

POLYMERIC MIXED MATRIX MEMBRANES INCORPORATED WITH GRAPHENE OXIDE FOR H₂/CO₂ SEPARATION

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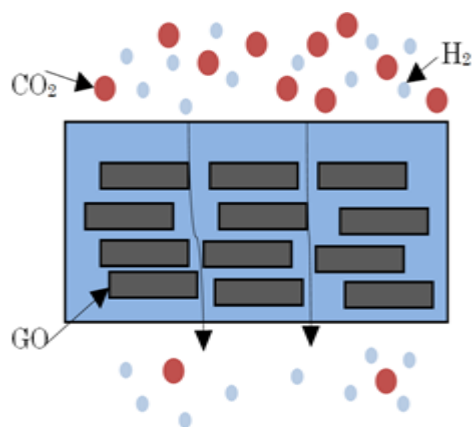
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Graphical abstract



Abstract

Biohydrogen is a potential alternative for fossil fuels and it can be produced from POME fermentation. Membrane technology has been a prominent separation approach for H₂ purification. However, membranes yield weakness in tradeoff between permeability and selectivity. The main objective of this project is to develop mixed matrix membrane with different polymeric bases of Polysulfone (PSF) and Polyimide (PI) with graphene oxide (GO) incorporation as inorganic filler for H₂/CO₂ separation. Gas permeability and selectivity results indicated that PI/GO membrane with 1 wt% of GO has the highest H₂ and CO₂ permeability at 501 GPU and 595 GPU at 1 bar, respectively, H₂/CO₂ selectivity of 1.01 at 5 bar and highest H₂ purity of 83 %. FESEM analysis indicated changes in the pore size and top layer of membranes due to the presence of GO. Zeta potential analysis proved that PI/GO 1wt% membranes is highly negative-charged (-56 mV). Contact angle results showed a decrease in contact angle value with the addition of GO. It can be concluded that PI/GO 1 wt% membranes demonstrated better results in the aspects of permselectivity and physicochemical properties compared to PSF membranes.

Keywords: POME, biohydrogen, MMMs, graphene oxide, gas separation

Abstrak

Biohidrogen merupakan satu alternatif yang berpotensi untuk bahan api fosil dan ia dapat dihasilkan daripada penapaian POME. Teknologi membran merupakan teknologi pemisahan yang terkenal untuk penulenan H₂. Namun, membran mempunyai kelemahan dalam penukaran antara kebolehtelapan dan pemilihan. Objektif utama kajian ini adalah untuk membentuk membran matriks bercampur yang berasaskan polimer polisulfona (PSF) dan polimida (PI) dengan penambahan grafin oksida (GO) sebagai pengisi bukan organik untuk pemisahan H₂/CO₂. Keputusan analisis kebolehtelapan dan pemilihan gas membuktikan bahawa membran PI/GO dengan 1 wt% GO mempunyai prestasi tertinggi dengan ketelapan H₂ dan CO₂ pada 501 GPU dan 595 GPU pada 1 bar, pemilihan H₂/CO₂ pada 1.01 pada 5 bar dan ketulenan H₂ yang tertinggi iaitu 83 %. Analisis FESEM telah menunjukkan perubahan saiz liang dan lapisan atas membran dengan kehadiran GO. Analisis keupayaan zeta menunjukkan membran PI/GO 1wt% adalah bersifat caj negatif yang tinggi (-56 mV). Keputusan sudut sentuhan juga menunjukkan penurunan nilai sudut sentuhan dengan penambahan GO. Ia dapat disimpulkan bahawa membran

PI/GO 1wt% menunjukkan keputusan yang lebih baik dalam aspek kepilihan dan sifat fisikokimia berbanding dengan membran PSF.

Keywords: POME, biohidrogen, MMMs, grafin oksida, pemisahan gas

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1.0 INTRODUCTION

We use energy sources in our daily lives. Extreme use of these energy sources like fossil fuel cause environmental pollutions. For this reason, it is necessary to find an alternative clean fuel such as hydrogen which is known to be environmental friendly. One of the main resources to produce hydrogen is through anaerobic fermentation of Palm Oil Mill Effluent (POME), in which hydrogen is produced along with carbon-dioxide as the final products. It is important to purify hydrogen in order for it to be used as fuel. Separation of hydrogen from impurities like carbon dioxide has been done using different technologies such as pressure and temperature swing adsorption, and cryogenic distillation which is known to be an expensive energy intensive process. Membrane technology is also a well-known technique due to its ease of operation and simplicity.

