Effect of Pebax coating on Gas Separation Properties of rGO-ZIF-8 PES MMMs

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Abstract- Mixed matrix membranes (MMMs) attract great attention due to their outstanding gas separation performance. The compatibility between the fillers and the polymer matrix is one of the key points for the preparation of high-performance MMM. In this study, MMMs consisting of 10 wt% in-situ synthesized rGO/ZIF-8 hybrid nanofillers were fabricated for gas separation. Pebax-1657 at 2, 3 and 4 wt% concentration was added as coating layer to study the effect of different concentration pebax on the permeability and selectivity of rGO-ZIF-8 PES MMMs. The pebax solution was prepared by dissolving it in a dilute ethyl alcohol in ratio of 70:30. The operating pressure of gas permeation varied from 1 bar to 5 bar. It was found that the permeation rate increase with higher pressure and decrease with increase coating time and concentration of pebax. Based on the result of 3%PEBAX/rGO-ZIF-8 PES MMMs, permeability of CO₂, CH₄, N₂, and O₂ gas shows 19%, 93% 86% and 79% decrease, in permeation rate for each gas respectively and the selectivity increase from 1.76 to 10.19 when compare to 3%PEBAX/PES. The XRD, FTIR TGA and BET analysis was done for the synthesized nanofillers and fabricated PES MMMs membrane of coated and uncoated. The 3%PEBAX/rGO-ZIF-8 PES gave the highest selectivity of 10.19, 3 bar with CO₂ and N₂ permeance of 79.68 and 7.82 respectively whereas for CO₂ no gas flow was recorded during the test.

Keywords — CO₂ selective membrane, Polymer/Zeolitic imidazolate framework composite membrane, rGO, ZIF-8, Pebax,

I. INTRODUCTION

Methane, a key component in natural gas composition contributing to 75% of natural gas, these energy resources comes primarily from natural gas and associated gas in oil reservoir. These natural gas reservoirs and associated gas derived from oil reservoir naturally contain numerous impurities in which needed gas separation process to produce a purified natural gas. The impurities include CO₂, H₂S, and N₂ gas. The conventional method for gas separation technique includes the pressure swing adsorption technique and cryogenic distillation. Both pressure swing and cryogenic distillation method typically used for very large operation which needed a high operating cost. Therefore, they switch to alternative method by using membrane for gas separation. The membrane gas separation has gained wide attention due to its simple fabrication and easy to operate. Hence reduce in the operating and maintenance costs. The membranes also exhibit excellence efficiency in gas separation as it can separate gas molecule at specific size of molecule particle [1]. There are three (3) types of membranes used in gas separation which are polymer [2], inorganic [2] and mixed matrix membranes (MMMs) [2]. MMMs consist of polymer as the continuous phase and inorganic filler as the dispersed phase. The combination between both component were supposed to overcome the Robeson upper bound [3] trade-off limits. The inorganic filler that is widely used in MMMs fabrication are zeolites [2], carbon nanotubes (CNT) [4], metal organic framework (MOF) [5] and graphene [6].

MOF have been used as nanofillers as its provide a good interaction with polymer matrix through its organic linkers [7], [8]. Zeolitic imidazole framework (ZIF-8), which is a subclass of MOF, exhibit excellent capacity for gas separations and this was proven by the study of Q. Song et al [9]. In his study, ZIF-8 with loadings up to 30 wt% shows a good adhesion within the polymer matrix, however, the pure gas (H₂, CO₂, O₂, N₂ and CH₄) permeation tests showed a very high permeability with low selectivity. This is due to an increase in the free volume caused by addition high ZIF-8 loading together with the free diffusion of gas through the cages of ZIF-8.

Reduced graphene oxide were 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, reduced graphene oxide (rGO) shows prominent use as hybrid nanofillers selection to ZIF-8 due to its inert properties which prevent diffusion of gasses bigger than helium gas. It also due to its aromatic ring electron density that repel all matter that trying to penetrate this graphene sheet [10]. The synergistic effect between both rGO and ZIF-8 nanofillers had been shown in the study of Gege et al. [11], where in electrochemical sensing field, they help to fasten the rate of mass transfer and contribute to high conductivity of the filler. These excellent properties of rGO/ZIF-8 nanofiller prompt them to be a candidate of modified material in MMMs for gas separation application.

