

# EFFECTS OF PEBAK COATING CONCENTRATIONS ON CO<sub>2</sub>/CH<sub>4</sub> SEPARATION OF RGO/ZIF-8 PES MEMBRANES

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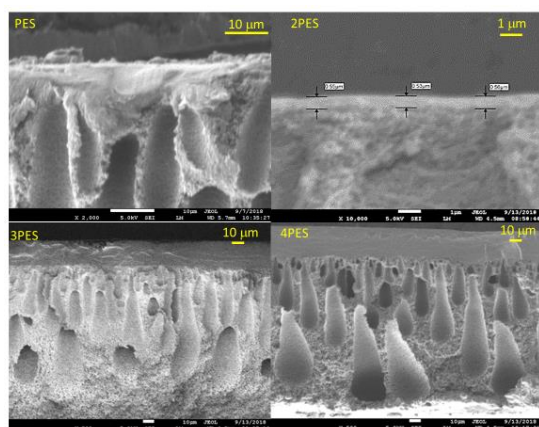
Najihah Jamil<sup>a</sup>, Nur Hidayati Othman<sup>a\*</sup>, Munawar Zaman Shahrudin<sup>a</sup>, Mohd Rizuan Mohd Razlan<sup>a</sup>, Nur Hashimah Alias<sup>a</sup>, Fauziah Marpani<sup>a</sup>, Lau Woe Jye<sup>b</sup>, Pei Sean Goh<sup>b</sup>, Ahmad Fauzi Ismail<sup>b</sup>

\*Corresponding author  
nurhidayati0955@uitm.edu.my

<sup>a</sup>Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM), Shah Alam, Selangor, Malaysia

<sup>b</sup>Advanced Membrane Technology Research Center (AMTEC), Faculty of Chemical and Energy Engineering, UTM, 81310 Johor Bahru, Johor, Malaysia

## Graphical abstract



## Abstract

The biggest challenge surrounding application of polymeric membranes for gas separation is their trade-off between gas permeation and selectivity. Therefore, the use of mixed matrix membranes (MMMs) comprising inorganic materials embedded into a polymer matrix can overcome this issue. In this work, PES flat sheet membrane and MMMs consists of 10 wt.% of rGO/ZIF-8 hybrid nanofillers were fabricated via dry/wet phase inversion process. Dip-coating technique was then used to deposit PEBAK selective layer onto the surface of rGO/ZIF-8 PES support. The effects of PEBAK coating solution concentrations (2, 3 and 4 wt.%) on the permselectivity of CO<sub>2</sub> and CH<sub>4</sub> were investigated. The as-prepared rGO/ZIF-8 nanofillers and MMMs were characterized by fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) prior to gas separation performance study. Gas permeation testing was carried out at operating pressure of 1, 3 and 5 bar using CO<sub>2</sub> and CH<sub>4</sub> gasses. It was observed that the prepared PES membranes and rGO/ZIF-8 PES MMMs did not have any selectivity towards the gases although their permeability was high. As the concentration of PEBAK coating solution increased, thicker coating layer was formed. Therefore, the permeability of CO<sub>2</sub> rapidly dropped but the CO<sub>2</sub>/CH<sub>4</sub> selectivity increased significantly up to 38.4. Results indicated that the use of 2 wt.% of PEBAK was not effective to form homogenous coating layers on PES membrane and to cover any defects on membrane surfaces, thus, possessing low selectivity of CO<sub>2</sub>/CH<sub>4</sub>. The high gas separation performances obtained in this work was due to the synergistic effect rGO and ZIF-8 crystals. In the rGO/ZIF-8 MMMs, the dispersibility are enhanced due to the presence of distorted rGO sheets, while the ZIF-8 component ensure the porosity of the nanofillers and permit gas interactions with the metallic sites and functional groups on the organic linker. These sites facilitate the reactive adsorption leading to enhanced CO<sub>2</sub> adsorption as compared to CH<sub>4</sub>.

Keywords: Reduced Graphene Oxide, Zeolitic Imidazole Framework -8, Mixed Matrix Membrane, Polyethersulfone, Pebax

## Abstrak

Cabaran terbesar di dalam ruang lingkup aplikasi membran polimer untuk pemisahan gas adalah perdagangan antara permeasi dan gas selektiviti. Oleh itu, penggunaan membran matriks campuran (MMMs) yang terdiri daripada bahan bukan organik yang terletak di dalam matriks polimer dapat mengatasi masalah ini. Dalam penyelidikan ini, komposisi membran PES dan MMMs terdiri daripada 10% rGO/ZIF-8 dihasilkan melalui proses fasa penyongsangan kering/basah. Teknik celupan kemudiannya digunakan untuk menyalut PEBAX sebagai lapisan selektif di atas permukaan membran rGO/ZIF-8 PES. Kesan kepekatan larutan lapisan PEBAX (2, 3 dan 4 wt.%) pada pemisahan CO<sub>2</sub> dan CH<sub>4</sub> juga telah dikaji. Ciri – ciri rGO/ZIF-8 pengisi nano dan MMM di analisa menggunakan spektroskopi Inframerah Transformasi Fourier (FTIR), analisis termogravimetrik (TGA), X-ray difraksi (XRD), mikroskop elektron pengimbasan (SEM) dan mikroskop elektron penghantaran (SEM) sebelum kajian prestasi pemisahan gas. Pengujian permeasi gas beroperasi pada tekanan 1, 3 dan 5 bar menggunakan gas CO<sub>2</sub> dan CH<sub>4</sub>. Melalui pemerhatian, dapat dilihat bahawa membran PES dan rGO/ZIF-8 PES MMM tidak selektif terhadap gas. Oleh kerana kepekatan larutan PEBAX meningkat, lapisan yang lebih tebal telah terbentuk menyebabkan kebolehtelapan CO<sub>2</sub> menurun dengan pesat, manakala selektiviti CO<sub>2</sub>/CH<sub>4</sub> meningkat dengan ketara sehingga mencapai 38.4. Keputusan menunjukkan pada 2 wt% kepekatan PEBAX, tidak berupaya untuk membentuk lapisan sekata pada membran PES membawa kepada selektiviti CO<sub>2</sub>/CH<sub>4</sub> yang rendah. Prestasi pemisahan gas yang tinggi yang diperolehi dalam penyelidikan ini adalah disebabkan oleh kesan sinergi rGO dan kristal ZIF-8. Dalam rGO/ZIF-8 MMM, interaksi penyebaran meningkat oleh kerana kehadiran kepingan tidak rata rGO, manakala komponen ZIF-8 memastikan keliangan pengisi nano membenarkan interaksi gas dengan tapak metalik dan kumpulan berfungsi pada organik penyambung. Ini memudahkan penjerapan reaktif yang membawa kepada peningkatan penjerapan CO<sub>2</sub> berbanding dengan CH<sub>4</sub>.