Polymeric membranes are known to be the most popular kinds of membrane used in gas separation industry because of their excellent basic transport properties, high ability of process, and their low cost [1]. A good polymeric membrane should have both high selectivity and permeability. However, membrane can only achieve either high selectivity or high permeability depending on the types of polymers. Other weaknesses of membrane include the properties of temperature resistance and mechanical strength [2-4]. Several studies have reported on the enhancement of membrane properties by introducing blend membranes or mixed matrix membranes (MMM) with the incorporation of inorganic fillers such as zeolite [5].

In this project, Polysulfone (PSF) has been selected as the basic polymer due to its rigid, strong, and transparent thermoplastic properties. It is one of the most used polymeric membrane materials for gas separation (such as stripping CO₂ from natural gas) due to its low cost, mechanical strength, thermal, and chemical stability [6]. However, high plasticization pressure is one of the major concerns for this polymer [7]. On the other hand, polyimide (PI) has been chosen for its excellent physical and chemical properties with good thermal stability and high glass transition temperature [8,9]. Another potential way to enhance membrane properties is through the incorporation of graphene oxide (GO) as inorganic filler. This is possible due to its good potential for easy membrane formation, solution-

processable casting, size controllable, possible pore engineering. Besides, it has excellent gas-barrier properties as polymer composites [10].

Hence, the main objective is to improve the performance of PSF and PI membranes in terms of permselectivity and physicochemical properties by adding graphene-oxide (GO) as inorganic filler in different concentrations, which is essential in the separation of H₂/CO₂ from the fermented gas mixture of POME.

2.0 METHODOLOGY

2.1 Materials

Polysulfone in granule form (PSF, Udel polysulfone P-1700) and polyimide in fibre form (P84 co-polyimide BTDA-TDI/MDI, co-polyimide of 3,3',4,4' benzophenone tetracarboxylic dianhydride and 80% methylphenylenediamine + 20% methylene diamine) were purchased from Goodfellow Cambridge Limited. The solvent used, 1-methyl-2-pyrrolidinone (NMP) was purchased from Merck KGaA. The properties of polymers and solvent are listed in Table 1. Graphene oxide (GO), prepared using Hummer's method as described in the study by Mahmoudi *et al.* [39] was supplied by the Membrane Lab, Universiti Kebangsaan Malaysia (UKM) [11].

Table 1 Properties of polymers and solvent

Properties	PSF	PI	NMP
Glass transition temperature(°C)	185	300	–
Density(g/cm ³)	1.24	1.2	1.033
Molecular weight(g/mol)	42.52	80,000	99.13

2.2 Synthesis of Polymeric Membranes

The basic polymeric membrane, PSF and PI, were prepared via phase inversion method with the polymer proportion of 18 wt% in 82 wt% of solvent. The solution was dissolved in NMP at 60 °C on a hot plate under continuous stirring (500 RPM) for 12 hours to obtain a homogeneous mixture. Next, the solution was degassed for 30 minutes in a sonicator. After degassing, the solution was casted at room temperature with a thickness of 200 micron. Then the casted membrane was put in a cold-water bath (18

°C) for one hour. Finally, it was rinsed with distilled water (25 °C) before it was kept at room temperature for 24 hours. In order to add GO into the polymeric solution in three different concentrations (0.1, 0.5, 1 wt%), it was first dissolved completely in NMP for a few hours, prior to addition polymeric solution under continuous stirring at 200 RPM for 12 hours at room temperature. A similar casting procedure was then performed as shown in Figure 1.

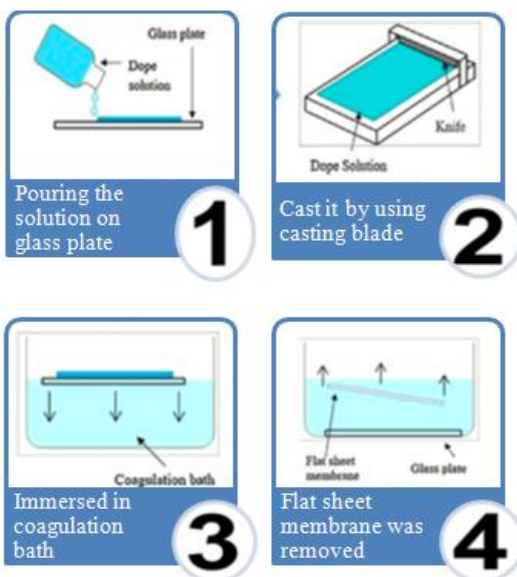


Figure 1 Membrane fabrication procedures

2.3 Characterizations

The resultant polymeric membrane and polymeric-GO membranes were characterised with the following characterisation analyses:

