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CARBON DIOXIDE/METHANE SEPARATION PERFORMANCE BY MIXED MATRIX MEMBRANE FROM POLYSULFONE/ HALLOYSITE NANOTUBES

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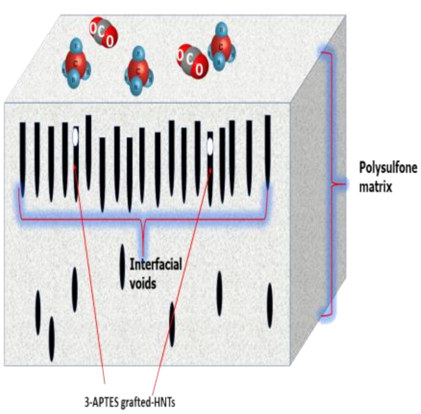
Graphical abstract



Abstract

Gas separation by using membrane-based technology is one of the rising technologies used in the industry. It has many advantages such as low in cost and energy consumption. However, this technology is limited because of the "trade-off" exists between permeability and selectivity of the membrane. Thus, in this study, an inorganic filler, halloysite nanotube is modified with 3-aminopropyl(triethoxysilane) and then incorporated into the polysulfone polymer and the performance of the mixed matrix membranes (MMMs) is investigated. MMMs were analyzed by using SEM, FTIR, tensile and gas permeation tests which studied the morphological differences, mechanical strength, and membrane permeability and selectivity towards CO_2 and CH_4 respectively. The performance of the MMMs was compared with neat membrane and MMMs with unmodified HNTs. SEM results show an increase of 111% on the thickness of the dense skin layer of MMMs with APTES-modified HNTs compared to the neat membrane and the MMMs with unmodified HNTs. Elongation at break for MMMs with 3-APTES-modified HNTs also increased to 24.22%. The gas separation performance of the MMMs with 3-APTES modified HNTs shows an overall increase of 25.37% in the membrane selectivity compared to MMMs with unmodified HNTs while when coating is done, the selectivity of the MMMs with 3-APTES modified HNTs shows an increase from 0.845 to 10.158 for a pressure of 2 bar showing that coating helps in increasing the selectivity of the membrane.

Keywords: Mixed matrix membranes, polysulfone, halloysite nanotubes, 3-APTES, gas permeation

Abstrak

Pemisahan gas dengan menggunakan teknologi berasaskan membran dan ia mempunyai banyak kelebihan berbanding teknologi pemisahan gas konvensional lain seperti kos dan penggunaan tenaga yang rendah. Namun, terdapat beberapa batasan dalam teknologi ini kerana "trade-off" yang wujud antara kebolehtelapan dan selektiviti membran. Untuk menyelesaikan masalah ini, membran matriks bercampur (MMMs) dibangunkan. Dalam kajian ini, sejenis nanofiller inorganik, nanotube halloysite diubah suai dengan 3-aminopropil (triethoxysilane) dan kemudian dimasukkan ke dalam polimer polysulfone dan prestasi MMM dikaji. MMM dikaji dengan menggunakan SEM, FTIR, ujian tegangan dan permeasi gas, yang masing-masing mengkaji perbezaan morfologi, kekuatan mekanikal, kebolehtelapan dan selektiviti CO_2 dan CH_4. Prestasi MMM dibandingkan dengan membran tulen dan MMM dengan HNT yang tidak diubah suai. Keputusan SEM menunjukkan peningkatan sebanyak 111% pada ketebalan lapisan kulit padat MMM dengan HNTs yang diubah suai menggunakan APTES berbanding dengan membran tulen dan MMM dengan HNT yang tidak diubah suai. Pemanjangan pada rehat untuk MMM dengan HNT yang diubah suai menggunakan APTES juga meningkat kepada 24.22%. Prestasi pemisahan gas MMM dengan HNTs yang diubah suai menunjukkan peningkatan keseluruhan 25.37% dalam selektiviti membran berbanding dengan MMM dengan HNTs yang tidak diubah suai manakala apabila salutan dilakukan, pemilihan MMM dengan HNTs yang diubah suai menggunakan 3-APTES menunjukkan peningkatan dari 0.845 hingga 10.158 untuk tekanan 2 bar, menunjukkan bahawa salutan membantu dalam meningkatkan selektiviti membran.

Kata kunci: Membran matriks bercampur, polysulfone, halloysite nanotubes, 3-APTES, penyerapan gas

1.0 INTRODUCTION

Carbon dioxide (CO_2) is a colorless, greenhouse gas that consists of carbon that is covalently bonded to two oxygen atoms. It is the component of natural gas, biogas and landfill gas and is the main combustion product of fossil fuel. It is naturally found in the natural gas stream at a level beyond 70% and as high as 80%. The existence of CO_2 in the natural gas stream will affect the selling price and reduces the energy content of the gas [1, 2]. It will also decrease the calorific value, increase the corrosiveness and acidity of the streams, reducing the gas compression and transport possibilities pipelines [2, 3].