*Kata kunci:* Pengurangan graphene oksida, ierangka Imidazole Zeolitic - 8, membran matriks campuran, polietersulfone, PEBAX

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## 1.0 INTRODUCTION

Methane is one of the key components in natural gas. However, this raw natural gas also contains other impurities such as water vapor, carbon dioxide, nitrogen and helium. As CO<sub>2</sub> can cause many operational problems such as pipeline corruptions [1], gas hydrate formation [2] and gas heating value reduction [3], therefore, the separation of CO<sub>2</sub> from natural gas is essential. There are several gas separation techniques available including adsorption, absorption cryogenic distillation and membrane separation. The conventional method is known to have reliable performance in CO<sub>2</sub> removal but owing to high installation and operating cost, membrane separation has become an established technology [4]. Membrane separation contributes to several advantages compared to conventional process such as no phase change, easy to operate, high process flexibility, smaller footprint, low cost and low maintenance. Thus, it has been regarded as one of the energy efficient and economical technology particularly for CO<sub>2</sub> removal at offshore platform [5].

Polymeric membranes are one of the most widely used for gas separation processes such as natural gas sweetening, hydrogen purification, air separation, and landfill gas recovery, owing to the materials flexibility to be processed into different types of modules [6]. However, the performances of polymeric membranes have been constrained by the Robeson "upper bound" trade – off line between the gas permeability and selectivity. In contrast, inorganic membranes have excellent chemical and thermal stability with high gas permeation and selectivity. However, they are also brittle and expensive, which limit their application.

Recently, mixed matrix membranes (MMMs) with hybrid characteristics of polymer and inorganic materials, have been introduced as an alternative approach to overcome these limitations. MMMs are considered as a class of composite membranes that incorporate inorganic materials into a continuous polymer matrix. [7, 8]. The synergy between both components allows higher selectivity and permeability relative to the existing polymeric membranes, resulting from the inherent superior

separation characteristics of inorganic particles. Among the widely used inorganic fillers in MMMs fabrication are zeolites [9], carbon nanotubes (CNT) [10–12], metal organic framework (MOF) [8, 13] and graphene [14, 15].

MOF are made of metal complexes that are linked by organic ligands to create highly porous frameworks particles. It is also expected to interact more easily with polymer matrix through its organic linkers [16, 17]. Zeolitic imidazole framework (ZIF-8) is a subclass of MOF that exhibit excellent capacity for gas adsorption and separation properties. Song *et al.* [18] founds that by using up to 30 wt.% loading of ZIF-8, good adhesion within the polymer matrix can be maintained while significantly improved the pure gas ( $H_2$ ,  $CO_2$ ,  $O_2$ ,  $N_2$  and  $CH_4$ ) permeation. This was due to an increase in free volume caused by the high loading of ZIF-8 together with free diffusion of gas through the cages of ZIF-8.

Reduced graphene oxide (rGO) is usually prepared by partial removal of oxygen containing group such as carboxylic acid (COOH), epoxy (COH) and hydroxyl (OH) from the edges and basal planes of graphene oxides (GO). Recently, rGO shows prominent use as hybrid nanofillers selection due to its inert properties which prevent diffusion of gasses larger than helium gas and owing to its aromatic ring electron density, it repels all matter that trying to penetrate the graphene sheet [19]. The synergistic effects between rGO and ZIF-8 nanofillers had been shown in the study of Wang *et al.* [20], where rGO was found to increase the high permeation flux and contributes to high conductivity of the filler. These excellent properties of rGO/ZIF-8 nanofiller prompt it to be a suitable candidate as nanofillers in the development of MMMs for gas separation application.

In order to minimize surface defects and improve separation performances of MMMs, surface coating of MMMs using polydimethylsiloxane (PDMS) and poly (ether block amide) (PEBAX) has been widely adopted. Wahab *et al.* [21] shows that through PEBAX coating, the selectivity of MMMs has been improved significantly from 1.09 to 13.69. This is because the addition of coated layer acts as a selective layer to withstand the gas pressure during transmittance of gas while the polymer matrix acts as transport channel for the separated gas [21]. Dip-coating method has been used for the deposition of selective layer onto membrane support. This technique smears a wet layer of coating material onto a dry porous support surface followed by a drying process. However, repeated coating-drying process will cause the reduction of the membrane permeation properties as the thickness of coating layer increased [6].

