Activated carbon and halloysite nanotubes membrane for CO$_2$ and CH$_4$ separation

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Abstract. In this study, mixed matrix membranes (MMMs) were prepared where activated carbon and halloysite nanotubes with a loading of 1 wt% is incorporated into the polysulfone membrane, and the performance of each membrane was investigated. The morphological properties, mechanical strength and their correlations with the gas separation performance for CO$_2$ and CH$_4$ for halloysite-mixed matrix membrane (MMMs-HNT) and activated carbon-mixed matrix membrane (MMMs-AC) was studied by using Scanning Electron Microscopy (SEM-EDX), tensile test and gas permeation test. From the characterization of MMMs, SEM shows an increase of 30.77% on the thickness of the dense layer of MMMs-HNTs compared to neat membrane and MMMs-AC. The EDX results also showed that HNTs evenly distributed in the polymeric matrix without any sign of agglomeration. Elongation at the break for MMMs-HNTs also decreases to 11.38%. The gas separation performance for MMMs-HNTs increased by about 55.43% compared to MMMs-AC at 2 bar. Furthermore, MMMs-HNTs also showed in increase in the selectivity of membrane towards CO$_2$ and CH$_4$ from 0.82 to 15.83 at 2 bar. In conclusion, the addition of 1 wt% of HNTs into PSF polymeric matrix showed a better permeance of CO$_2$ and a greater selectivity compared to the neat membrane and the MMMs-AC and thus is the optimum inorganic filler for the mixed matrix membrane.
1. Introduction

Carbon dioxide in the atmosphere increases the greenhouse effect, which then causes global warming. Eventually, it is the source of the temperature rise, that having an effect on the world’s climate. Carbon dioxide, with its most considerable involvement in climate change which causes about 60% of the heat trapped in the atmosphere [1]. Natural gas is also known as the prince of hydrocarbon, and it is kind of petroleum which often occurs in association with fossil oil. The main prevailing element in natural gas is methane, with a composition of about 70-90%, but it still contains some most substantial and lighter hydrocarbons and also some impurities like carbon dioxide.

One of the world’s energy supply is natural gas and also known as the source of hydrocarbon for petrochemical feedstocks. Natural gas mostly considered clean compared to other fossil fuels, but natural gas not necessarily clean and free from contaminants found in a reservoir. Carbon dioxide should be removed to overcome problems related to process bottlenecks and to meet its standard quality specification as consumer fuel. Special priority on the removal of carbon dioxide from natural gas because it is the leading supplier for GHG emissions, a major contaminant in natural gas, and one of the challenging gas separation problems. The presence of carbon dioxide in natural gas reduces the energy content in natural gas, affects the transportation of natural gas in the pipeline to a very far distance, increases the acidity of the stream, and causes corrosion in the pipeline. Current technologies used for purification of natural gas are absorption, cryogenic separation, and adsorption. Another emerging conventional technology is membrane-based technology.

Membrane technology could become a piece of robust equipment for gas separation because it has small footprints, energy-efficient, do not require phase change, reduce the potential use of hazardous chemicals, smaller than other conventional systems, easy scale-up, flexible and lack of mechanical complexity. Polymeric membrane dominates in gas separation market due to its ability to be used in many applications and low cost [2].

Examples of polymeric membranes used in gas separation are polyamide, polytetrafluoroethylene, cellulose acetate, polysulfones, and polyethersulfones. Polysulfones (PSf) are preferable in the gas separation industry due to their toughness, stability at high temperature, high critical pressure of plasticization, higher selectivity, and good permeability in gas separation. Polysulfones are a family of high-performance thermoplastics. It is composed of a sulfonyl group, aromatic group, and ether groups. The ether group allows free rotation of the polymer chain. This improves mechanical properties and reduced the melting point. The biphenylsulfonyl group helps the polymer to be resistant towards heat, oxidation resistant and has high stiffness at elevated temperature. Despite that, due to some hindrance faced by polymeric membrane it is desirable to synthesis a more durable membrane with higher selectivity and permeability towards carbon dioxide.