M. Shafiq et al [12] shows that coating using pebax helps to improve the selectivity of MMMs and decrease the permeability of the membrane. The addition of coated layer believed to act as a selective layer for the separation process by withstand the gas pressure during transmittance of gas, the hard segment of polyamide provide a strong mechanical strength to the copolymer while the soft segment of polyether act as a transport channel for the separation process [12]. The coating process uses the dip-coating method which implement a wet layer upon a porous support by smear the dry support surface with a particle dispersed suspension or solution followed by a sintering process. Repeated coating-sintering process will cause the reduction of the membrane permeation properties [2].

In this work, the effect of different concentration of pebax (2, 3 and 4 wt%) was introduced as a coating layer to PES substrate. The addition of coated layer on top of PES MMMs and 10%rGO-ZIF-8 PES MMMs was believed to act as selective layer for the separation process. The PES membrane and 10%rGO-ZIF-8 PES MMMs both coated and uncoated was then test with single gas permeation at 1, 3 and 5 bar to investigate the permeability and selectivity of CO₂, N₂

and CH₄. The chemical structure and thermal stability of the membranes were confirmed X-ray diffraction (XRD) analysis, Fourirer transform infrared spectroscopy (FTIR) analysis and thermogravimetric analysis (TGA). The corresponding separation mechanism of rGO-ZIF-8 nanofillers in MMMs for the gas separation was also discussed.

II. METHODOLOGY

A. Chemicals and Materials

Graphite powder (Mw = 12.01g/mol) was purchased from Merck. Potassium permanganate (KMnO4, Mw = 158.05 g/mol), sulphuric acid (H₂SO4, 95-98%) and sodium nitrate (NaNO₃, 98%) were purchased from R&M Chemicals. L-ascorbic acid (C₆H₈O₆) purchased from SYSTERMS. Hydrogen peroxide (H₂O₂) was purchased from MERCK. Hydrochloric acid (HCl) and methanol (MeOH) from MERCK and SYSTERMS respectively. Zinc nitrate hexahydrate (Zn(NO₂)₃.6H₂O, Mw = 297.49 g/mol) and 2methylimidazole (H-MeIM, Mw = 82.10g/mol) were purchased from Sigma-Aldrich. PES powder (MW = 22,000 g/mol) was from Veradel. N-Methyl-2-pyrrolidone (NMP, 85% C₅H₉NO) was purchased from Merck (Germany). Polyether Block Amide, pebax pellet from ARKEMA and ethanol (95% concentration) was purchased from SYSTERM.

B. Synthesis of rGO-ZIF-8 nanofiller

The graphene oxide (GO) was prepared from graphite powder by using the modified Hummer's method [6]. In brief, 10 g of graphite powder along with 5 g of NaNO3 were mixed with 400 ml of H₂SO4 in a 2000 ml beaker. The solutions in the beaker were kept in an ice bath at temperature below 15°C. The mixture was stirred for an hour using magnetic stirrer at 350 rpm. 60 g of Potassium Permanganate (KMnO₄) was added portion-wise, and the mixture was further stirred for 1 hour at a temperature below 15°C. Then, the mixture was continuously being stirred for another 2 hours while maintaining the temperature below 15°C. The ice bath was removed and the mixture was continuously being stirred for another 22 hours at room temperature. Then, the temperature was increased and maintained at 70 °C for 1 hour while slowly added 100 ml of distilled water into the mixture. The temperature was then increase to 90 °C and continuously being stirred for another 1 hour while slowly added another 100 ml of distilled water. Next, 60 ml of hydrogen peroxide (H₂O₂) was added into the mixture in order to stop the reaction and the solution is constantly stirred for 1 hour. The solution was then left overnight. Afterward the suspension was washed 2 times with diluted HCl (160 ml:1840 ml) and 2 times with distilled water. The mixture afterward was then centrifuged at 15°C temperature with speed of 10,000 rpm for 25 minutes. The producing supernatant was filtered and check for pH value. Afterward, distilled water was and centrifuged again at with speed of 10,000 rpm for 15 minutes. The produced solid precipitate was then washed with acetone. GO was obtained as brownish powder after drying in an oven at $60^{\circ}\text{C} - 70^{\circ}\text{C}$ temperature for 24 hours. After drying, the GO powder was then milled to obtain a fine powder.