In this work, 10 wt.% of rGO/ZIF-8 nanofillers were embedded in the PES substrate and their performances were compared with bare PES membrane. This study aims to further improve the membrane performances with the addition of different concentrations (2, 3 and 4 wt.%) of PEBAX which serves as selective layer to PES substrate. The

properties of synthesized rGO/ZIF-8 and membranes were investigated in terms of its chemical structure, and thermal stability morphology. The membrane performances were measured with a single gas permeation using  $CO_2$  and  $CH_4$  gasses at various operating pressure.

## 2.0 METHODOLOGY

### 2.1 Materials

Graphite powders (MW=12.01 g/mol, Merck),  $H_2SO_4$  (98%, R&M Chemicals),  $NaNO_3$  (84.99 g/mol, SYSTEM),  $KMnO_4$  (158.05 g/mol, R&M Chemicals),  $H_2O_2$  (30%, Merck), HCl (Merck) and ascorbic acid were used as the raw material for rGO synthesis. Zinc nitrate hexahydrate ( $Zn(NO_3)_2 \cdot 6H_2O$ , MW = 297.49 g/mol) and 2-methylimidazole (H-MeIm, MW = 82.10g/mol) were purchased from Sigma-Aldrich used for synthesizing rGO/ZIF-8 nanofillers. Commercial PES powder (MW = 22,000 g/mol) was obtained from Veradel. N-Methyl-2-pyrrolidone (NMP, 85%  $C_5H_9NO$ ) was purchased from Merck (Germany). Polyether block amide (PEBAX) pellet was supplied by ARKEMA and ethanol (98 % concentration) was purchased from SYSTEM.

### 2.2 Preparation of rGO/ZIF-8 Nanofillers

Graphene oxide was synthesized based on our previous works [22]. Then, 400 mg/L of GO suspension was prepared and sonicated for 2 hours until no visible particulate matter. 1.5 g of ascorbic acid was then added into the solution and the solution was stirred for 30 minutes. Ammonia was then added until the pH of the solution reaches 9-10 and the solution was stirred vigorously at 95 °C for 2 hours. The resulting product was isolated using vacuum filter and washed repeatedly with deionized water before dried in an oven for 24 hours at 60-70 °C to form rGO.

rGO/ZIF-8 nanofillers was synthesized by using templated growth of ZIF-8. 4.8 g of  $Zn(NO_3)_2 \cdot 6H_2O$  and 10.6 g of 2-Hmim were dissolved in 180.8 ml of methanol separately and stirred for an hour. Then, 70 mg of rGO suspension was immersed in the  $Zn(NO_3)_2$  methanol solution and sonicated before adding the solution into the  $Zn(NO_3)_2$  solution. The mixture was continually stirred and sonicated for another 1 hour and 8 hours, respectively. The precipitate was then collected by centrifugal and wash with 50 mL of methanol for 3 times to remove any leftover precursor. The samples were dried at 60 °C for 24 h under vacuum to obtain the rGO/ZIF-8 nanofillers.

### 2.3 Preparation of PES MMMs

PES MMMs were prepared using rGO/ZIF-8 and the compositions of the prepared membranes are given in Table 1. The dope solution was prepared by dissolving 10 wt.% of rGO/ZIF-8 nanofiller in NMP

solvent. The solution was then sonicated for an hour prior left for magnetic stirring overnight at room temperature to obtain a homogenous dispersion of filler. A pre-determined amount of PES was then added gradually into the rGO/ZIF-8 – NMP solution and continually stirred until the polymer was completely dissolved. The dope solution was then left magnetically stirred overnight until a homogenous solution was obtained, sonicated and degassed for an hour to remove bubbles in the solution prior fabricating process. Phase inversion based on immersion precipitation technique was used to fabricate the MMMs where the solution was casted onto a glass plate using a casting knife at the gap of 130  $\mu\text{m}$  – 200  $\mu\text{m}$ . The fabricated membrane sheet was immediately immersed into a coagulation bath for 24 hours before transferred into another coagulation bath for 1 hour to remove any residual solvent followed by air-dried for 24 hours at room conditions [23,24]. Bare PES membrane was also prepared and used as a control membrane.

**Table 1** Composition of dope solution

Samples	PES	rGO/ZIF-8	NMP
Uncoated PES	20	0	80
rGO/ZIF-8 PES	18	2	80

In order to investigate the effect of PEBA coating layer thickness, 3 different concentrations of PEBA solution was prepared (2, 3 and 4 wt.%). 2 wt.% of PEBA solution was prepared by dissolving 2 g of overnight dried PEBA pellets in a mixture of 70 wt.% ethanol and 30 wt.% of water under reflux at 70 °C for 2 hours until a homogenous transparent solution was obtained. The PEBA solution was then sonicated for an hour prior coating on the surface of PES MMMs. The dip-coating method was used where 3 ml of 2 wt.% PEBA solution was poured inside a petri dish. The shiny surface of the membrane was then dip coated for 30 sec. The coated MMMs were dried at 60 °C for 2 hours to allow solvent vaporization. Similar procedure was repeated by using 3 wt.% and 4 wt.% of PEBA.

## 2.4 Characterization and Gas Permeation Testing

The crystalline species of the prepared samples was determined by using X-ray diffraction (XRD, X'pert PRO) at 2 $\theta$  range from 5 - 80°. The equipment voltage and ampere were set at 40kV and 40mA, respectively.

