K.J. Balkus and J.P. Ferraris, 2013. "Surface Cross-Linking of ZIF-8/Polyimide Mixed Matrix Membranes (MMMs) for Gas Separation." Industrial & Engineering Chemistry Research, 52(21): 6991-7001.

Liu, Y., M.L. Ching, T.S. Chung and R. Wang, 2003. "Effects of amidation on gas permeation properties of polyimide membranes." Journal of Membrane Science, 214(1): 83-92.

Zhang, Y., J. Sunarso, S. Liu and R.Wang, 2013. "Current status and development of membranes for CO2/CH4 separation: A review." International Journal of Greenhouse Gas Control, 12: 84-107.