The reduction of GO into rGO was conducted by using chemical method. Briefly, 1.5 g of GO powder was dispersed in 500 ml distilled water inside a 600 ml beaker to form 1.5 g/600 ml of graphene oxide suspension. The mixture was sonicated at 150 W for 2 hours until solution become clear with no visible particulate matter. 15 g of l-ascorbic acid was added into the resulting graphene mixture under continuous stirring for 30 minutes. 25 ml of NH₄OH solution was added until the mixture reached alkalinity of 9-10 pH reading and continuously stirred for another 30 minutes. The mixture was heated to 95°C under vigorous stirring for 2 hours. The product obtained was then isolated using vacuum filter and washed repeatedly using distilled water. The produce rGO was dried in an oven for 24 hours at $60^{\circ}C - 70^{\circ}C$. Afterward the rGO are milled to

a powdery form.

The procedure to synthesize the rGO-ZIF-8 hybrid using zinc nitrate hexahydrate, reduce graphene oxide and 2-methyl imidazole with the use of methanol as a solvent. [6], [13]–[15]. A 70 mg of rGO were added into one-day aged mother liquor (ML) and stirred for 30 min. The solution was then sonicated for 1 hour at 60° C. 1.3g of NaOH was added and the solution quickly turns into greyish color. The solution was stirred for 4 hours at 60° C and left at room temperature for 12 hours before being vacuum filtered and washed several times with acetone and distilled water (DW). The filtered products rGO-ZIF-8 was dried for 12 hours at 100°C.

C. Membrane Preparation

The fabrication of the rGO-ZIF-8 PES MMMs utilizes the process of phase inversion method [6], [16]. Dope solution was prepared by blending 80 wt% of NMP solvent. 2 wt% of rGO-ZIF-8 powder by slowly added into the solution at room temperature until solution become completely homogenized and left to stir overnight. Next the 18 wt% of PES that was previously dried were slowly added into the solution at room temperature until solution become completely homogenized and left to stir overnight. The dope solution was sent to be sonicated and degas using Elma 5180H Ultrasonic machine for 1 hour prior to casting. The synthesized casting solution was cast over the glass plate and in which it was being layered gently using casting knife at the gap of $130 \,\mu\text{m} - 200$ µm. The fabricated membrane sheet was immediately immersed into a coagulation bath that constitute of distilled water for 24 hours then afterward transfer into another coagulation bath for 1 hours to remove any residual solvent. The rGO-ZIF-8 PES membranes was rinse with distilled water and dried at room temperature for 24 hours until dry membrane sheet was obtained. The process is repeated for PES Bare membrane by not adding the rGO-ZIF-8 powder.

Table 1: Sample composition

Samples	PES (wt%)	rGO-ZIF-8 (wt%)	NMP (wt%)
Bare PES	20	0	80
10 rGO-ZIF-8 PES	18	2	80

To prepare a 2 wt% solution of pebax, the pebax pellet are first dried in the oven at 60°C and left overnight to remove moisture. 2 g of overnight dried pebax pellets were dissolved in a mixture of 70 wt% ethanol and 30 wt% of water under reflux at 70 °C for 2 hours until a homogenous clear and diluted solution was obtained. The 2 wt% of pebax solution was then sonicated for 1-hour prior coating on the surface of PES MMMs. The dip-coating method was used for coating preparation where 3 ml of 2 wt% pebax solution are poured inside a petri dish. The membrane was then dip one side for 30 sec. Pebax was coated on the PES bare and rGO-ZIF-8-PES substrate at 2, 3 and 4 wt% as in Table 2 where every coating the membrane was dried at 60°C for 2 hours to let the solvent vaporize. The procedure was then repeated for 3 and 4 wt% of pebax concentration.