A new approach so-called mixed matrix membranes (MMMs), is considered to be most practical in the future application. MMMs is a cost-effective heterogeneous membrane which involves a combination of homogeneously interpenetrating inorganic particle for high selectivity and permeability, hence the polymer matrix eases the processability above the Robeson Upper-bound limit [3]. The fillers in MMMs such as carbon molecular sieve and zeolite with the molecular sieving effect can discriminate different molecules that present in feed mixture gas based on size and shape [4][5]. The polymeric membrane is mostly used in the purification of natural gas. The reason is due to their low cost, high processability, and excellent intrinsic transport properties. Due to some limitations such as suffer from a trade-off between selectivity and permeability of membrane in Robeson upper bound, that eventually constrains the upper limits of membrane separation performances [6][7]. Thus, the problem overcome by introducing MMMs that consists of a dispersion of inorganic filler within continuous polymer matrix while retaining the benefits of the polymeric membrane [8][9].

In MMMs, the porous layer only provides mechanical support, and the skin layer involves the gas separation of the membrane. The fillers improve the gas selectivity towards carbon dioxide by introducing molecular sieving effect, changing the free volume of the polymer matrix and chain rigidity of polymers [10][11][12][13]. Thus, the presence of fillers in MMMs helps in transporting the carbon..
dioxide gas, which then increases the performance of gas separation due to the filler’s superior textural properties.

In this study, an effort was made to examine the impact of activated carbon (AC) and halloysite nanotubes (HNTs) incorporation into PSF polymer matrix on the functional group, morphological properties, tensile test, and gas separation performances in MMMs. Although research works on activated carbon and halloysite nanotubes in MMMs has been done, yet there is still a lack of studies on the comparative performances by using HNTs and AC in PSF polymeric matrix for CO$_2$/CH$_4$ gas separation. The main goal of this work is to fabricate an asymmetric membrane with a loading of 1 wt% of halloysite nanotubes and activated carbon (MMMs-HNTs and MMMs-AC) for CO$_2$ and CH$_4$ separation.

2. Methodology

2.1. Polymer

Polysulfone (PSf) was used to form a continuous matrix phase in mixed matrix membrane formation. PSf was chosen for membrane fabrication because it is durable, rigid, has excellent strength and thermal properties. PSf was purchased from Sigma Aldrich that had a weight-averaged molecular weight of 35,000. The melt index of about 6.5 g/10 min. Polymer pellets were dried in the oven at 60 °C for 24 hours before the dope preparation.

2.2. Solvents

N-methylpyrrolidone (NMP) [(C$_5$H$_9$NO), 99.13 g/mol] and methanol [(C$_3$H$_7$OH), 32.04 g/mol] were purchased from Merck, Germany. Methanol was used to remove excess solvent. Polydimethylsiloxane (PDMS) was used for the membrane coating that was supplied by Dow Corning. NMP was used due to its low toxicity. All the chemicals stated above were used without any further purification.

2.3. Inorganic fillers

Inorganic fillers that were used in this study were halloysite nanotube and activated carbon. All the chemical and physical properties of the fillers were listed. Halloysite nanotubes (HNTs) was purchased from Sigma-Aldrich, Germany. The chemical composition of HNTs was Al$_2$(OH)$_4$Si$_2$O$_5$, 2H$_2$O with the molecular weight of 294.19 g/mol. The physical properties of HNTs AC are shown in Table 1. Activated carbon was a highly porous molecular sieve material, which was purchased from Sigma-Aldrich, Germany.

| Table 1. Physical Properties of HNTs and AC |
|------------------------------------------|
| Physical properties | Values |
| Outer diameter | HNTs 50 nm | AC - |
| Inner lumen diameter | 15 nm | - |
| Pore diameter | 1-3 μm | 2-50 nm |
| Length of tube | 64 m$^2$/g | 960 m$^2$/g |
| Surface area (S/A) | 1.26-1.34 mL/g | 1.56 mL/g |
| Pore volume | 1.54 | - |
| Specific gravity | 2.53 g/cm$^3$ | 2.05 g/cm$^3$ |
2.4. Preparation of membrane solution
In this study, three types of membrane solutions were prepared. The three membranes solution consists of a neat membrane (Neat) solution, activated carbon membrane (MMMs-AC) solution, and halloysite nanotubes membrane (MMMs-HNTs) solution.