The advancement in technology for the separation of CO_2 from the gas streams has become significant because the CO_2 removal will result in the production of high energy content fuel and preventing the corrosion dispute in the pipeline for gas transportation system [3].

Current technologies that are practiced for the purification of natural gas include adsorption, cryogenic separation, and absorption. Another type of technology that has been garnering attention for its many advantages is the membrane-based technologies. It is an essential technology that is cost-saving and demonstrates advantages in terms of a smaller footprint, lower weight, modular installation, easier maintenance and also requires low labor and minimum requirement of utilities [4].

Polysulfone (PSf) is one of the examples of membranes that is widely used in membrane-based technology for gas separation. It is used broadly due to its good permeability, selectivity in the gas separation, low in cost, resistance to degradation and also gives a high critical pressure of plasticization and it also consists of carboxyl group and aromatic ring making it suitable for CO_2 separation [4]. However, the limit of selectivity and permeability for currently available industrial polymeric membrane has been reached, pushing the industry to make improvements on the performance of the membrane by introducing new techniques of dispersing of inorganic materials into the polymer matrix giving new context in the membrane technology which is the mixed matrix membranes (MMMs) [5]. The introduction of MMMs in the industry improves gas separation by introducing the molecular sieving effect and increasing the specific membrane-pervasive interaction [6].

HNTs was selected as the inorganic filler as it is an environmental friendly material and naturally abundant. It can give a better diffusion path of the selected gas as it has a multiwalled tubular structure.

In this study, HNTs will be modified by 3-APTES and grafted onto the PSf by using the phase inversion technique. By grafting this silane, amine groups will be introduced and increase the boning properties of polymer-clay interface.

The aim of this report is to study the performance of the MMMs with HNTs that is modified using 3-APTES on the separation of carbon dioxide (CO_2) and methane (CH_4). The difference of phase structure and chemical composition between the unmodified and 3-APTES modified HNTs was examined and the morphological structure, mechanical strength and the gas separation performance of the membrane are also further examined.

2.0 METHODOLOGY

2.1 Materials

The polymer web used in this research is PSf and it is supplied by Sigma Aldrich Co. in the form of transparent pellets while the solvent used is the 1-methyl-2-pyrrolidone (NMP) and n-hexane are supplied by Merck. Ethanol with a purity of 96% for the modification of the HNTs and methanol to remove the residual solvent from the membrane are also supplied by Merck. The filler used, which is the halloysite nanotubes (HNTs) and the silane used for the modification of the filler which is the (3-Aminopropyl) triethoxysilane (APTES) is also supplied by Sigma Aldrich Co. PDMS used for the membrane coating is supplied by Dow Corning.

2.2 Membrane Solution Preparation

1 wt % of unmodified and modified HNTs were added to the neat polymer solution containing PSf and NMP with a ratio of 25:75 respectively [7]. The HNTs were modified using 3-APTES according to the method used form the previous study by Carli *et al.,* (2013). 20 g of HNT was dispersed in 120 mL of ethanol and the solution is then stirred vigorously until the HNT dissolves completely. The 3-APTES with a ratio of 1:0.2 (HNT:silane), is added to the mixture and stirred for 2 hours. Butchner funnel is used to collect the modified sample and filtered then washed with 96% ethanol. The filter cake obtained from the filtration is dried at room temperature for 24 hours and then dried under vacuum for 8 hours at 70 °C until a constant weight is obtained. The preparation of the membrane solution is according to the method proposed by Ismail *et al.,* 2017.

For membrane fabrication, a small amount of MMMs solution was poured onto a clear, clean and flat glass plate and spread evenly on it. The thin film were first immersed in a coagulation bath (tap water) and then the membrane formed was transferred into another tap water. The membrane were left overnight in the tap water before soaked in methanol for 4 hours to further remove the solvent. Then the membrane were dried at temperature for 3 days.

2.3 Membrane Coating

Membrane coating is carried out by using polydimethylsiloxane (PDMS) that is prepared by mixing the elastomer and hardener in a ratio of 10:1 in n-hexane solvent. The proposed methodology is similar to the one used by Murali *et al.,* (2014) and Zulhairun *et al.,* (2014). The solution is then stirred for 3 hours until it is well mixed by using overhead stirrer. Each of the membrane samples that had been cut into a small circle with an outer diameter of 5.5 cm is then immersed separately for 10 minutes and is left to dry at room temperature for 5 days before the gas permeation test [12].

2.4 Characterization of Unmodified and Modified HNTs

Unmodified and modified (APTES-grafted) HNTs are characterized by using X-ray Powder Diffraction Data Analysis (XRD) and Fourier-Transform Infrared Spectroscopy (FTIR).