Table 2: Pebax concentration for each sample.

Samples	Pebax concentration
Bare PES	2, 3 and 4 wt%
10 rGO-ZIF-8 PES	2, 3 and 4 wt%

D. Characterization of nanofillers and membrane properties

XRD

The crystalline properties of nanofillers and membranes was determined by using X-ray diffraction, (X'pert PRO) at room temperature. GO, rGO, rGO-ZIF-8, PES bare, PEBAX/PES, and rGO-ZIF-8 PES was analyzed by using 20 range from 5-80 degree.

The voltage used was set at 40 kV and 40 mA.

TGA

The thermal stability of all the samples were investigated using thermogravimetric analysis (TGA) by a Mettler Toledo Analyzer. The analysis was conducted from room temperature up to 800 ^oC under nitrogen condition. The mass of the samples is monitored during the cooling and heating process in a furnace in this analyser

BET

Nitrogen adsorption-desorption isotherm and surface area properties of the samples are determined by using the Brunauer Emmet Teller (BET) Surface Area and Porosity Analyzer (Micromeritics, ASAP 2020). The characterization is based on nitrogen N₂ adsorption and desorption isotherm. The samples first are degasses for 8 hours of holding time at 300 $^{\circ}$ C with the ramping rate is 10 $^{\circ}$ C/min.

FTIR

Perkin Elmer Fourier Transform Infrared (FTIR) Spectroscopy was used to examine the surface functional group of the membranes selective layer which incorporated with either pebax coated or rGO-ZIF-8 PES Based MMMs.

E. Gas transport performances measurement

The pure gas permeabilities were determined by a constant volume and variable pressure method using a 316 stainless steel gas permeation cell, designed in-house with an effective area of 22.9 cm2. Four gases (purity of 99.999%) having various kinetic diameters, CO₂ (3.30 Å), CH₄ (3.80 Å), N₂ (3.64 Å) and O2 (3.46 Å) were used during this study. All the gases were used without further purification. In each experiments, the prepared membranes were cut into desired circular shape. The gas permeabilities were determined from the flow rate of the permeating gas as well as permeability and selectivity of the membrane.



Fig 1. Schematic diagram for permeation using flat sheet membrane module.

Each membrane sample was tested for its gas permeate volumetric flowrate for 3 times and the gas permeability was then calculated using the following equation [6], [17]:

$$Permeability = \frac{QxL}{A \times \Delta P}$$
(1)

where L is the membrane thickness(m), Q is the permeate volumetric flowrate (mol/s), ΔP is the pressure difference and A is the area.

The selectivity equation was determined by using the following equation [6]:

$$Gas Selectivity = \frac{Pi}{Pj}$$
(2)

where the Pi permeability of component i while Pj permeability of component j.

III. RESULTS AND DISCUSSION

A. Nanofiller synthesis

XRD

XRD analysis was carried out to identified the crystal structures of the nanofillers and membranes prepared in this work. From Fig 1, it can be seen that rGO exhibit a broad peak at diffraction angle (2Θ) of 25.05. The result consistent with the previous study done by Najihah et al [6] which indicates an amorphous structure that presence due to multilayer domains. The ZIF-8 and rGO-ZIF-8 shows a crystalline diffraction peaks which consistent with the result obtain by K. Daeok et al [18], Surendar et al [13] and Najihah et al [6].



Fig. 2: XRD results of rGO, ZIF-8, rGO-ZIF-8

The XRD spectra of PES membrane shows primarily amorphous and shows singular broad peak at 2O at 18° which is similar to the reported peak for pure PES [19]. The PES membrane with added rGO-ZIF-8 and PES membrane coated with pebax also shows no other characteristic peaks when compared to XRD characteristic of rGO-ZIF-8 and PEBAX [6], [18], [20].