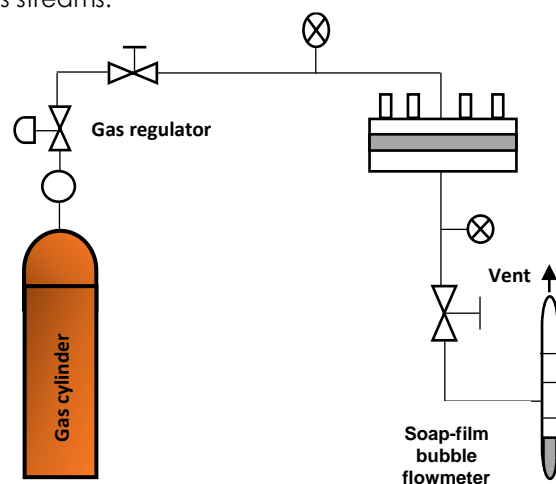
The surface area properties of the samples and Nitrogen adsorption-desorption isotherm are determined by using the Brunauer Emmet Teller (BET) Surface Area and Porosity Analyzer (Micromeritics, ASAP 2020). The characterization is based on nitrogen (N<sub>2</sub>) adsorption and desorption isotherm. The samples were first degassed for 8 hours at 120 °C.

The thermal stability of the samples was then investigated using thermogravimetric analysis (TGA, Mettler Toledo Analyzer). The analysis was conducted from room temperature up to 900 °C under nitrogen

condition. The mass of the sample was monitored during the cooling and heating process to determine the total weight loss of samples.

The morphology of the samples was performed using Hitachi S-300N scanning electron microscopy (SEM) and transmission electron microscope (TEM). Prior to SEM analysis, the sample was sputtered coated with a thin layer of gold to prevent electrical charging effect.

Gas separation performance was determined by a constant volume and variable pressure method using an in-house 316 stainless steel gas permeation cell with an effective area of 19.64 cm<sup>2</sup>. In each experiment, the prepared MMMs were cut into desired circular shape. Two gases (purity of 99.99%) having various kinetic diameters, CO<sub>2</sub> (3.30 Å), and CH<sub>4</sub> (3.80 Å) were used during this study. A bubble flow meter was used to measure the permeation rate of gas streams.



**Figure 1** Schematic diagram for permeation using flat sheet membrane module soap-film bubble flowmeter

Each permeation testing was carried out for 3 times and the average value was reported. The membrane permeance was determined using the permeate flow rate obtained from the soap-film bubble flow meter and using the following equation [25]:

$$P = \frac{22414}{A} \times \frac{l}{P_2 - P_1} \times \frac{P_1}{RT} \times \frac{dV}{dt} \quad (1)$$

where A representing membrane area (cm<sup>2</sup>), P<sub>1</sub> and P<sub>2</sub> are the transmembrane pressure, R is the universal gas constant (6236.56 cm<sup>3</sup>.cmHg/mol.K), T represents absolute temperature (K), dV/dt is the volumetric displacement rate (cm<sup>3</sup>/s) and 22,414 cm<sup>3</sup>.(STP)/mol is the number of penetrant per mole. The ideal separation factor (selectivity) of a membrane for gas i to gas j is evaluated as follows [24]:

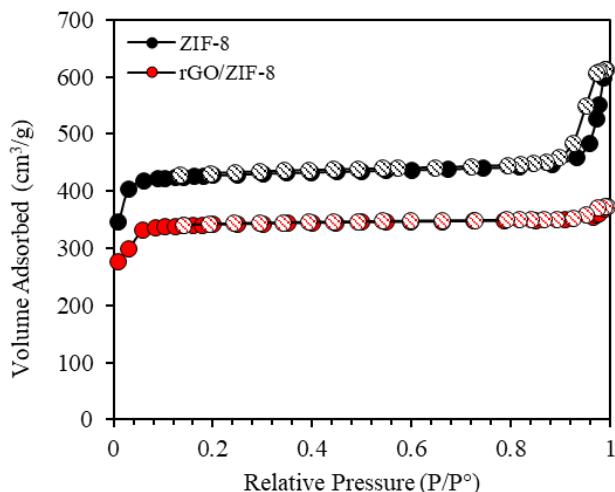
$$\text{Selectivity} = \frac{P_i}{P_j} \quad (2)$$

where the P<sub>i</sub> permeability of CO<sub>2</sub> gas while P<sub>j</sub> permeability of CH<sub>4</sub> gas.

### 3.0 RESULTS AND DISCUSSION

#### 3.1 rGO/ZIF-8 Nanofillers Properties

Figure 2 shows the N<sub>2</sub> sorption isotherms of ZIF-8 and rGO/ZIF-8. Typical Type I isotherms with rapid increases in N<sub>2</sub> adsorption at low relative pressure were obtained for both samples, which suggests the microporous nature of the nanofillers. However, the behaviour of ZIF-8 isotherms was observed to change to Type IV when the values of P/P<sub>0</sub> > 0.95, indicating the existence of large pores due to intra aggregate voids in ZIF-8.