For XRD, the unmodified HNTs and the modified (APTES-grafted) HNTs in powder form is characterized by using Philips X-pert Pro diffractometer to study on the effect of the modification to the phase structure of the HNTs. The diffractometer is equipped with copper anode material with Kα (λ_1=1.54056 and λ_2=1.54439).

FTIR is used to determine the infrared emission of the sample. It is conducted by using Perkin Elmer Spectrum 100 spectrometer. The frequency used is between 4000 cm^{-1} and 400 cm^{-1} with a total of 4 scans. The sample is first crushed finely and then is put onto the scanning plate. The absorbance spectra are then generated on the computer screen.

2.5 Characterization of Membrane

The prepared neat membrane and MMMs will be characterized by using Scanning Electron Microscopy (SEM) and tensile test. SEM (S-3400N, Hitachi) is used to study the morphological behavior of all the membranes. For this test, the membrane was cut by using a microtome knife into a small piece of membrane with a dimension of 5 mm × 5 mm. The sample is then mounted on a stab by using carbon tape, masking on a stand inside the sputter coater and then sputter-coated with gold before it is examined by using SEM. The samples were observed with a potential of 15 kV and magnification of 420× for the membrane cross-section.

For the tensile test, Universal Testing Machine (UTM) is used. For each type of membrane, three samples were cut with a dimension of 25×50 mm^2 and tested with a crosshead speed of 5 mm/min. The elongation at break and the tensile strength of each of the samples were then analyzed.

2.6 Gas Permeation Test

A gas permeation test is done to study the separation performance of the membrane. The test is done by using CO_2 and CH_4 gas in which will permeate through the membrane that is placed on a metal plate. The test is done at room temperature with a pressure of 2 bar. Figure 1 shows the schematic diagram of the whole system for the gas permeation test.

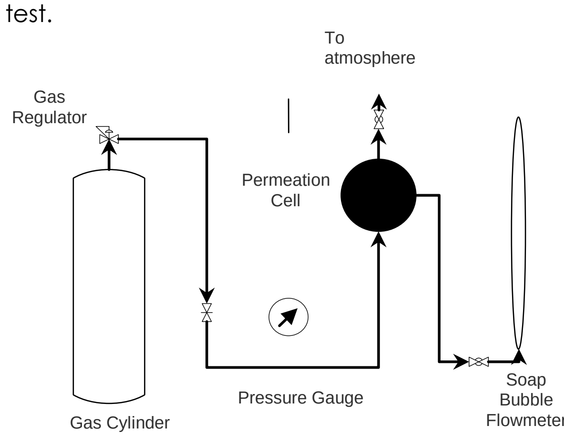


Figure 1 Schematic Diagram for Gas Permeation Test

The permeability and the selectivity of the membrane are determined by calculating the flux and comparing the permeability of both gases to find the selectivity. The pressure-normalized flux can be calculated by using the formula below:

$$\left(\frac{P}{l}\right)_i = \frac{Q_i}{(\Delta p)(A)} \qquad (1)$$

Where Q_i is the volumetric volume of the selected gas at STP, Δp is the transmembrane pressure difference and A is the membrane active surface that is exposed to the gas. The permeance is then expressed in GPU unit which is as follows:

$$GPU = 1 \times 10^{-6} \frac{cm^3(STP)}{cm^2 \sec cmHg} \qquad (2)$$

The pure gas selectivity can be then determined by taking the ratio of the permeance of the membrane towards the pure gas. It can be expressed by using the following formula:

$$\alpha_{i/j} = \frac{(P/l)_i}{(P/l)_j} \qquad (3)$$

3.0 RESULTS AND DISCUSSION

3.1 Determination of Phase Change of Powdered HNTs

The study of the phase structure differences between the unmodified and modified HNTs to study if phase change occurs when the HNTs are modified with 3-APTES. The XRD data for unmodified HNTs in Figure 2 shows two distinct reference peaks at an angle of 11.9° and 19.9°. Both peaks correspond to a d-spacing of 7.43 Å and 4.46 Å respectively. These results are slightly different from the reported characteristic peaks but still in the range of the reported value. The characteristic peaks for unmodified, raw HNTs is at 13° and 20.5° which was based on the research done by Murali *et al.*, (2014). The characteristics peaks of the 3-APTES grafted HNTs can be seen in Figure 2 at the angle of 12.04° and 19.85° with a d-spacing of 7.34 Å and 4.47 Å. There is a shift of angles to a lower angle in the APTES-modified HNTs showing that there is an increased interlayer spacing of the clay [13].