2.5 Preparation of Polysulfone homogenous membrane
The preparation of this membrane does not contain any filler (neat membrane) and acts as a control membrane. First, the 50 g of the dried polymer was added slowly into the laboratory bottle containing 150 g of NMP solvent. Then, the mixture was stirred using the overhead stirrer at 215 rpm until a clear and viscous solution was obtained. Once a homogenous solution formed, the mixture was left in a water bath stirrer at 25 °C for 125 rpm around 40 minutes. The dope solution was left for one day in order to remove any air bubbles that formed during mixing. Due to the bubbles in the casting solution, it can cause the formation of holes during membrane formation.

2.5.1. Preparation of mixed matrix membrane solution.
The preparation of mixed matrix membranes was quite similar as for the preparation of neat membrane; however, several additional methods were added. In this study, mixed matrix membranes were prepared with 1 wt% loading of activated carbon and halloysite nanotubes. The composition of each material for the fabrication of MMM is tabulated in Table 2. For comparison purpose, 1 wt% is the ideal loading and also to prevent agglomeration in the membrane.

Table 2. Composition of materials for fabrication of membrane

| Filler  | Loading (wt%) | Psf (wt%) | NMP (%) |
|---------|--------------|-----------|---------|
| AC      | 1            | 25        | 75      |
| HNTs    | 1            | 25        | 75      |

The MMMs solution was prepared by adding 0.51 g of activated carbon into a laboratory bottle containing 150 g of NMP solvent. Then the solution was mixed using a magnetic stirrer for 1 hour at 300 rpm to avoid aggregation in AC and enhance the homogeneity of the AC dispersion in the solution. After stirring, the polymer was introduced into the casting solution. Add 50 g of PSF polymer into the casting solution and was stirred using overhead stirrer at 215 rpm until a clear, viscous, and stable solution was obtained. Once a homogenous solution formed, the mixture was left in a water bath stirrer for 25 °C at 125 rpm for 40 minutes. The casting solution was kept in the bottle for one day in order to remove any air bubbles that formed during mixing. The same procedure repeated for the formation of MMMs-HNTs.

2.5.2 Fabrication of membrane. A smooth, dry, flat, and a dust-free rectangular glass plate was used as a casting template. Acetone was used to clean and remove any dust that present on the glass surface and glass rode. Both the sides of the glass plate were tapped by using cellophane tape. Casting or dope solution was then poured across the glass plate edge. As the glass rode was pulled towards the user, a uniform wet film of the membrane was produced across the glass plate surface. Time taken for casting each membrane was recorded. Without delay, the glass plate was transferred into the water bath. Next, the membrane was peeled off from the glass surface and immediately transferred into another basin containing a water bath hence left overnight in order to remove the solvent on the membrane. After one day, the membrane was submerged into methanol for 4 hours and then dried for three days. This method was repeated for the fabrication of MMMs-AC and MMMs-HNTs.
2.6 Characterisation of neat and mixed matrix membrane

Neat and mixed matrix membrane was characterized by using Fourier-Transform Infrared Spectroscopy (FTIR). FTIR was used to determine the functional group present in the three samples of the membrane. In the present work, all the infrared spectrums and functional group were recorded using Fourier Transform Infrared Radiation (FTIR), (Perkin Elmer Spectrum 100). Spectrums were obtained in the range of between 4000 cm\(^{-1}\) and 400 cm\(^{-1}\).