**Figure 2** Nitrogen sorption isotherms of ZIF-8 and rGO/ZIF-8 samples

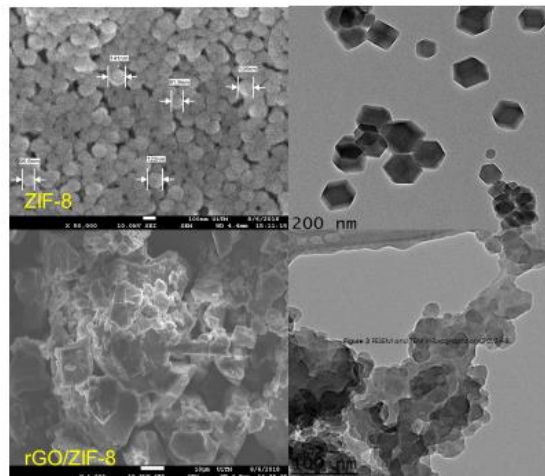
The surface area and pore volume of the ZIF-8 and rGO/ZIF-8 samples are shown in Table 2. The BET surface area of ZIF-8 and rGO/ZIF-8 was 1144 m<sup>2</sup>/g and 986 m<sup>2</sup>/g and the total pore volume = 0.41 and 0.324 cm<sup>3</sup>/g, respectively. These results are in good agreement with the literature [26]. There was a significant reduction of the surface area and pore volume of rGO/ZIF-8 which indicates an interaction between ZIF-8 and rGO molecules. However, owing to the structural features of ZIF-8 such as high surface area, large spherical cavities (11.8 Å) and structural flexibility [27], the hybrid rGO/ZIF-8 nanofillers prepared is still considered very attractive materials for adsorption of CO<sub>2</sub> due to an improved porosity and accessibility of ZIF-8 crystal in rGO/ZIF-8 composites as observed by Kim *et al.* [28].

**Table 2** Surface area and pore volume of ZIF-8 and rGO/ZIF-8

Samples	Surface area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)
ZIF-8	1,144	0.410
rGO/ZIF-8	986	0.324

The morphology and size of the prepared ZIF-8 and rGO/ZIF-8 were examined by SEM and TEM (Figure 3). ZIF-8 exhibited a well-defined polyhedral shape, tightly distributed nanoparticles with the nearly same size. The average particle size was approximately 200 nm.

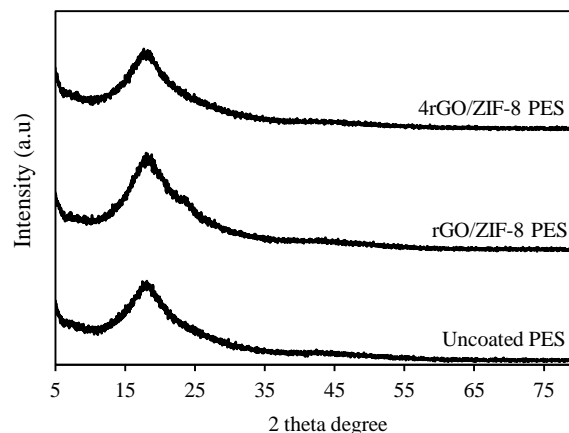
For rGO/ZIF-8 structure, obvious wrinkles without any noticeable pore are observed in accordance with characteristics of rGO [20] indicating that ZIF-8 was anchored and grew on the rGO template. The size of ZIF-8 nanoparticles was observed to reduce to around 100 nm suggesting an interaction between rGO and ZIF-8.



**Figure 3** FESEM and TEM micrographs of rGO/ZIF-8

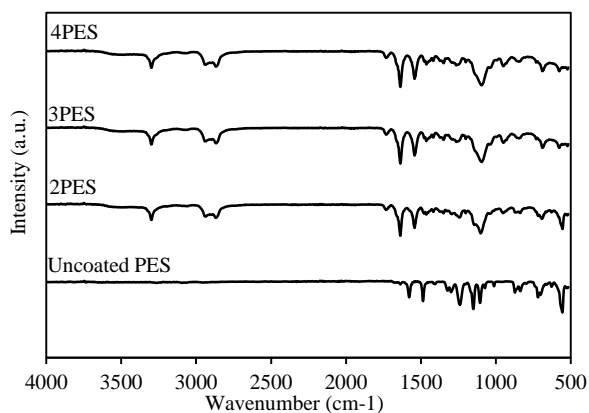
#### 3.2 rGO/ZIF-8 PES MMMs Chemical and Thermal Properties

Figure 4 compares the XRD spectra of bare PES, rGO/ZIF-8 PES MMMs and PEBAX-coated rGO/ZIF-8 PES MMMs. The XRD pattern of PES membrane shows primarily amorphous and singular broad peak 2θ at 17 ° which is similar to the reported peak for pure PES [29]. Upon addition of rGO/ZIF-8 nanofillers, the amorphous nature of the PES was observed to remain intact, although its amorphous peak shifted slightly to lower 2θ values. The decrease of the value implies that the d-spacing of the membrane increases where greater d-spacing indicates the interstitial chain-chain distance and the fractional free volume (FFV) of the MMMs increases [24, 28, 30].



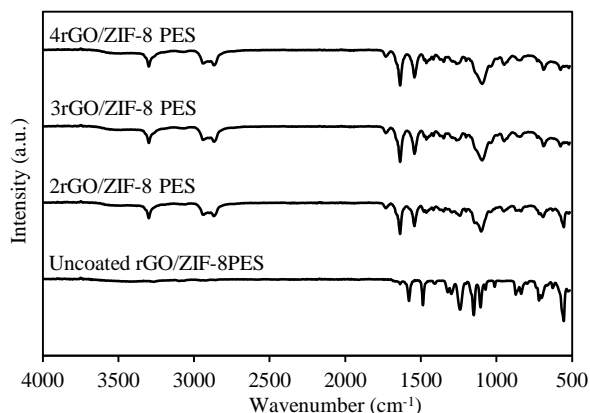
**Figure 4** XRD results of uncoated PES membrane, uncoated rGO/ZIF-8 PES MMMs and 4wt% PEBAX coated rGO/ZIF-8 PES MMMs

Figure 5 compares the FTIR result for uncoated and PEBA coated PES membranes. The uncoated PES membrane showed a typical trait of PES including benzene ring at  $1588\text{ cm}^{-1}$ , C–C bond stretching at  $1490\text{ cm}^{-1}$  and aromatic ether C–O–C stretching at  $1253\text{ cm}^{-1}$  [31]. After the PEBA coating, new absorption band appeared such as absorption band at  $3300\text{ cm}^{-1}$  (–N–H–),  $1620\text{ cm}^{-1}$  (–H–N–C=O–) and  $1771\text{ cm}^{-1}$  (–O–C=O–). The spectra observed are belong to functional group in the hard polyamide (PA) segment of PEBA [31].