Fig. 3: XRD results of PES, rGO-ZIF-8 PES MMMs and PEBAX/PES

FTIR

The FTIR of rGO shows peaks at 1750 cm-1 (C=O) and 1584 cm-1 (C=C). ZIF-8 peak at 2980 cm-1 (C-H), 1583 cm-1 (C=N), 1180 cm-1 (C-H) 750 cm-1 (Zn-O) and 700 cm-1 (Zn-N). The rGO-ZIF-8 shows peak at 2980 cm-1 (C-H), 1584 cm-1 (C=C), 1583 cm-1 (C=N), 1180 cm-1 (C-H) 750 cm-1 (Zn-O) and 700 cm-1 (Zn-N).



Fig. 4: FTIR results of ZIF-8, rGO and rGO-ZIF-8

The PES bare membrane shows peak at 1578 cm⁻¹, 1486.73 cm⁻¹, 1298.90 cm⁻¹, 1240 cm⁻¹, 1152 cm⁻¹, 1107 cm⁻¹, 872 cm⁻¹, 719 cm⁻¹ and 555.32 cm⁻¹. 2,3, and 4% PEBAX/PES shows peaks at 1094, 1731, and 2867 cm⁻¹ are the stretching vibrations of C-O, C=O, and –CH3 respectively. 1637, and 3298 cm⁻¹ were the H-N-C=O and N-H respectively. [20]. The pebax coated membrane shows similar FTIR pattern which were conducted by Bai et al [20].



Fig. 5: FTIR results of PES bare, 2, 3, and 4%PEBAX/PES

The rGO-ZIF-8 PES membrane shows broad peak at 3265 cm⁻¹ and peak 1637 cm⁻¹, 1578 cm⁻¹, 1486 cm⁻¹, 1240 cm⁻¹, 1150 cm⁻¹, 1105 cm⁻¹, 872 cm⁻¹, 719 cm⁻¹ and 555.32 cm⁻¹. 2,3 and 4% PEBAX/rGO-ZIF-8 PES shows similar peaks at 1101, 1732, and 2868 cm⁻¹ are the stretching vibrations of C-O, C=O, and –CH₃ respectively. 1637, and 3298 cm⁻¹ were the H-N-C=O and N-H respectively. The pebax coated membrane shows similar pattern to pebax membrane FTIR result conducted by Bai et al [20].



Fig. 6: FTIR results of rGO-ZIF-8 PES, 2, 3, and 4%PEBAX/rGO-ZIF-8 PES

The thermal stability of rGO, ZIF-8 and rGO-ZIF-8 were shown in Fig 6. It shows that constant decrease in mass loss from 100 to 73% at 800°C. ZIF-8 shows lower mass loss from 0 to 620 by 14% mass loss but increase significantly after 620°C. The rGO-ZIF-8 shows better thermal stability than ZIF-8 with similar pattern in mass loss at 12% which include significant decrease in mass loss at 604°C.



Fig. 7: TGA results of ZIF-8, rGO and rGO-ZIF-8

The thermal stability of PES bare and rGO-ZIF-8 PES membrane were shown in Fig 7. It shows that minor decrease in mass loss from 100 to 96% at 475°C and 97% at 454°C respectively. Both shows sudden mass loss after 475 and 454 to 57% and 58% respectively.



Fig. 8: TGA results of ZIF-8, rGO and rGO-ZIF-8

BET

The surface area for rGO-ZIF-8 are $986 \text{ m}^2/\text{g}$ and pore volume of 0.324 cm3/g was found to be higher compared to Najihah et al [6] result.



Fig. 9: BET for rGO-ZIF-8

B. Effects of different concentration and coating time of pebax on membrane separation performance.

Based on the figure 14 obtained, it shows that sample which coated with 30 sec durations and 2%PEBAX/PES shows insignificant change hence prove that the coating is inadequate to provide a considerable effect from the coating towards the permeation of the membrane. This prove by comparing the sample of PES bare membrane with 30 sec coating time and 2%PEBAX/PES with the similar concentration with 60 sec coating duration time permeability.