Other than that, the diffraction peaks in both samples show similarity in the diffraction peaks pattern. This shows that the modification of HNTs does not affect the phase structure of the HNTs as it is only grafted on the surface hydroxyl group of the tubular halloysite [14]. A study done by Yuan *et al.*, (2008) and Ge *et al.* (2017) also shows the same results as the XRD pattern is similar for both unmodified and modified HNTs. Thus, it can be concluded that the modification of the HNTs does not affect the phase structure of the nanotubes and the modification of the HNTs with 3-APTES is partially successful.

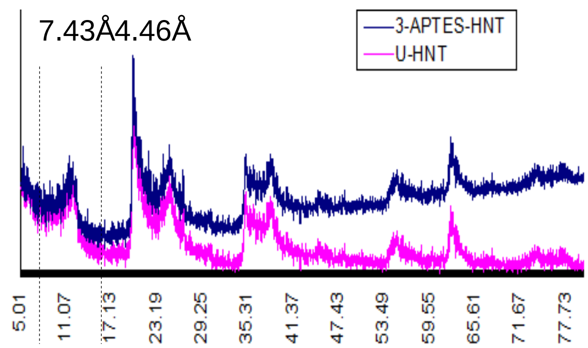


Figure 2 XRD patterns for unmodified HNTs and 3-APTES grafted HNTs

3.2 Determination of Functional Group by Using FTIR

Figure 3 shows the FTIR results for both unmodified and modified HNTs. The characteristic peak of the halloysite nanotube can be observed at 3693 cm^{-1} and 3621 cm^{-1} that corresponds to the stretching of the O-H group of the HNTs in which 3693 cm^{-1} belongs to the O-H stretching of the inner-surface of the hydroxyl groups while 3621 cm^{-1} belongs to the O-H stretching on the inner hydroxyl groups. Characteristic peak of 906 cm^{-1} contributes to Al-OH blending vibration while the peak at 792 cm^{-1} contributes to the surface hydroxyl translation. Strong adsorption at 998 cm^{-1} belongs to the asymmetric flexible vibration of the O-Si bond due to the existence of O-Si-O groups on the HNTs outer surface (Qin *et al.*, 2016). Al-O stretching vibration can be seen at the peak of 460 cm^{-1} [18].

APTES-grafted HNTs, on the other hand, shows a new peak at 641 cm^{-1} suggesting the deformation of the sulfonic group. A weak band at 1630^{-1} cm^{-1} is assigned to the adsorbed water while a broader band at 3548 cm^{-1} suggesting the $N\text{-}H_2$ asymmetric stretching vibration exists. Characteristic peak of the stretching CH_2 at 2939 cm^{-1} cannot be observed due to the low molar concentration [18]. A broader band at 1630 cm^{-1} corresponds to the adsorbed water in the sample.

These results agree with the previous study done on the modification of HNTs by using APTES although there are some peaks cannot be observed in the spectrum. This might be due to the low weight percent of the APTES that is grafted into the HNTs surface. In conclusion, based on the previous results stated, it can be said that the HNTs were semi-successfully grafted with 3-APTES.