**Figure 5** FTIR results of uncoated PES and 2, 3, 4 wt.% PEBA coated PES membranes

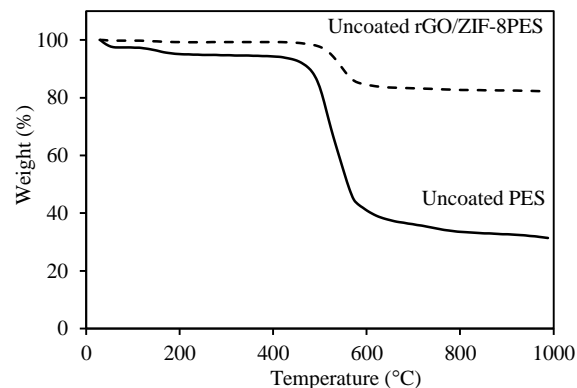
Figure 6 shows FTIR results for uncoated rGO/ZIF-8 PES MMMs and 2, 3 and 4 wt.% of PEBA coated PES MMMs. The FTIR results indicate typical spectrum of PES and PEBA without any additional peak observed as per Figure 5. This might be due to the low amount of rGO/ZIF-8 added into the PES polymer matrix. It also be said that this is due to the nanofillers is diffuse inside the polymer chain and dispersed homogenously [32].



**Figure 6** FTIR results of uncoated rGO/ZIF-8 PES and 2, 3, 4 wt.% PEBA coated PES MMMs

Figure 7 shows the TGA analysis of uncoated PES membranes and rGO/ZIF-8 PES MMMs. PES membrane shows a single step weight loss where the decomposition temperature was observed at around 500 to 600 °C. For rGO/ZIF-8 PES MMMs, no obvious

weight loss was observed until the temperature reached 550 °C, which might be due to the decomposition of PES [33]. The incorporation of 10 wt.% rGO/ZIF-8 into PES membranes was found to significantly increases the thermal stability of the membranes. The total weight loss of PES MMMs was around 17% as compared to PES membranes (70 %). This thermal stability improvement might be due to the formation of hydrogen bonds between rGO/ZIF-8 nanofillers and functional group of PES, which resulted in higher decomposition temperature of PES MMMs [34,35].



**Figure 7** TGA results of BP and 10 PRG uncoated

### 3.3 Membrane Separation Performances

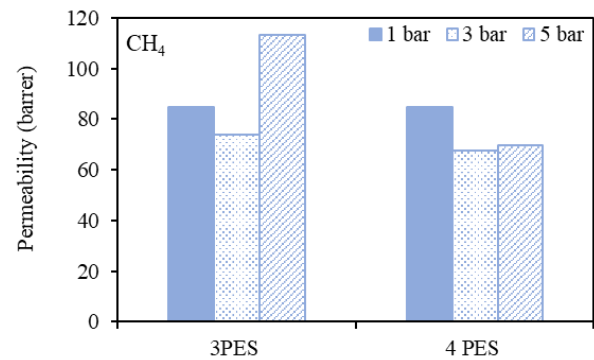
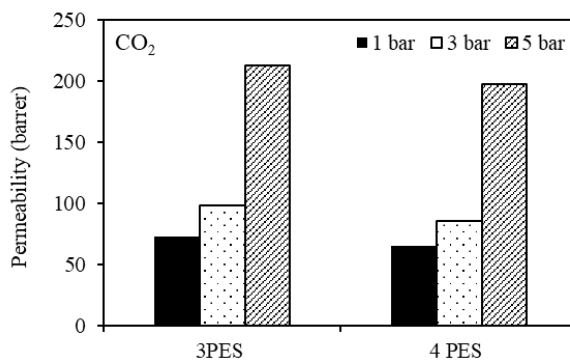
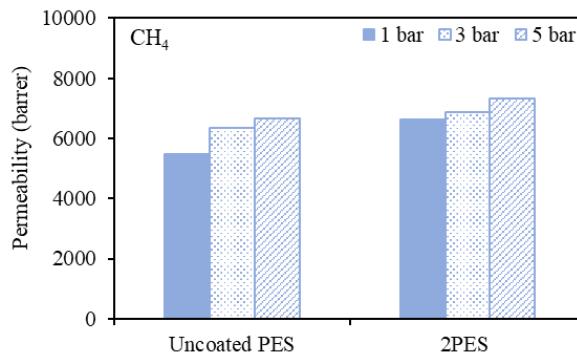
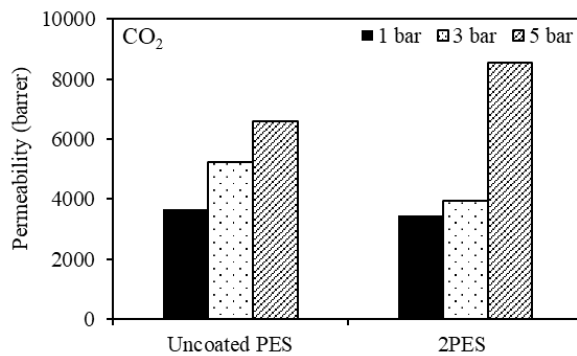
In order to study the effects of rGO/ZIF-8 incorporation on  $\text{CO}_2/\text{CH}_4$  separation performances, the gas permeability and selectivity of uncoated and coated PES membranes are measured and compared with rGO/ZIF-8 PES MMMs. The effect of surface coating thickness was also evaluated, and the results are shown in Figure 8 and Table 3. The uncoated membrane shows higher gas permeability for both  $\text{CO}_2$  and  $\text{CH}_4$  gases. As the PEBA concentration increases, the permeability value for both membranes decreased. The  $\text{CO}_2/\text{CH}_4$  selectivity of uncoated PES and 2, 3, 4 wt.% PEBA coated PES membranes obtained in this work are in the range of 0.99 to 2.83 suggesting that PES is not selective to  $\text{CO}_2$ .