- FTIR (Fourier Transform Infrared Radiation): To identify the functional groups in the sample [12]. It was determined by using Nicolet 6700 FTIR-ATR (Thermo Scientific, USA), whereby each sample was cut in the measurement of 1cm×1cm and analysed in the wave number of 400-4000cm⁻¹.
- Contact Angle measurement: To determine the hydrophobicity/hydrophilicity of the samples [13]. It was measured using contact angle meter (Kruss GmbH, Germany) with Drop Shape Analysis software with accuracy of +/- 0.10°.
- Zeta potential analysis: To determine the surface charge of the membrane [14]. The zeta potential of membrane surface was measured in water at pH 7 using polystyrene latex particles as the tracer particles, with Malvern Surface Zeta Potential Cell (Malvern Instruments, UK) by applying field strength of 25 V/cm.
- Tensile Strength Test (Mechanical properties): To measure the mechanical strength of a material by providing the burden of the opposing forces in a straight line [15]. Each membrane sample was cut with the measurement of 25mm×75mm

and was put in the grips. It was analyzed using CT3-100 Texture Analyzer (Brookfield, USA), with the tension test trigger, deformation, and speed set at 0.5 g, 15 mm and 5mm/s, respectively. Membranes were dried and tested at ambient conditions.

- FESEM (Field Emission Scanning Electron Microscopy): To obtain the membrane surface and cross-sectional morphology [16]. It was carried out by using FESEM (Zeiss 55VP SUPRA, USA), in which the membranes samples were initially prepared by soaking in liquid nitrogen (N₂) to crack membranes' top and cross section.

2.4 Gas Performance Testing

a) Gas Permeance Study

Gas permeance was measured using an apparatus which consisted of a bubble flow meter and pressure gauge at the bottom of the cell. The gas separation performance was evaluated in terms of selectivity and permeability with pure compositions of CO₂ and H₂ at pressures from 1 to 5 bar. The gas permeation equipment is shown in Figure 2. Based on the study by Mohamad *et al.* [40] the gas inlet ratio for H₂/CO₂ was confirmed at equal proportion [17]. Hence, the specially-mixed gas consisted of 50 % of H₂ and 50 % CO₂ (supplied by NIG gases Sdn. Bhd.) was flowed into the gas permeation test unit, as a substitution of fermented gas from POME for further performance evaluation. The permeability and ideal H₂/CO₂ selectivity were calculated using Equations 1 to 3, respectively.

$$\frac{P_{CO_2}}{L} = \frac{1}{\Delta P} \quad (1)$$

$$\frac{P_{H_2}}{L} = \frac{1}{\Delta P} \quad (2)$$

$$\alpha = \frac{P_{H_2}/L}{P_{CO_2}/L} \quad (3)$$

Where:

J = flux

ΔP = pressure (KPa)

L = membrane thickness(μm)

P = permeability

α = selectivity

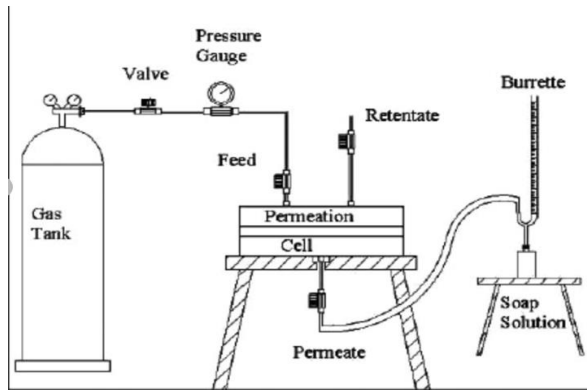


Figure 2 Gas permeation equipment schematic diagram

b) Gas composition study

Gas chromatography (GC) (SRI 8600C, USA) was used to analyze the gas composition, permeation, and retention after separation. The peak readings (retention time) for composition of H₂ and CO₂ were taken at 1.6 minutes and 10.5 minutes, respectively.