The fabricated neat and mixed matrix membranes were characterized by using Scanning electron microscopy (SEM-EDX), and tensile test. By using SEM (S-3400N, Hitachi), the morphology for all the three samples was determined. The membrane was cut into small pieces by using a knife in a dimension of 5mm X 5mm. The cross-section of the membrane surface observed under the magnification of 420x. The surface of the membrane examined under magnification of 500x, 1500x, and 10kx. For the characterization of the membrane, it was initially fractured in liquid nitrogen to obtain a clear cut of a cross-section. The purpose of immersing those membranes in liquid nitrogen was to make membrane-less brittle. The sample was then mounted on stab by using carbon tape, and then sputter-coated with gold/platinum before analyzing it by using SEM. All the elemental composition in the three samples was analyzed using elemental dispersion composition (EDX). EDX method plots the abundance of an element alongside a line. This method was conducted using SEM-EDX (S-3400N, Hitachi).

This tensile test widely used and one of the best ways to measure the mechanical properties. A universal testing machine (UTM) was used to measure mechanical strength. The membrane was clamped between grips and pulled to the opposite direction with a constant grip separation rate. From there, elongation at break and mechanical strength was measured. The sample with an area of 25 × 50 mm\(^2\) was tested with a crosshead speed of 5 mm/min. The test was carried out by using a universal testing machine (Shimadzu Trapezium lite x version 1.1.2) at room temperature, and a minimum of four samples was tested.

2.7 Gas Performance Analysis

For gas performance analysis, the membrane samples were coated by using a PDMS solution. Once it was coated, the membranes were analysed by using CO\(_2\) and CH\(_4\) gas.

2.7.1 Post-treatment before gas permeation test. Each of the membrane samples was cut into a small circle with an outer diameter of 5.8 cm. To reduce the generation of voids and pinholes formation on the fabricated membranes, they were immersed in the coating solution consists of 3 wt% polydimethylsiloxane in n-hexane for 3-5 seconds. Then, the membranes were placed in the oven for 3 days at 60 °C in order to cure the coating. Afterwards, the coated membrane was tested for the gas separation performance of pure carbon dioxide and methane gas.

2.7.2 Gas permeation test. The analysis test for the coated membrane was evaluated using the gas permeation unit. This test was done to study the performance of each membrane on separating the gas. Pure gas carbon dioxide (CO\(_2\)) and methane (CH\(_4\)) was used, which permeate through the membrane placed on the cell permeation test. Gas with a different feed pressure of 2, 4, 6, 8, and 10 bar was used. The test was based on the pressure on feed steam and measure the gas flux across a known area and thickness of the membrane on the permeate phase. All the test was carried out at a temperature of 25 °C. The data measurement was taken for the permeate gas [(CO\(_2\)), (CH\(_4\))] to reach a volume of 1 cm. By using a bubble flow meter, the gas for volume was measured. Thus, the pressure-normalized flux or gas permeance was calculated by using equation (1).

\[
\frac{Q_i}{A \times (\Delta P)} = \frac{P_i}{\Delta P}
\]  

(1)
Where $\Delta P$ is the differential pressure across the membrane (bar), $A$ was the surface area of membrane ($cm^2$), $Q$ was the volumetric flow rate of gas at standard temperature and pressure. The gas permeance was expressed in the unit of GPU, which stated in equation (2).

$$GPU = 1 \times 10^{-6} \left(\frac{cm^3 (STP)}{cm^2 \text{ sec cm Hg}}\right) \quad (2)$$

The ideal selectivity of the membrane was the ratio of gas permeance, as shown in equation (3).

$$\alpha_i/j = \frac{P_i}{P_j} \quad (3)$$

### 3. Results and Discussion

#### 3.1. Characterization of Neat membrane and mixed matrix membrane

The addition of halloysite nanotubes and activated carbon into the polysulfone membrane are further characterized by using FTIR. The objective of this characterization is to validate the presence of the HNTs and AC. The membranes were also characterized by using SEM and EDX to study the morphology structure of membranes and the effect of the addition of activated carbon and halloysite nanotubes on the changes in the morphology structure of membranes and elemental dispersion in MMMs. On the other hand, tensile strength is studied to determine the mechanical strength of mixed matrix membranes after the effect of the addition of activated carbon and halloysite nanotubes on the changes in mechanical strength compared to the neat membrane.

