The incorporation of graphene oxide into polysulfone mixed matrix membrane for CO_2/CH_4 separation

K Zahri[1], P S Goh[2], A F Ismail[3]

Advanced Membrane Technology Research Centre (AMTEC), *Universiti Teknologi Malaysia*, 81310 UTM Skudai, Johor Darul Ta'zim, Malaysia

E-mail: [1]zkhalisah@gmail.com, [2]peisean@petroleum.utm.my, [3]afauzi@petroleum.utm.my

Abstract. Carbon dioxide (CO_2) is often found as the main impurity in natural gas, where methane (CH_4) is the major component. The presence of CO_2 in natural gas leads to several problems such as reducing the energy content of natural gas and cause pipeline corrosion. Thus it must be removed to meet specifications ($CO_2 \leq 2$ mol%) before the gas can be delivered to the pipeline. In this work, hollow fiber mixed matrix membrane (MMM) were fabricated by embedding graphene oxide (GO) into a polysulfone (PSf) polymer matrix to improve membrane properties as well as its separation performance towards CO_2/CH_4 gas. The membrane properties were investigated for pristine membrane and mixed matrix membrane filled with filler loading of 0.25%. The synthesized GO and properties of fabricated membranes were characterized and studied using TEM, AFM, XRD, FTIR and SEM respectively. The permeance of pure gases and ideal selectivity of CO_2/CH_4 gas were determined using pure gas permeation experiment. GO has affinity towards CO_2 gas. The nanosheet structure creates path for small molecule gas and restricted large molecule gas to pass through the membrane. The incorporation of GO in PSf polymer enhanced the permeance of CO_2 and CO_2/CH_4 separation from 64.47 to 86.80 GPU and from 19 to 25 respectively.

1. Introduction

The key characteristics of membrane to be used in gas separation process are its permeability and selectivity. Powel *et al.* [1] has stated that other than permeability and selectivity, membrane for gas separation has to be chemically, thermally and physically stable. Furthermore, they should be resistant towards plasticization and aging effect which influences final cost and modularity. Polysulfone (PSf) based membrane has been an ideal choice as they possess the before listed characteristic [2-3]. However, neat polymeric membrane suffers the trade-off problem common with gas separation membrane, between permeability and selectivity [4]. The idea of incorporating inorganic particle into polymer matrix is expected to solve this problem.

Graphene oxide (GO) is a new material from the graphene nanomaterials family which has fascinating properties and characteristics that offers viable solutions in this industry. Shrier *et al.,* [5] has conducted a molecular simulation study to investigate the effect of graphene surface adsorption towards CH_4, CO_2, N_2, O_2, H_2S SO_2 and H_2O. The study proved that graphene was applicable for CO_2

[1-3] To whom any correspondence should be addressed.

capture and separation. GO is derived from graphene, owing the same carbon sheet structure as graphene but has oxygenated functional groups attached on its planar sheet. These active functional groups such as epoxy, hydroxyl and carboxyl groups help to enhance its dispersion in polymer substrate, which affects membrane gas separation performance [6]. GO filled in polymer nanocomposite membrane has shown promising improvement in its properties, thermally and mechanically [3]. Other than that, in terms of separation performance, GO act as barrier, which creates tortuous path in polymer matrix for gas with smaller molecules size to easily pass through the MMM, and hinder gas with larger molecule size from pass through it [7]. The incorporation of GO in MMM is expected to surpass the Robeson separation trade-off boundary by overcoming the polymeric membrane's drawbacks.

A literature survey reveals the gap of previous works on gas permeation studies for GO incorporated in PSf hollow fiber MMM. In this work, GO was embedded in glassy PSf polymer. The study aim was to prove that the incorporation of GO in PSf polymer improve gas separation performance as compared with pristine PSf. The properties of synthesized GO were investigated in terms of its structure and morphology. Further on, the membrane was characterized by SEM and a gas permeation study was conducted with pure CO_2 and CH_4 gas.

2. Experimental and characterization method

2.1 Materials
Polysulfone (PSf Udel-3500) was purchased from Amoco Chemicals. Dimethylacetamide (DMAC), tetrahydrofuran (THF) and ethanol were supplied by Acros, Merck and Fisher Scientific respectively. Natural graphite flake ($\leq$ 20 µm) and Potassium permanganate ($KMnO_4$) were purchased from Sigma Aldrich. Concentrated sulphuric acid (H_2SO_4, 95-97 wt%), hydrochloric acid (HCl) and hydrogen peroxide aqueous solution (H_2O_2, 30 wt%) were bought from Merck. All the reagents were purchased in analytical grade and used without further purification. PSf and graphite flake were dried in oven for 24 h at 60°C to completely remove moisture. Reverse osmosis water processed from Milipore system (Milli-Q) was used throughout experiments.