Gas Permeation



Fig. 10: Permeation Test Result of PES bare - 60 sec



Fig. 11: Permeation Test Result of 2%PEBAX/PES - 60 sec



Fig. 12: Permeation Test Result of 3%PEBAX/PES - 60 sec



Fig. 13: Permeation Test Result of 4%PEBAX/PES - 60 sec



Fig. 14: Permeation Test Result of 2%PEBAX/PES - 30 sec



Fig. 15: Permeation Test Result of 3%PEBAX/PES - 30 sec



Fig. 16: Permeation Test Result of 4%PEBAX/PES – 30 sec



Fig. 17: Permeation Test Result of rGO-ZIF-8 PES



Fig. 18: Permeation Test Result of 2%PEBAX/rGO-ZIF-8 PES - 30 sec



Fig. 19: Permeation Test Result of 3%PEBAX/rGO-ZIF-8 PES - 30 sec



Fig. 20: Permeation Test Result of 4%PEBAX/rZ8 PES - 30 sec

C. Effect of rGO-ZIF-8 nanofiller on PES membrane separation properties

ZIF-8 possesses large cavities without any polar functional groups that can selectively adsorb CO2, so it is very difficult for ZIF-8 to increase the CO₂/CH₄ selectivity for polymeric membranes, which already have decent selectivity. Furthermore, a high loading of filler often lowers a membrane's mechanical stability and there by limits its practical applications. Based on these results, it is hypothesized that rGO could serve as the secondary filler, which would enable the drawbacks of ZIF-8 filler, such as its poor CO2/CH4 selectivity and negative effects on the membrane's mechanical strength, to be overcome. When ZIF-8 was added, the permeability of the membrane increased, due to increase in chain mobility and free volume [Metal-organic framework-reduced graphene oxide composites: a facile method to highly improve the CO₂ separation performance of mixed matrix membranes]. The CO₂ permeability of ZIF-8 PES was higher than other membranes because ZIF-8 possesses a larger BET surface area and micropore volume, as well as higher affinity and adsorption capacity for CO2 due to interaction between quadrapole CO2 molecules and the positive charges of the unsaturated metal sites.

This observation confirmed the incorporation of ZIF-8 created extra microvoids within the mixed matrix membrane, possibly due to the distortion of the original well-packed polymer chain structure [21]. Improved operational stability of pebax-based gas separation membranes with ZIF-8. A comparative study of flat sheet and composite hollow fibre membranes. Specifically, for the pure pebax benchmark the CO₂ permeability was much higher than the other tested gases, which could be attributed to the rubbery PEO block in pebax having a strong affinity to the polar gas (CO₂) over the non-polar gases (N₂, O₂ and CH₄).

By comparing PES bear with rGO-ZIF-8 PES MMMs based on type of gas and pressure used using the equation [22],

$$Percentege \ different = \frac{|P_2 - P_1|}{P_1} X100 \tag{3}$$

the effect of the nanofiller on the separation properties of the membrane can be measured. The result show increase in permeability of all gas in which N_2 gas shows the most significant increase, but a reduction in permeability toward O_2 gas.

Table 4: Comparison between PES bare and 10 rGO-ZIF-8 PES MMMs permeability.

initial per incubinity.				
Pressure,	CO ₂	CH ₄	N_2	O ₂
Bar				
1	189	373	673	73
3	162	307	542	71
5	233	451	393	65

This shows that the nanofiller increases the permeability for CO₂, CH_4 and N_2 , in which it increases the permeability of N_2 significantly ranging from 393 to 673% depending on the pressure which lower pressure have greater effect. The methane shows percentage difference from 307 to 451% and CO₂ range from 162 to 233%. While O₂ shows decrease in permeability ranging from -65 to - 73%. Interestingly, different behavior was observed for rGO-ZIF-8 PES where momentous increased in the CO₂ permeance (35%) while the CO₂/CH₄ selectivity remains unchanged. Using rGO-ZIF-8 as filler tends to increase the CO2 permeance while PEBAX/rGO-ZIF-8 promotes more selective membrane while sacrificing its permeance. This research show that the modification approach of ZIF-8 is crucial in resulting either more permeable and/or more selective membrane. This is likely contributed by the porosity of rGO-ZIF-8 that provides permeation channels for all gases that overwhelm the slight membrane rigidification [23].