3.0 RESULTS AND DISCUSSION

3.1 FTIR Analysis

In Figure 3 (a) it can be seen that the peaks reflected the presence of respective functional groups in PSF. All these functional groups showed the existence of C-O bond (2968 cm⁻¹), O=S=O bond (1245 cm⁻¹), which is a functional group in PSF, while peaks of 1294 cm⁻¹ and 1151.4 cm⁻¹ were related to asymmetric and symmetric stretching vibrations which originated from C-O-C bond. The peaks between wave numbers of 2900 cm⁻¹ and 3100 cm⁻¹ were associated to aromatic groups and the stretching vibration of C-H bond. For pure PI membranes (see Figure 3 (b)), the symmetric and asymmetric stretching of the C=O group (imide groups) were observed at 1727.6 and 1780 cm⁻¹. The peak related to C=C stretching of the aromatic ring was observed at 1512 cm⁻¹. The band observed at 1164 cm⁻¹ was ascribed to the presence of C₆H₄. The peak due to aromatic ring bending vibrations was observed at 863 cm⁻¹. These results were in accordance with previous studies [18, 21, 22]. Furthermore, the addition of GO into PI, the peaks of O-H and C-O-C was observed at peaks of 1367.9 and 1105.5 cm⁻¹, respectively. It has been proven that, due to the existence of oxygenated functional groups in GO which includes carboxyl (C=O), hydroxyl (C-OH) and epoxy (C-O-C), the interaction between GO and polymer could be enhanced with improved hydrophilic [19, 20]. Observations on characteristic peaks of GO basically showed that by increasing GO concentration, the peaks also increase.

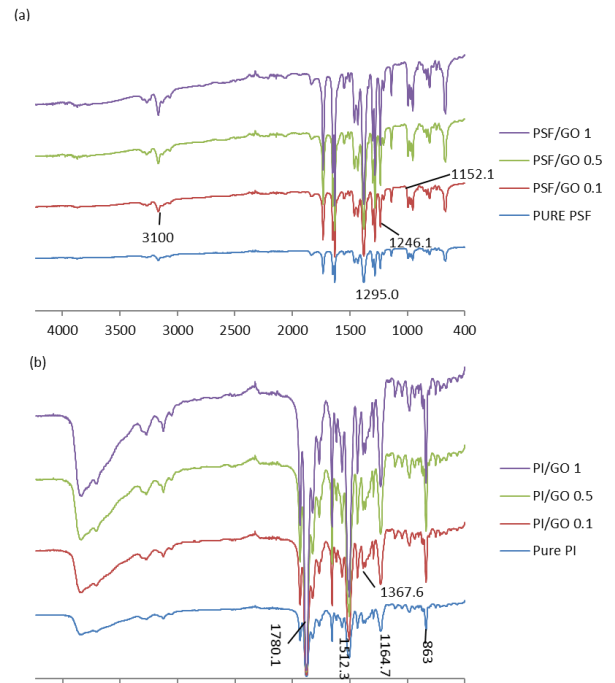


Figure 3 FTIR analysis of a) PSF-based membrane b) PI-based membrane

3.2 Contact Angle Analysis

In Table 2, it can be seen that pure PI membrane has the highest contact angle of 91°. It was shown that the addition of GO, contact angle decreased due to the addition of hydrophilic groups which includes carboxyl (C=O), hydroxyl (C-OH) and epoxy (C-O-C). Furthermore, the lowest contact angle in PI-based membrane is around 58° which indicates more hydrophilic membrane surface. As for PSF-based membrane, the highest contact angle belongs to pure PSF which is around 69° while the lowest is around 65°. Besides, these observations can be supported by previous studies which show that the addition of GO into membrane has decreased the contact angle due to addition of hydrophilic groups [20, 23, 25].

Table 2 Contact angle

Sample	Contact Angle
Pure PI	91.4 ± 0.07
PI/GO0.1	88.9 ± 0.07
PI/GO 0.5	84.7 ± 0.08
PI/GO 1	58.4 ± 0.07
Pure PSF	69.7 ± 4.35
PSF/GO 0.1	68.9 ± 0.03
PSF/GO 0.5	67.2 ± 0.04
PSF/GO 1	65.9 ± 0.04