2.2 Preparation of GO nanosheets
GO was prepared by oxidation of graphite using modified Hummer's method [8-10]. Graphite powder (3.0 g) was dissolved in concentrated H_2SO_4 (100 ml) while the mixture was stirred in an ice bath to maintain temperature of 0 °C. Then, $KMnO_4$ (9.0 g) was added to the mixture gradually as the mixture was being stirred for 2 hrs at temperature below 10 °C. Next, the mixture temperature was increased to 35 ± 2 °C and vigorous stirred for 30 mins. After that, 150 ml of RO water was added to the mixture slowly, producing a large exotherm up to 100 °C. The temperature was assured to be below than 100° C and was stirred under this condition for 20 mins. Additional water (500 ml) was added to the mixture, followed by 15mL of 30% H_2O_2. The mixture was filtered and further washed with 3% HCl and amount of RO water to remove metal ions and neutralize the filtrate respectively. The suspension was subjected to 1 hr sonication during the first RO water washing to remove the large and un-exfoliated GO. The resulting GO was dried in vacuum oven overnight and was ground to obtain GO powder.

2.3 Dope solution preparation
The preparation of pristine PSf membrane consists of PSf pellets, DMAC, THF and EtOH, with weight ratio of 30/35/30/5 respectively. The composition of dope solution was determined according to procedure described in elsewhere [11]. Initially, PSf pellets was added gradually to the solvent mixture of DMAC and THF and was left under medium speed of mechanical stirrer for 24 hrs. After ensuring the polymer pellets was dissolved, EtOH was added to the dope solution and was subsequently stirred for 2 hrs.

For the fabrication of MMM dope solution, 0.25% of GO nanosheets from the total solid of solution were added into DMAC whilst the operation of ultrasonic bath and was left under sonication for 30 min. THF was added to the suspension and stirred for 1 hr for wetting procedure. For optimum wetting procedure, 10 wt.% of total PSf was added into the suspension subsequently for 4 hours of priming. The remaining PSf pellets were added to the solution gradually and stirred overnight for complete dissolution of the polymer pellets. Finally, EtOH was added into the solution and further stirred for 2 hrs for completion of the formulation above. The solution was placed in an ultrasonic water bath for 1 hr and was left overnight at room temperature to remove trapped bubbles that may exist during dope solution preparation.

2.4 Asymmetric hollow fiber membrane fabrication
Asymmetric hollow fiber membranes were fabricated by spinning process via dry/wet phase inversion process. Details about spinning process described are elsewhere [11]. The dope solution were extruded using spinneret dimension of 0.6/0.3 mm (OD/ID) at air gap distance of 7.0 cm, bore fluid flow rate and dope extrusion rate ratio of 1:2. The fabricated membranes were collected at rate of 15 m/min. Tap water was used as the coagulant during the whole fabrication process. Then, the fabricated membranes were immersed into water coagulation bath for 2 for complete solvent exchange. After that, the membranes were post-treated in methanol for 8 hours. Subsequently, the membranes were left to dry at room temperature for at least 2 days before ready for further characterization.

2.5 Characterization and gas permeation test
The surface morphology of GO was observed using a transmission electron microscope (TEM, Hitachi HT7700). The GO dimension was characterized using an atomic force microscope (AFM, XE-100 Park System, Korea).

The crystalline properties of GO and membranes were investigated using X-Ray diffractometer (XRD, Siemens D5000). The analysis was carried out using copper Kα radiation (λ= 1.541nm), in the scanning range of 2θ angle ranging from 5° to 60° with a step size of 2 degree.

The chemical structure of GO was analysed using Fourier transform infrared spectrophotometer (FT-IR, Perkin Elmer, Spectrum One). The morphology of prepared membranes was investigated using scanning electron microscopy (SEM, TM3000 Hitachi Japan).

The gas permeation test was conducted with a bubble soap flow meter to measure the membrane performance towards selected gases. Pure CO_2 and CH_4 gas were used and tested at room temperature with operating pressures of 5 bar. The pressure normalized flux or permeance (P_i/l) of hollow fiber membrane and its selectivity was calculated using equation described in elsewhere [11].