D. Effect of pebax coating on different type of membrane

Using the same method that uses equation 1, the effect of pebax coating on separation properties of PES and rGO-ZIF-8 PES MMMs are shown at the table below.

Table 5: Comparison between 2%PEBAX/PES and 2%PEBAX/rGO-71E 8 PES permeability

ZIT-6 TES per incability.				
Pressure,	CO ₂	CH_4	N_2	O_2
Bar				
1	197	193	255	289
3	437	493	503	383
5	151	748	705	577

Table 6: Comparison between 3%PEBAX/PES and 3%PEBAX/rGO-ZIF-8 PES MMMs permeability.

Pressure,	CO ₂	CH4	N_2	O ₂
Bar				
1	-	-	-	-
3	19	93	86	79
5	65	90	85	81

Table 7: Comparison between 4%PEBAX/PES and 4%PEBAX/rGO-ZIF-8 PES MMMs permeability.

Pressure, Bar	CO ₂	CH4	N ₂	O2
1	-	-	-	-
3	39	99	88	64
5	71	96	91	71

Based on the table above, the effect of pebax coating on PES coated membrane compared to rGO-ZIF-8 PES MMMs shows overall decrease in for all gases except for 2%PEBAX/rGO-ZIF-8 PES MMMs which shows increasing permeability for all the gases. However, from comparing previous figure 11 and 14 it shows that the coating time and concentration were inadequate hence reflected on the figure 18. The figure 19 and 20 shows that for pressure 1 bar for 3 and 4%PEBAX/rGO-ZIF-8 PES were unobtainable due to no gas flow which similar to previous study by Wahab et al [12].

E. Membrane Selectivity

The CO₂/N₂ gas selectivity of 3 and 4% PEBAX/rGO-ZIF-8 PES shows 10 and 6.7 selectivity respectively and shows no gas flow for CH4. PEBAX/PES membranes shows CO₂/Methane selectivity that show value of 0.5 to 3, and similar range for CO₂/Nitrogen. The gas selectivity for PEBAX/rGO-ZIF-8 PES shows higher selectivity with adequate coating of the pebax in which show by the 3 and 4% PEBAX/rGO-ZIF-8 PES MMMs while uncoated and 2% PEBAX/rGO-ZIF-8 PES show lower gas selectivity.



Fig. 21: Gas selectivity based on permeation test result of PES bare, 2, 3 and 4%PEBAX/PES membrane CO₂/Methane selectivity



Fig. 22: Gas selectivity based on permeation test result of PES bare, 2, 3 and 4%PEBAX/PES membrane CO₂/Nitrogen selectivity



Fig. 23: Gas selectivity based on permeation test result of rGO-ZIF-8 PES and 2%PEBAX/rGO-ZIF-8 PES CO₂/Methane selectivity



Fig. 24: Gas selectivity based on permeation test result of rGO-ZIF-8 PES and 2, 3, and 4%PEBAX/rGO-ZIF-8 PES CO₂/Nitrogen selectivity

IV. CONCLUSION

It shows that 30 second and 3 percent concentration are the minimum amount of duration and concentration respectively needed to achieve a profound effect of pebax coating on the gas separation properties of the membrane. The pebax solution with concentration of 2 wt%, 3 wt% and 4 wt% are dissolve using a diluted ethyl alcohol n ratio of 70:30.

A systematic study also conducts to differentiate the effect of different concentration of pebax coating on different membrane and its effect toward different type of gas permeability at different pressure setting. The permeation rate increase with higher pressure and decrease with increase coating time and concentration of pebax. However, for pebax coated membrane, CO₂ shows increase in permeation rate with increasing pressure and smaller decrease in permeation rate compare to other gases hence increase it selectivity

towards CO2 gas.

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