3.3 Zeta Potential Analysis

The surface charge of membranes is mostly described by surface zeta potential which is determined by electro-kinetic measurements [25, 26]. Basically, if both membrane and molecules have the same charge, there will be repulsion which leads to less fouling. However if they are in opposite charge, there will be attractive forces which leads to easy fouling and reducing the performance [27]. As can be seen in Figure 4, the surface zeta potential for all membranes is negative which is due to the existence of electronegative functional groups [20, 26]. It was also observed that as the GO concentration increased, the zeta potential also increased due to homogenous dispersion of more functional groups in mixed matrix membrane. This can be supported by a study which reported that the appearance of negative charge surface by adding GO into membrane takes place during phase inversion process when hydrophilic functional groups in GO move to the surface [26]. Furthermore, it can be determined that the zeta potential for PI based membranes is higher than PSF-based membrane. Increasing the concentration of GO and preparing a homogenous solution by blending GO into the membrane, caused an increase in hydrophilic groups density, hence leads to higher negative surface charge which was also supported by studies done by Zhao *et al.* [26]. Furthermore, having a high surface charge on membrane, leads to less fouling of the membrane which leads to better performance [29]. Finally, it can be concluded that since PI-based membrane has higher negative surface charge, it is better compared to PSF-based membranes.

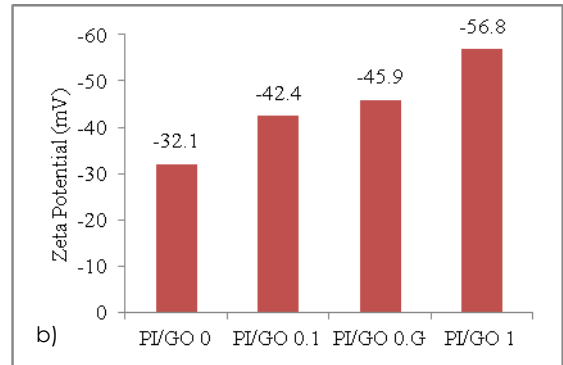
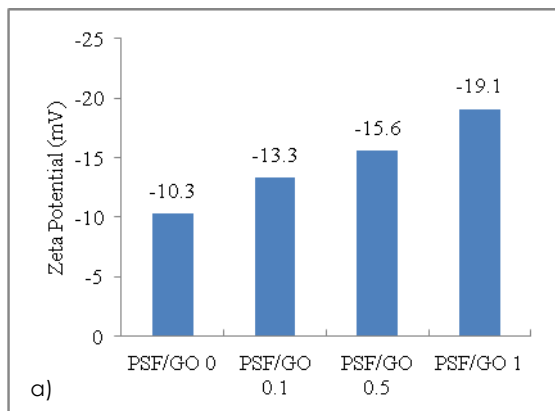


Figure 4 Zeta potential vs GO content a) PSF-based membrane, b) PI-based membranes

3.4 Mechanical Properties

Figure 5 shows peak load of each membrane vs GO content. Increasing the concentration of GO, increased tensile strength due to the enhancement in membrane structural strength [30]. It can also be determined that the tensile strength for PI based membranes was much higher than PSF based membranes which might possibly be due to better interaction of GO with PI [31]. Furthermore, it can be observed from the graph that PI/GO with 1 wt% concentration has a higher peak load of 2778.5g, while the lowest peak load was 1522.5g for pure PSF. The result showed that PI-based membranes yield higher tensile strength which signifies better mechanical properties compared to PSF-based membranes.

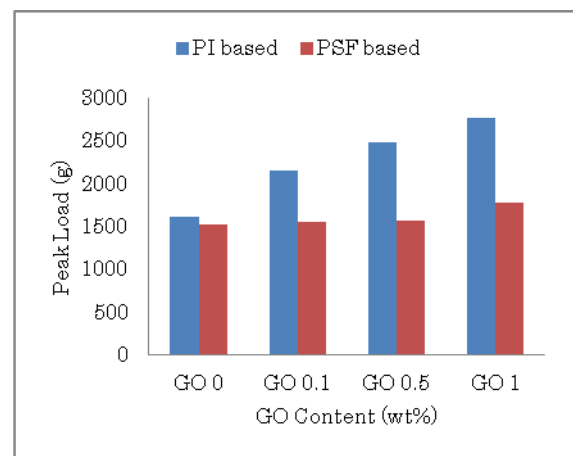


Figure 5 Tensile strength vs GO content

3.5 FESEM Analysis

As shown in Figure 6 (a), some pores were found in pure PSF membrane. However, for PSF/GO 1 wt% (see Figure 6 (b)), smoother surface can be seen which is due to the development of integrated selective skin layer that led to less formation of open porous structure causing generation of selective layer [30, 31]. Meanwhile, cross-sectional image of PSF membrane incorporated with GO 1 wt% revealed long finger-like pores which are larger at the bottom part of the membrane. The shape of the pores was also different as can be seen in the cross-sectional image of pure PSF (see Figure 6 (e)). Several studies on this have determined that addition of GO into the PSF membranes, changed the pore shape which might affect the gas permeation properties [20, 34]. It was also observed that addition of GO into the PSF, caused changes in the pore size which might be due to the increase in viscosity value [19].