3. Result & Discussion

3.1 Characterization of GO nanosheets

3.1.1 TEM and AFM analysis
Various functional groups were introduced to graphite structure by oxidation process via Hummers' Method. During the oxidation process, the functional groups are introduced to the graphite's lamellar interlayer structure, making them suitable to be expanded into few layer or monolayer of GO after ultrasonication [12]. The morphologies of GO nanosheets were characterized using transmission electron microscopy (TEM) and atomic force microscopy (AFM). Figure 1(a) shows the typical structures of GO nanosheets from TEM analysis. The thickness of the nanosheets was measured via AFM analysis and the value was 0.716 nm which was same as reported by previous work [13]. Figure 1(b) shows the topography image of GO nanosheets while Figure 1(c) shows its line profile. The results indicated that the synthesized GO was successfully exfoliated into monolayer nanosheets.
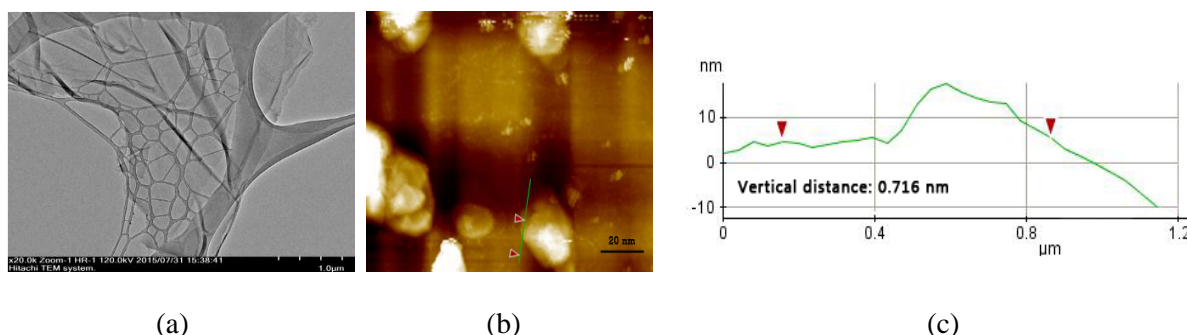
(a)   (b)   (c)

Figure 1. (a)TEM image, (b) AFM topography image, and (c) line profile of GO nanosheets

3.1.2 XRD analysis

The microstructure of GO was characterized using x-ray diffraction (XRD) analysis. Figure 2 shows the graphite powder exhibit a sharp diffraction peak at $2\theta = 26.41°$, corresponding to a d-spacing of 0.373 nm [14-15]. The peak of GO appeared at peak $2\theta = 10.5°$ with d-spacing 0.842 nm, which was consistent with value reported in literature [15] and also in line with AFM result. The GO d-spacing value was obviously larger than pristine graphite, which indicates the exfoliation of GO due to the attachment of functional groups during oxidation process and the absorbed water between GO interlayers [9,16].
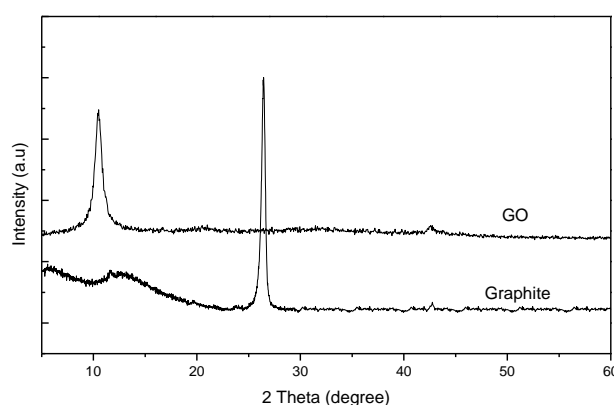

Figure 2. XRD patterns for graphite and GO

3.1.3 FTIR analysis

Figure 3 shows FTIR spectrum of pristine graphite and GO. The characteristic of pristine graphite FTIR spectrum shows vibration peak of C-C at wavelength 1600cm^{-1} [9] and two –CH$_2$- peaks at wavelength 2920 cm^{-1}, 2850 cm^{-1} [10]. Compared with pristine graphite, more significant peaks of GO are observed on the GO spectrum after being oxidized. The spectrum shows broaden peak at 3450 cm^{-1}, attributed to water content adsorbed by polar functional groups on GO surface such as –OH [17]. Other vibration spectrum are observed at peak 1720 cm^{-1}, 1390 cm^{-1}, 1230 cm^{-1}, 1050 cm^{-1}, which corresponds to carboxyl (C=O), hydroxyl (C-OH), epoxy (C-O-C) and C-O respectively. Therefore, the existences of oxygenated functional groups are confirmed as well as in literature [9,18]. In addition, those oxygenated functional groups attached to GO are expected to improve the interaction between GO and polymer [19].
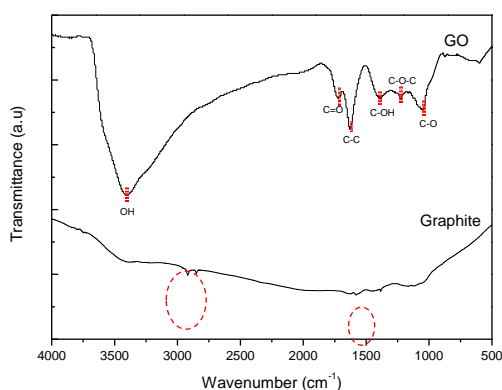
Figure 3. FTIR patterns for graphite and GO