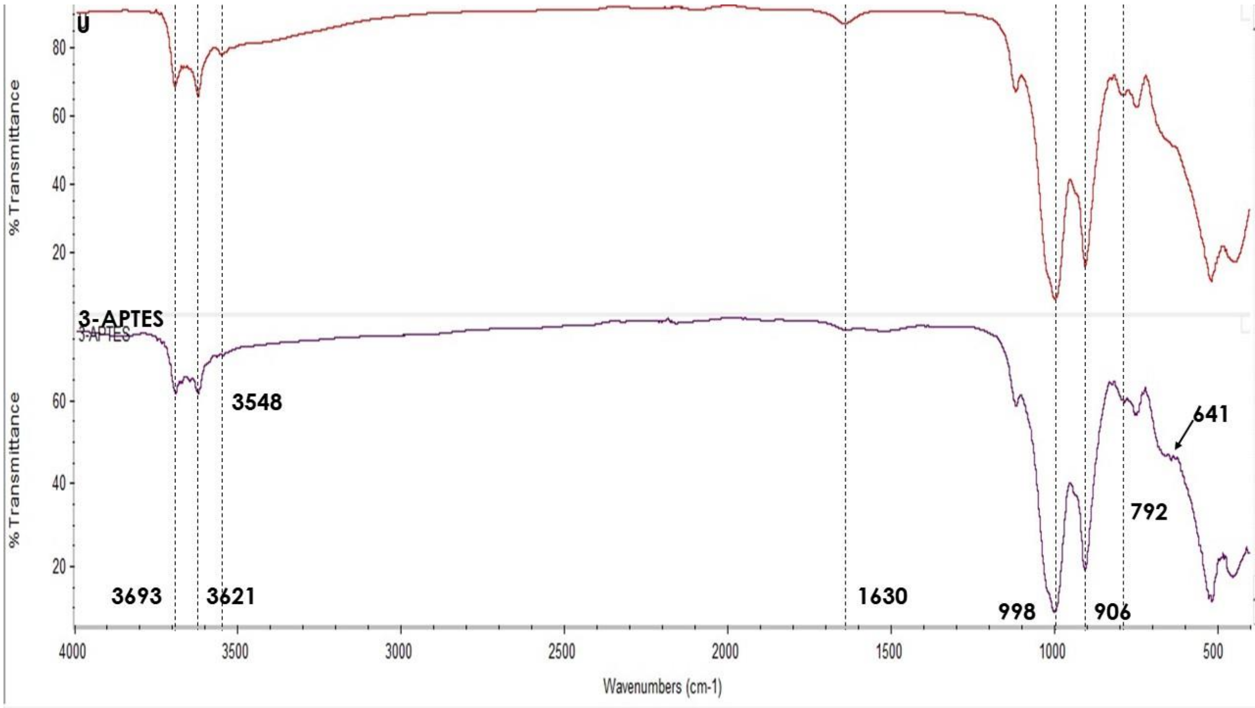


Figure 3 FTIR Results for Unmodified and 3-APTES Modified HNTs

3.3 Determination of Membrane Morphological by Using SEM

The morphology of the membranes which is the neat membrane, MMMs with unmodified HNTs and MMMs with 3-APTES modified HNTs is further studied by using SEM. Figure 4(a), (b) and (c) show the cross-sectional micrographs of the neat membrane and both MMMs.

Neat membrane, which only contains polysulfone (PSf) shows a small dense layer with teardrop-like structures embedded in the porous structure. It agrees with other results that were reported by Ismail *et al.,* (2017) and Suleman *et al.,* (2018).

Membrane with unmodified and 3-APTES modified HNTs shows a slightly different morphology in terms of the number of the teardrop-like structure compared to the neat membrane containing pure PSf only. Figure 4(b) and Figure 4(c) show the morphology of the MMMs with unmodified HNTs and MMMs with modified HNTs respectively. The thickness of the membrane increased in overall from neat membrane to MMMs with unmodified HNTs and MMMs with 3-APTES modified HNTs. The thickness of the dense skin layer for the neat membrane is 8.03 µm, MMMs with unmodified HNTs is 15.1 µm and MMMs with 3-APTES modified HNTs is 17.0 µm.

MMMs with unmodified HNTs shows an increase in 88.04% in the thickness of the dense skin layer. On the other hand, MMMs with 3-APTES modified HNTs shows an increase of 111.7% compared to neat membrane and an increase of 12.58% compared to the MMMs with unmodified HNTs. The increased in the thickness of the denser layer may due to the diluent evaporation on the top surface of the membrane. From the image, there are no HNTs can be seen in the skin layer which might be due to the relatively low amount of HNTs embedded.

Another distinct difference that can be observed is the decreased in the teardrop-like structure. Neat membrane in Figure 4(a) exhibits more teardrop structure as compared with the two MMMs that have been incorporated with HNTs. When adding the 3-APTES modified HNTs into the polymer matrix, the teardrop-like structure can be seen to be disappearing more than the MMMs with unmodified HNTs. Thus, it can be concluded that the modification of the HNTs with 3-APTES gives a better morphology of the membrane compared to the neat membrane and the MMMs with unmodified HNTs.