With respect to PI-based membranes, pores were found in pure PI membrane while for PI/GO 1 wt%, due to addition of GO, the skin layer of the membrane is more dense which leads to lower number of pores and emerge of macroscopic defect. (see Figures 6 (c) and (d)). Cross sectional images (see Figures 6 (g) and (h)) also showed no significant difference. In addition, it can be determined from the cross section image of PI/GO 1 wt% (see Figure 6 (h)) that a dense skin top layer was formed, whereas pure PI usually has a sponge like structure. This observation on the addition of GO is supported by Ge *et al.* who stated that due to GO homogeneous dispersion in the polymeric matrix based of PI and GO interaction, the surface is smooth, and no cracks, pores or other defects can be observed [22].

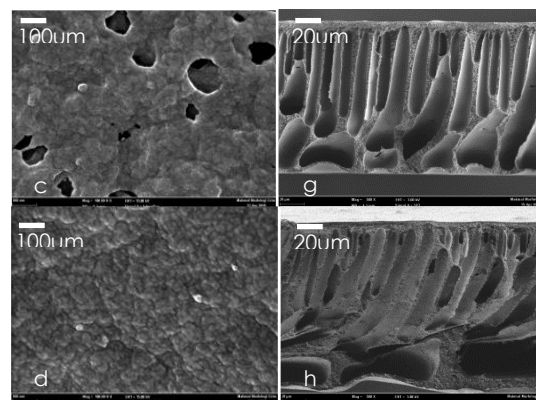
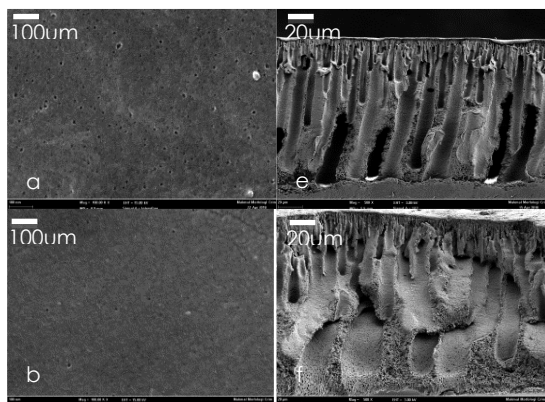


Figure 6 Membrane surface (a-d) with magnification of 100.00KX and cross section (e-h) with magnification of 500X, Pure PSF (a and e); PSF/GO 1wt% (b and f); pure PI (c and g); PI/GO 1wt% (d and h)

3.6 Pressure Effect on Gas Permeation

The gas permeation properties of the produced membranes were evaluated as one of the main parameters in membrane gas separation.

a) Gas Permeation for PSF-based Membranes

Figures 7 (a) and (b) show the effects of adding GO into PSF polymer on both CO₂ and H₂ permeability. As can be seen from Figure 7(a) hydrogen permeability increases by increasing GO concentration from 0 to 1 wt%. It can also be determined from the figure that the permeability change is almost steady for all PSF-based membranes. The highest permeability was for PSF membranes incorporated with GO with 1 wt% at 3 bar which was 439 GPU. On the other hand, the lowest permeability was for pure PSF at 5 bar which was 133 GPU. According to Kapantaidakis *et al.* [35] the permeability of gases like H₂, He, N₂ and O₂ have no interaction with membrane matrix; by increasing pressure, the permeability remains almost steady. A similar effect can be seen in Figure 7 (a). Several studies have shown that at a higher gas sorption, compression of membrane and plasticization can be met by increasing the pressure [4]. Basically, it means as the pressure increases, more gas molecules attach to the surface of the membrane which cause higher gas sorption. The membrane compaction or fouling is a phenomenon that causes a decrease in membrane transport properties especially in pressure driven processes which is blockage of membrane surface and pores [36]. With respect to plasticization, it usually occurs at high pressure which mainly affect the physical properties of the membrane in contact with CO₂ [37]. Furthermore, it has been proven that by increasing the pressure, diffusion also increases. However due to the compaction of membrane, increasing the pressure leads to less diffusion of hydrogen gas which also leads to less permeability [4, 38]. A similar observation can be made for pure PSF membrane as the permeability increases at first and then decreases.