3.2 Membrane characterization

3.2.1 SEM analysis of MMM
Figure 4 shows the SEM images of fabricated pristine PSf hollow fiber membranes as compared with PSf-GO hollow fiber MMM incorporated with 0.25% GO loading. From the SEM cross section images, a typical morphology of asymmetric membrane for gas separation consisting active dense skin layer structure supported by porous sub-layer comprising small sponge like structure sandwiched by large macrovoid structure were observed. It can be observed that the addition of GO to the membrane shorten the elongation of tear drop structure at the membrane lumen side and supress the formation of circular microvoid structure beneath the outer surface layer, which leads to a more dense and thicker active skin layer. The difference of dope polymer viscosity can explain this phenomena. This phenomenon was supported by previous study conducted by Ismail *et al.* [20] which suggested that the incorporation of filler influenced the membrane morphology structure due to change in polymer dope viscosity. The addition of GO increased the dope viscosity value and this affects the formation of asymmetric membrane structure. Higher viscosity delayed the solvent-nonsolvent exchange rate which restrained the formation of larger tear drops. Thicker and denser skin layer is expected for higher viscosity. However, the skin layer thickness cannot be measured via SEM analysis.
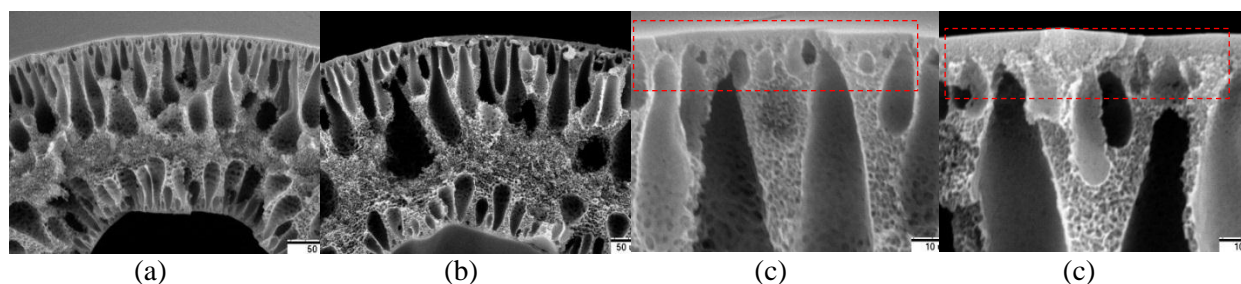

Figure 4. SEM cross section images of (a) pristine PSf, (b) PSf-GO MMM at magnification x1.5k, (c) pristine PSf and (d) PSf-GO MMM at magnification at magnification x10k

3.2.2 The permeation and selectivity of MMM towards CO_2/CH_4 gas

Table 1. Gas permeation properties for CO_2 and CH_4 measured at 5 bar and 25 ± 7 °C

Membrane	P_{CH4} (GPU)	P_{CO2} (GPU)	Selectivity
PSf	3.36	64.47	19.20
PSf-GO	3.34	86.80	25.98

Table 1 shows the effect of adding GO into PSf polymer on the gas permeation characteristic. Based on previous study, the incorporation of GO into rubbery polymer matrix enhanced the permeation of selective gas without major reduction in selectivity [7]. Li *et al.* [8] has reported that polyethyleneglycol-polyethylineimine GO nanosheets embedded into Pebax polymer matrix has improved MMM gas separation performance. However, the membrane performance deteriorated with the addition of filler at certain threshold amount. The present study shows that the addition of 0.25% GO nanosheets into PSf polymer does improve the MMM performance, especially for CO_2 gas permeation. CO_2 permeance significantly increased from 64.47 GPU to 86.80 GPU. It was observed that the permeation of CH_4 gas slightly reduce from 3.36 GPU to 3.34 GPU, which resulted improvement in CO_2/CH_4 selectivity by 35% with respect to the pristine PSf.