Interestingly, it can be seen that the 2 wt.% PEBA coating did not significantly reduced the gas permeability as compared to 3 and 4 wt.%. The gas permeability value decreased from thousand barrer to hundreds barrer when 3 wt.% of PEBA was used. This indicates that the 2 wt.% of PEBA is not effective to form homogenous and good integrity coating layers on PES membrane. The integrity results were confirmed through SEM analysis on the coated membrane (Figure 9). It can be seen that by using 2 wt.% of PEBA, a thin coating layer of  $0.7\ \mu\text{m}$  was deposited as compared to  $40\text{--}60\ \mu\text{m}$  thickness when 3 and 4 wt.% thickness was used. Thus, the 2rGO/ZIF-8 PES MMMs might still have defects allowing higher gas to permeate. The excessive use of PEBA could also negatively affect the permeability because the

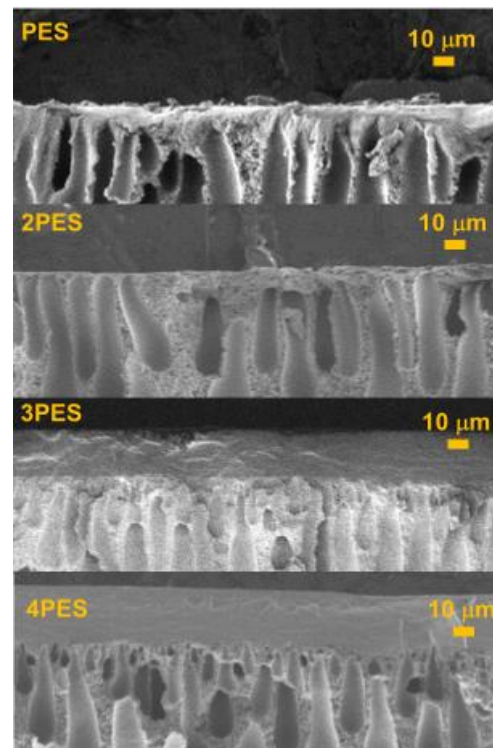
coating layer became thicker, thus creates more resistance for gas to diffuse. Therefore, optimization of PEBA coating thickness is very important to control trade-off between membrane permeability and selectivity.

**Table 3** Selectivity of uncoated PES and 2, 3, 4 wt.% PEBA coated PES membranes

Samples	CO <sub>2</sub> /CH <sub>4</sub> Selectivity		
	1 bar	3 bar	5 bar
Uncoated PES	0.67	0.82	0.99
2PES	0.52	0.57	1.16
3PES	0.86	1.33	1.88
4PES	0.93	1.27	2.83



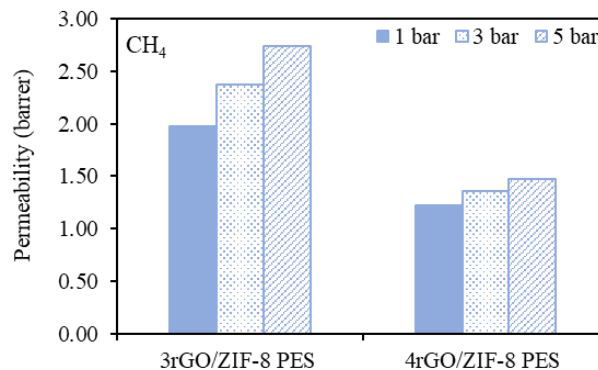
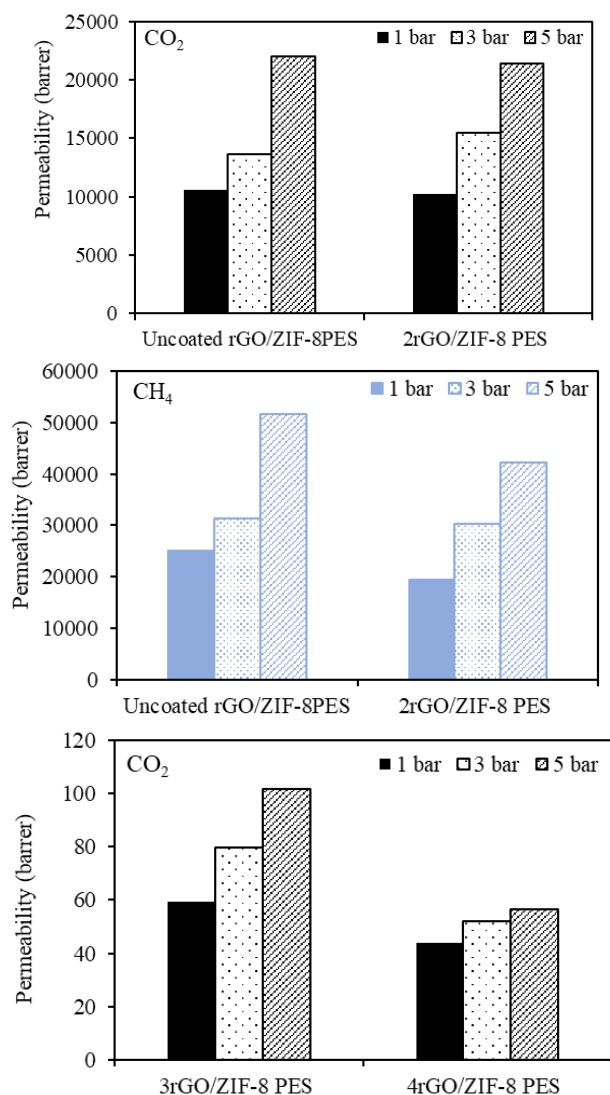
**Figure 8** CO<sub>2</sub> and CH<sub>4</sub> permeability of uncoated PES and 2, 3, 4 wt.% PEBA coated PES membranes