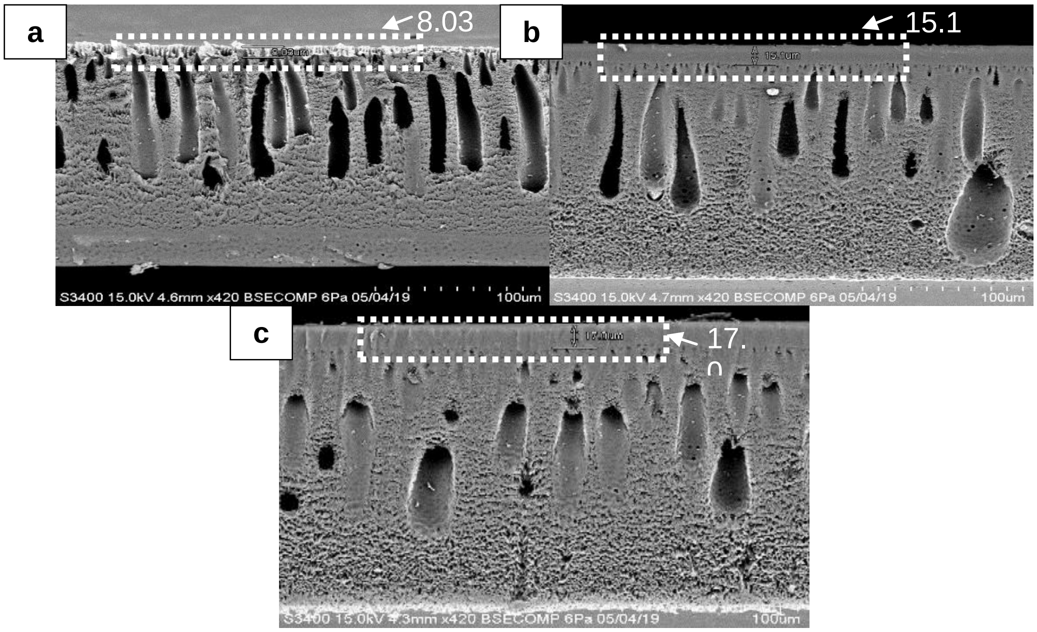


Figure 4 Cross-sectional morphology for a) Neat membrane b) MMMs with unmodified HNTs c) MMMs with 3-APTES modified HNTs (×420 magnification

3.5 Determination of Mechanical Strength

Based on the SEM results, the morphology of the membrane altered due to the incorporation of the HNTs. The alteration of the structure of the membrane also affects the mechanical properties of the membrane [20]. Hence, to determine the mechanical strength of the membrane, a tensile test is done and the tensile strength and average elongation at break are studied.

Table 1 Tensile Test Results for the Membranes

Type of Membrane	Neat	MMMs with unmodified HNTs	MMMs with 3-APTES modified HNTs
Average tensile strength (MPa)	8.02	9.11	7.5
Average elongation at break (%)	19.26	21.56	24.22
Elastic modulus (MPa)	212.89	252.13	203.90
Maximum load (N)	49.95	49.01	58.24

Table 1 shows the average tensile strength and the elongation at break for the neat membrane, MMMs with unmodified HNTs and MMMs with modified HNTs. The average tensile strength of the mixed matrix membrane incorporated with HNTs shows an increase of 13% compared to neat membrane. This proves that the addition of HNTs into the polymer matrix increased the tensile strength of the membrane. However, the MMMs with modified HNTs shows a different result compared to the unmodified HNTs. There is a 6% reduction in the average tensile strength of the membrane which is very significant. The reduction of tensile strength contradicts other research as the tensile strength of the membrane should increase when there is an incorporation of the filler. It might be because of the aggregation of the modified HNTs in the polymer matrix forming a weak junction zone that is vulnerable towards external force [21].

The average elongation at break for all types of membranes, however, shows an increased pattern compared to the average tensile strength of the membrane. By adding filler into the membrane, the average elongation of break increased from 19.26% to 21.56% and 24.22% respectively. Thus, it can be said that the membrane flexibility increased when the HNTs and APTES-modified HNTs is added into the polymer matrix. Figure 5 and Figure 6 shows the bar chart of average tensile strength and elongation at break of all three different types of membrane.

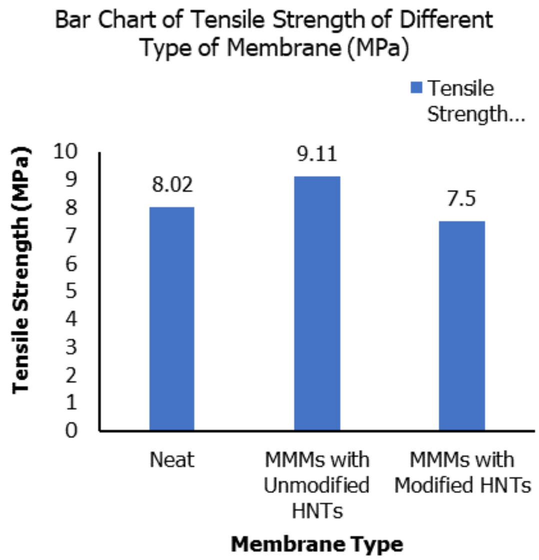


Figure 5 Bar Chart of Tensile Strength of Different Type of Membrane

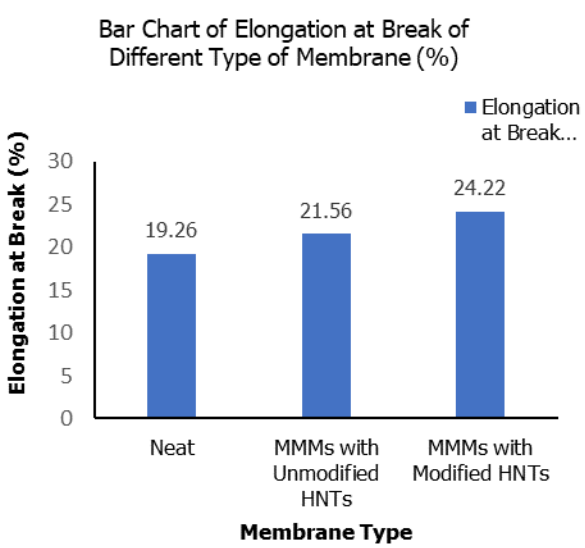


Figure 6 Bar Chart of Elongation at Break of Different Type of Membrane

3.6 Permeability and Selectivity of the Membrane

3.6.1 Effect of Adding HNTs and Modified HNTs on the Gas Separation Performance

The prepared membranes are tested to find their permeability and selectivity for the separation of CO_2/CH_4. In this section, the effect of the addition of the unmodified and 3-APTES modified HNTs is studied at the pressure of 2 bar for uncoated membranes. The result is as shown in Figure 7 and Figure 8.