The increasing of CO_2 permeation can be contributed by the GO itself which possesses high absorption properties towards selective gas. GO own π-π stacking bond that has interaction with CO_2 gas and high affinity towards that polar gas [9]. Other than that, GO contained active functional groups which helped to improve its interaction with PSf molecular chain resulting in better GO dispersion in polymer matrix. These phenomenon's explains the significant increment of CO_2 permeation in MMM.

The low loading of GO can increase the nanoparticles aspect ratio by preventing GO sheets from agglomerating and restack back to multilayers GO. In addition, the oxygenated functional groups as mentioned above help GO to have good dispersion in polymer matrix and prevent interphase problem between GO and polymer matrix from occur. Other than that, GO structure in nanosheets or few layers sheet form creates tortuous diffusion path in polymer matrix which allows smaller gas molecule (CO_2: 3.3Å) to diffuse with less resistance and restricts the larger gas molecule (CH_4: 3.8 Å) from diffusing through the MMM [8]. This explains the slight reduction of CH_4 permeation and significant increment of CO_2/CH_4 selectivity.

4. Conclusion
PSf-GO hollow fiber MMM was fabricated. The characteristic of synthesized GO and membranes in term of its morphological structure as well as gas separation performance were analysed. From this work, the GO nanosheets have been successfully synthesized. The incorporation of GO nanosheets into PSf polymer gives significant improvement to gas separation properties even at low loading (0.25 wt.%). The special properties present in GO consisting of polar groups and π-π conjugate bond helps to improve CO_2 permeance in MMM by 34%, correspondingly increased the selectivity of CO_2/CH_4 gas.

5. References

[1]   Powel C E and Qiao G G, 2006 *J. Membr. Sci.* **279** 1
[2]   Ganesh B M, Isloor A M and Ismail A F 2013 *Desalination* **313** 199
[3]   Ionita M, Vasile E, Crica L E, Voicu S I, Pandele A M, Dinescu S, Predoiu L, Galateanu B, Hermenean A and Costache 2015 *Composites: Part* B **72** 108
[4]   Robeson L M 2008 *J. Membr. Sci.* **320** 390
[5]   Schrier J 2011 *ACS Appl. Mater. Interfaces* **3** 4451
[6]   Yang X, Wang X, Yang J, Li J and Wan L *Chem. Phys. Lett.* **570** 125

[7]   Berean K J, Ou J Z, Nour M, Field M R, Alsaif M M Y A, Wang Y, Ramanathan R, Bansal, Kentish V S, Doherty C M, Hill A J, McSweeney C, Kaner R B and Kalantar-zadeh K 2015 *J. Phys. Chem.* C **119** (24) 13700

[8]   Li X, Cheng Y, Zhang H, Wang S, Jiang Z, Guo R and Wu H 2015 *ACS Appl. Mater. Interfaces,* **7** 5528

[9]   Zhao L, Cheng C, Chen Y F, Wang T, Du C H and Wu L G 2015 *Polym. Adv. Technol.* **26** 330

[10]   Zhao Y, Ding H and Zhong Q 2012 *J. Appl. Surf. Sci.* **258** 4301

[11]   Zulhairun A K, Ng B C, Ismail A F, Surya Murali S and Abdullah M S 2014 *Sep. Purif. Technol.* **137** 1

[12]   Wang T, Zhao Li, Shen J N, Wu L G and Bruggen B V 2015 *Environ. Sci. Technol.* **49** 8004

[13]   Li X, Ma L, Zhang H, Wang S, Jiang Z, Guod R, Wu H, Cao X Z, Yang J and Wang B 2015 *J. Membr. Sci.* **479** 1

[14]   Cao K, Jiang Z, Zhao J, Zhao C, Gao C, Pan F, Wang B., Cao X and Yang J 2014 *J. Membr. Sci.* **469** 272

[15]   Chen J, Li Y, Huang L, Li C and Shi G 2015 *Carbon* **81** 826

[16]   Szabo T, Berkesi O and Dekany I 2005 *Carbon* **43** 3181

[17]   Jin T X, Liu C, Zhou M, Chai S G, Chen F and Fu Q 2015 *Composites: Part* A, **68** 193

[18]   Guo H L, Wang X F, Qian Q Y, Wang F B and Xia X H 2009 *ACS Nano.* **3** 2653

[19]   Wang T, Zhao L, Shen J N, Wu L G and Bruggen B V 2015 *Environ. Sci. Technol.* **49** 8004

[20]   Ismail N M, Ismail A F and Mustafa A 2015 *Procedia CIRP* **26** 461