**Figure 9** SEM images of uncoated PES and 2, 3, 4 wt.% PEBA coated PES membranes

Figure 10 and Table 4 shows the effect of surface coating on the rGO/ZIF-8 MMMs performance with respect to gas permeation and selectivity. It can be observed that generally the addition of 10 wt.% rGO/ZIF-8 nanofillers resulted in increased permeability up to 5 folds. This is because the incorporation of nanofiller introduces more free volume, enhances the flexibility of membrane, creates more diffusion for gas penetrants and hence improves the diffusivity of gases through the membrane [36]. Mahdavi *et al.* [37] show the formation of non-selective voids from polymer-filler interaction can significantly increases the permeability but at the same time, decreased in selectivity especially when the void size form inside the membrane is larger than the permeate gas molecules [38,39]. However, our findings are opposite as

compared to his work, in which the gas permeability and selectivity increased simultaneously upon addition of rGO/ZIF-8 nanofillers. One of the reasons is due to the properties of rGO/ZIF-8 nanofillers itself where the CO<sub>2</sub> saturation capacities are higher due to synergistic effect rGO and ZIF-8 crystals. In the rGO/ZIF-8 hybrid, the dispersive interactions are enhanced due to the presence of distorted rGO sheets, while the ZIF-8 ensure the porosity of the nanofillers and permit the gas interactions with the metallic sites and functional groups on the organic linker [40]. These sites facilitate the reactive adsorption leading to enhanced CO<sub>2</sub> adsorption capacities.



**Figure 10** CO<sub>2</sub> and CH<sub>4</sub> permeability of uncoated rGO/ZIF-8 PES and 2, 3, 4 wt.% PEBAX coated PES MMMs

It was also observed that the CO<sub>2</sub>/CH<sub>4</sub> selectivity improves significantly from 0.4 up to 38.45 when the concentration of PEBAX increases. This is because the rubbery PEO block in PEBAX is known to have greater affinity towards polar gas (CO<sub>2</sub>) compared to non-polar gas (CH<sub>4</sub>) and this contributed to greater CO<sub>2</sub> permeability and CO<sub>2</sub> selectivity [41]. Besides, the PEBAX also could cover all the defects and pores on the PES MMMs surface that might be caused by rGO/ZIF-8 nanofillers, thus, improves the membrane selectivity. The result for CO<sub>2</sub>/CH<sub>4</sub> in this work was on a par with the recent study on MMMs PEBAX coating for CO<sub>2</sub>/CH<sub>4</sub> separation.

**Table 4** Selectivity of uncoated rGO/ZIF-8 PES and 2, 3, 4 wt.% PEBAX coated PES MMMs

Samples	CO <sub>2</sub> /CH <sub>4</sub> Selectivity		
	1 bar	3 bar	5 bar
Uncoated rGO/ZIF-8 PES	0.42	0.44	0.43
2rGO/ZIF-8 PES	0.53	0.51	0.51
3rGO/ZIF-8 PES	30.00	33.54	37.14
4rGO/ZIF-8 PES	36.00	38.42	38.45

Table 5 compares the performances of the membranes prepared in this work with other MMMs. It was observed that the CO<sub>2</sub>/CH<sub>4</sub> separation is higher due to synergistic effects of rGO and ZIF-8, allowing pore structure control without blocking the pathways for gas to diffuse across the membrane.

**Table 5** Comparison of CO<sub>2</sub>/CH<sub>4</sub> separation performance

Membranes	Test condition	CO <sub>2</sub> /CH <sub>4</sub>	Ref
3wt%Pebax/ImGO	4 bar, 25 °C	25.1	[42]
4wt%ZIF-8/PEBAX/PES	2 bar, 30 °C	14.5	[43]
4rGO/ZIF-8 PES	5 bar	38.45	This work



## 4.0 CONCLUSION

In this study, the effects of 10 wt.% of rGO/ZIF-8 nanofillers incorporation into PES membranes and the effects of PEBAX coating were studied and compared with bare PES membranes. It was found that incorporation of rGO/ZIF-8 nanofillers increases the permeability of CO<sub>2</sub> and CH<sub>4</sub> gas. However, the selectivity for this type of membrane was poor. Therefore, PEBAX was added as selective layer on the surface of PES membrane. The effects of surface coating concentration on PES and rGO/ZIF-8 MMMs performance with respect to gas permeation and selectivity was investigated. Results showed that the rGO/ZIF-8 MMMs performed better separation as compared to PES membranes. The MMMs coated with 3 and 4 wt.% of PEBAX exhibited excellent gas permeability and CO<sub>2</sub>/CH<sub>4</sub> selectivity (up to 38.45) in comparison to the uncoated- (0.43) and 2 wt.% coated- (0.51) MMMs. From the morphology analysis, it can be concluded that 2 wt.% of PEBAX is not effective to form homogenous and good integrity of coating layers on PES membrane, thus explain the low selectivity of CO<sub>2</sub>/CH<sub>4</sub>.

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