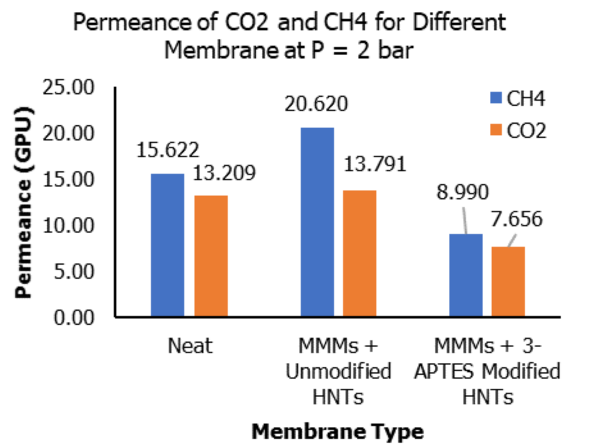


Figure 7 Permeance of the Membrane at a Pressure of 2 bar

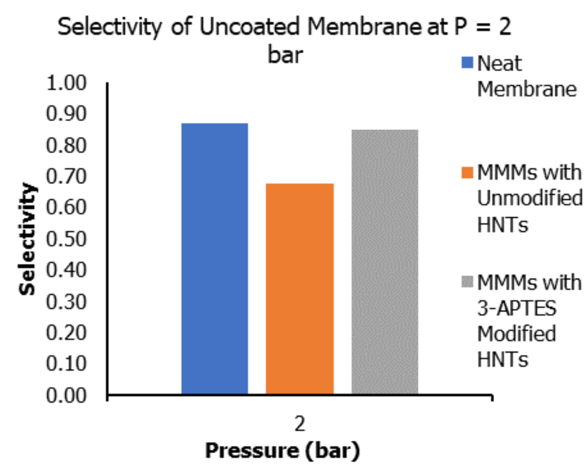


Figure 8 Selectivity of the Uncoated Membrane at a Pressure of 2 bar

The overall results show an increase in the permeability of the membrane. At the pressure of 2 bar, the CH_4 and CO_2 permeance are 20.62 and 13.79 respectively compared to neat membrane which is 15.62 and 13.21 respectively, showing an increase of 0.32% for CO_2 permeance and 0.04% for CH_4 respectively. This may be due to the increased in the HNT/polymer interfacial volume thus increasing the diffusivity of the gas [16].

The selectivity of the membrane increased overall for the MMMs with 3-APTES modified HNTs from 0.674 to 0.845 that accounts to 25.37% increased from MMMs with unmodified HNTs. It shows that the modification of HNTs with 3-APTES helps in increasing the selectivity of the membrane towards CO_2 and CH_4. However, the selectivity of the MMMs with unmodified HNTs and 3-APTES modified HNTs shows a decreasing selectivity compared to neat membrane due to the agglomeration of the filler inside the polymer matrix causing void structure inside the membrane. Similar results by Hashemifard *et al.* (2011) and Murali et. al. (2014) can be observed from previous research where the selectivity of the gas decrease when HNTs is incorporated into the polymer matrix. The increase in the selectivity of the gas in MMMs with 3-APTES modified HNTs is the result of the increase in the dense layer thickness compared to the neat membrane as previously discussed in the SEM characterization.

3.6.2 Effect of Coating on the Gas Separation Performance

The effect of coating for all three types of membrane is studied and the percentage of increase in the permeability and selectivity of the membrane is discussed. Figure 9 shows the selectivity of the uncoated and coated membrane