On the other hand, in Figure 7(b) it can be seen that adding GO into PSF membrane and increasing its concentration, increased CO₂ permeability. It can also be determined from the figure that by increasing the pressure; the permeability of the gases through the membranes incorporated with GO decreased. This is probably due to the decrease in amount of available free volume [39]. It can also be determined from Figure 7(b) PSF/GO 1 wt% has the highest permeability of 288 GPU at 1 bar, while pure PSF has the lowest permeability which is 7 GPU at 5 bar. It has been proven that the addition of GO into PSF polymer, increased CO₂ permeability due to the high adsorption properties of GO toward CO₂. Furthermore, GO contains an active functional group which improves GO and PSF interaction with each other preventing interphase problems between GO and PSF resulting in better GO dispersion. Hence, it improves CO₂ permeation [19, 26, 40].

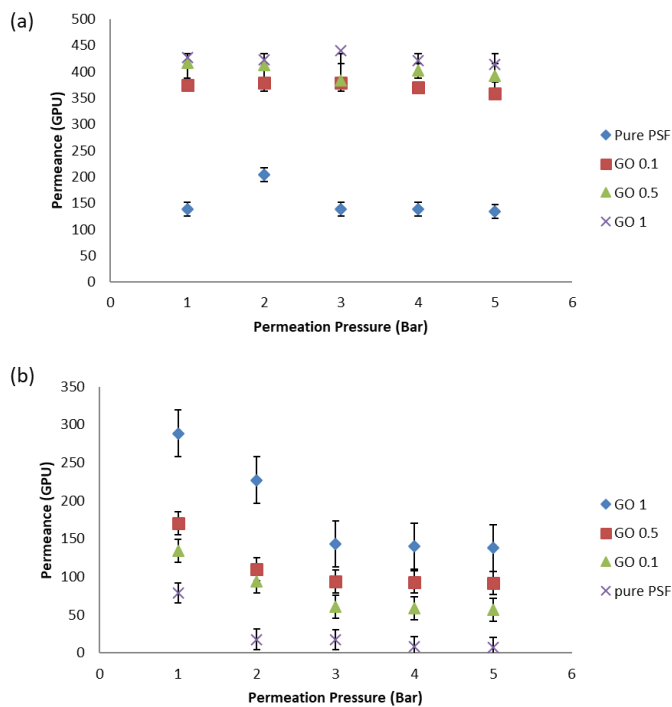


Figure 7 Gas permeation properties for PSF-based membrane at 25 °C a) H₂ permeability b) CO₂ permeability

b) Gas Permeation for PI-based Membranes

Figure 8 shows the effects of both pressure and concentration on gas permeation. It can be seen in Figure 8(a) that increasing the pressure, permeability of hydrogen in all membranes has insignificant changes. Besides, it also shows that as the concentration of GO increases the permeability of hydrogen also increases which is due to GOs' adsorption properties towards gas. The highest permeability recorded was for PI membranes incorporated with GO with concentration of 1 wt% at

1 bar which was 501 GPU and the lowest was observed at 5 bar for pure PI which was 92 GPU.

By increasing the pressure, the permeability of CO₂ decreases which might be due to the deduction in free volume (see Figure 8 (b)). Furthermore, it can be seen that increasing the concentration of GO, increases the permeability of CO₂. The highest permeability was recorded for PI membranes incorporated with GO with 1wt% at 1 bar which was 595 GPU. On the other hand, pure PI at 5 bar had the lowest permeability which was 57 GPU.