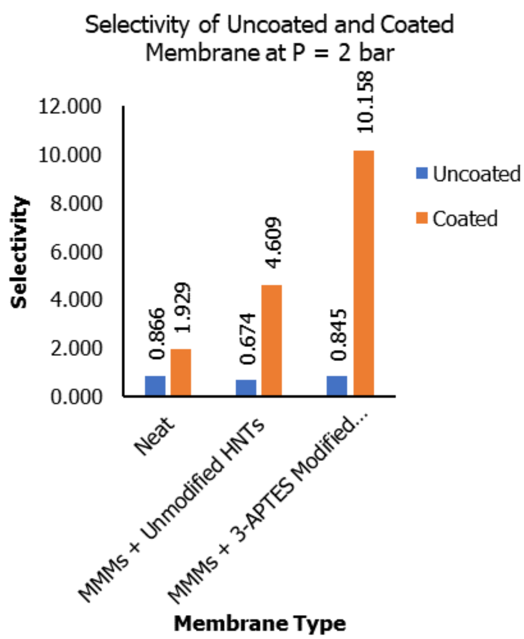


Figure 9 Selectivity of Uncoated and Coated Membrane at P = 2 bar

As shown in Figure 9, selectivity for the uncoated membrane is higher than the selectivity for the PDMS-coated membrane. The large difference of the permeance may due to the membrane defects that exist on the uncoated membrane allowing the gas to be more permeable thus decreasing the selectivity of the gas. Coating the membranes with PDMS help in reducing the pinholes and defect that exist in the membrane [10]. Coating decreases the permeance of both CO_2 and CH_4 but increases the selectivity of the gas. Compared to uncoated MMMs with 3-APTES modified HNTs, the selectivity of coated MMMs with 3-APTES modified HNTs increased from 0.845 to 10.158 for a pressure of 2 bar. This is due to the modification of HNTs with 3-APTES that increased the membrane selectivity towards the gas and also when the membrane is coated, the defect (pinholes) on the membrane is fully covered giving an increased in the permeability and selectivity of the gas. The introduction of amine group helps to improve filler dispersion as well as the MMMs permeability.

Overall, when the membrane is coated, the permeability and selectivity of the gas increased thus it can be concluded that coating helps in the gas separation performance of the membrane. These results agree with previous studies done by Jomekian *et al*. (2011) and Zulhairun *et al.*, (2015) that show an increase in the selectivity of the gas when it is coated with PDMS.

4.0 CONCLUSION

4.1 Conclusion

In this study, the modification of the HNTs with 3-APTES has been made and incorporated in the MMMs. Based on the study, it can be concluded that the modification of the HNTs with 3-APTES did not affect the phase structure of the HNTs which agree with other research done in the past. Although the FTIR results show slightly different results from other research, some characteristic peaks can be observed suggesting that the HNTs did indeed undergo modification with HNTs. There are also no changes in the physical structure of the HNTs and the mass of the HNTs after the modification decreases from 20 g to 17.5 g.

For the MMMs characterization, SEM images have proved that the modification of HNTs has been made. The decrease in the teardrop-like structure and the increase in the dense layer of the membrane to up to 111.71% for the MMMs with 3-APTES modified HNTs suggested that the modification had been made. The results show an increase in the gas separation performance compared to neat membrane that is being prepared. Tensile strength, however, shows slightly different results for the MMMs with modified HNTs compared to MMMs with unmodified HNTs. This may be due to the formation of weak junction zone in the MMMs due to the agglomeration of the modified HNTs as for the elongation at break, the results agree with previous studied that shows that MMMs with 3-APTES modified HNTs have a higher elongation at break.

Gas performance of the membrane in overall shows an increased pattern. The selectivity of the MMMs towards the gas increased compared to the neat membrane. MMMs with 3-APTES modified HNTs shows a superior result compared to the other two membranes as to have increased the selectivity of the membrane to 10.16 compared to neat membrane that has a selectivity of only 1.93 and MMMs with unmodified HNTs have a selectivity of only 4.61. This shows an increase of 426.42% compared to neat membrane and 120% compared to MMMs with unmodified HNTs. This can be supported by the SEM results that are obtained as for the MMMs with 3-APTES modified HNTs, the thickness of the dense layer increase and the number of the teardrop-like structure decrease hence only permeable to certain gas thus can increase the selectivity of the membrane. However, these results are at 2 bar and there is a discrepancy of results at other pressure that is due to the swelling of the membrane and the membrane was not properly coated allowing the gas to pass through the pinholes that are not covered by the coating.

In a nutshell, the modification of the HNTs with 3-APTES helps in increasing the gas separation performance of the membrane. This can be supported by the results that had been found on the modification of the HNTs and the characterization of the membrane. Although the results were not consistent, the available data shows an improvement in the performance of the membrane.

4.2 Recommendation

For future work, some suggestions that can be made to observe a more distinct difference in the gas separation performance of the membrane is by increasing the loading of the filler. In this study, the loading used is 1 wt% and by increasing the loading of the filler, the results can be observed more distinctly. Other than that, different grafting method can also be done to ensure that the HNTs is dispersed well in the solution and the modification with 3-APTES can be done successfully.

Finally, for the modification of the HNTs, other characterization methods can be done to see more clearly the effect of modification of HNTs such as TGA to study the thermal characteristics of the membrane. For the characterization of the membrane, FTIR can be done to study the incorporation of the filler in the MMMs. To improve the results for the gas separation performance, different coating method such as method done by Zulhairun *et al.* (2015) and Saedi *et al.* (2014) by drying the membrane in the oven instead of drying it at room temperature to ensure that the membrane is completely dried.

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