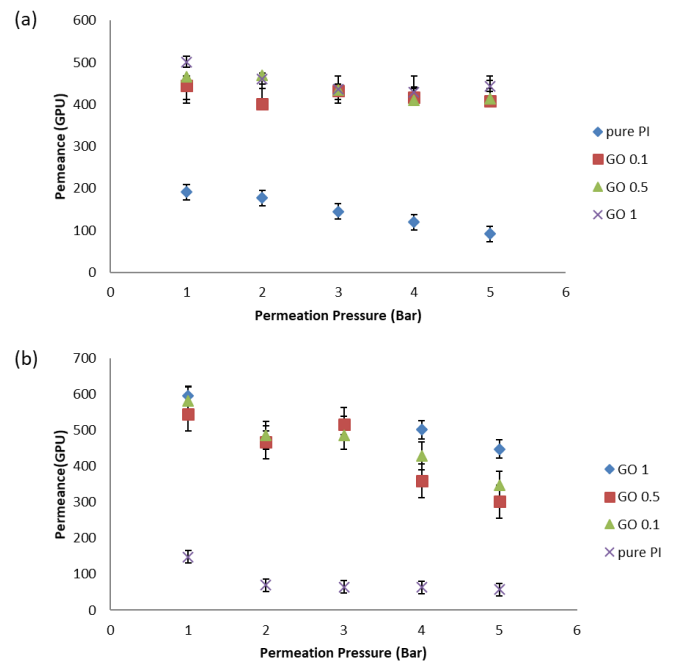


Figure 8 Gas permeation properties for PI-based membrane at 25 °C a) H₂ permeability b) CO₂ permeability

3.7 Gas Selectivity through Membranes

Finally, as shown in Figure 9 the H₂/CO₂ selectivity in PI-based membranes was higher than in PSF-based membranes at 5 bar. The highest selectivity belongs to PI/GO 1wt % which was 1.3 while the lowest was 0.05 and belongs to pure PSF membrane. Thus it can be determined that PI-based membranes have the best results. In addition, in this category, PI membranes incorporated with GO with 1 wt% showed the best results. These results can be supported by analysis in the previous section, that as PI-based membranes have better physicochemical properties especially for PI/GO 1 wt% which has higher negative surface charge and the least contact angle which resulted in better performance. The drop in PI/GO 0.5 wt% is related to permeability which might be due to incomplete dispersion of GO into polymeric base [26].

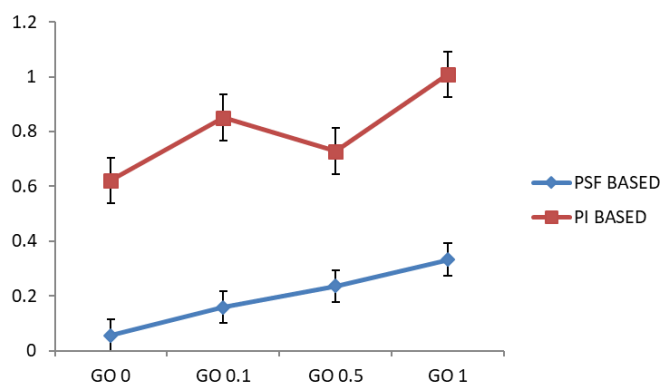


Figure 9 Selectivity vs GO concentration for PSF-based and PI-based membranes at 5 bar

3.7 Gas Composition Analysis

Gas composition was analysed after permeation of mixed H_2/CO_2 with 50/50 concentration. From Table 3 it can be seen that hydrogen composition was higher for each sample. Furthermore, hydrogen composition was slightly higher in PI-based membranes. It was also observed that the composition of hydrogen for membranes incorporated with GO with 1 wt% has a higher hydrogen composition indicating that more hydrogen pass through the membrane. The findings of this study can be supported by several studies which reported that membranes incorporated with GO, smaller molecules pass through more than the bigger molecules [19, 41].

Table 3 Gas composition after gas permeation test

Sample	CO ₂ Composition %	H ₂ Composition%
Pure PI	24	76
PI/GO 1wt %	17	83
Pure PSF	24	76
PSF/GO 1wt%	18	82

4.0 CONCLUSION

The performance of PSF-based and PI-based membranes for CO_2 and H_2 permeance and selectivity at pressures of 1 to 5 bar was successfully measured and characterized with the incorporation of various GO concentrations. The results from gas permeability and selectivity shows that PI/GO with concentration of 1 wt% has the highest performance with H_2 permeability of 501 GPU and CO_2 permeability of 595 GPU at 1 bar, while for H_2/CO_2 selectivity, the highest belongs to PI/GO 1 wt% of 1.3 at 5 bar. Meanwhile, gas composition analysis showed that hydrogen composition after permeation through the membrane was highest for PI/GO 1 wt% which was 83 %. As for FTIR analysis, oxygenated functional groups were observed with GO addition. The zeta potential analysis showed that surface charge negatively increased with the addition of GO

and the highest was -56mV which belongs to PI/GO 1wt%. Besides, FESEM analyses showed the change from droplet-like shape to finger-like for PSF-based membranes and denser structures for PI-based membranes. The addition of GO also leads to higher hydrophilicity with the contact angle of 58 for PI/GO 1wt%. It could be concluded that PI/GO 1 wt% membranes has exhibited enhanced gas permeation and physicochemical properties compared to PSF membranes with the incorporation of GO.

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