**3.1.1 Functional Groups present in Different Membrane.** The FTIR spectrum for the neat membrane, which portrays a graph of the percentage of transmittance versus wavenumber is shown in Figure 1. The characteristics peak for this neat membrane were at a wavenumber of 2967.47 cm$^{-1}$ which corresponds to the symmetric and asymmetric stretching vibration of C-H that involves the entire methyl group [14].

On the other hand, characteristics peak of 1486.93 cm$^{-1}$ and 1584.58 cm$^{-1}$ contributes to aromatic C=C bond stretching in the PSF chain [14]. Phenyl ring substitution band can be seen at the peak of 833.73 cm$^{-1}$ meanwhile, amine stretching is noticed at 1105.35 cm$^{-1}$ respectively. The most important functional group detected, which is symmetric O=S=O stretching of sulfonate group at characteristics peak of 1149.76 cm$^{-1}$[15].

![Figure 1. FTIR Results for Neat Membrane](image_url)
Figure 2 depicts the FTIR spectrum for MMMs-AC, where activated carbon mixed with polysulfone membrane. By referring to the spectrum, it can be observed that the characteristics peak for MMMs-AC contains some peak as the neat membrane with the addition of some new functional groups from activated carbon. MMMs-AC shows a new peak at 1676.08 cm\(^{-1}\) suggesting the quinones reflected in the C=O band. In characteristics peak of 1149.72 cm\(^{-1}\), shows a stretching vibration of the C-O group in ester, ether, phenol and alcohol [16][17]. Meanwhile, a band at 1409.20 cm\(^{-1}\) contributes to oxygen-containing functional group, which are C-O and C=O stretching vibration in the carboxylic group [18].

\[ \text{Figure 2. FTIR Results for MMMs-AC} \]

Figure 3 shows the FTIR spectrum for MMMs-HNTs, where halloysite nanotubes mixed with the polysulfone membrane. From Figure 3, it can be observed that MMMs-HNTs also consist of similar functional group as the neat membrane, with a few additions of a new functional group from elements in HNTs. In MMMs-HNTs, a peak at 3616.31 cm\(^{-1}\) shows a stretching vibration of Al-OH groups in the inner surface of HNTs [19]. The MMMs-HNTs spectrum is further characterized by stretching vibration of Si-O-Si group which the functional group comprises absorption peak at 1005.28 cm\(^{-1}\) [20]. Therefore, this FTIR analysis results confirm the presence of elements of activated carbon and halloysite nanotubes in the mixed matrix membrane.
3.1.2 Membrane morphology by using SEM. Membrane morphology of neat membrane, MMMs-AC, MMMs-HNTs is studied by using SEM. The effect of the addition of porous fillers (activated carbon, halloysite nanotubes) on the morphological properties is observed from the thickness of the skin layer to the development of micro-voids. Surface and cross-sectional of SEM micrographs of the different fabricated membranes are presented in Figure 4 and Figure 5.

The filler particles are homogeneously dispersed on the surface of all the membranes, as shown in Figure 4. Since the loading of fillers used was 1 wt% only, no severe agglomeration is visible (Figure 4). Figure 4(c) shows that at 1 wt% loading of halloysite nanotubes, a good dispersion of filler was observed on the membrane surface and smooth surface was formed due to the excellent compatibility of fillers with polymer matrix. The presence of halloysite nanotubes particles on membrane shown in Figure 4(c) confirmed by FTIR results for MMMs-HNTs as depicted in Figure 3. Since there are functional groups found on their exterior surface of halloysite nanotubes, this promotes better dispersion in the polymer matrix [21]. Meanwhile, in Figure 4(b), few formations of pinholes were visible, which may contribute to loss in the selectivity of gases.
Figure 4. SEM images for surface area of membranes at (Magnification ×1.50k) (a) Neat membrane, (b) MMMs-AC, (c) MMMs-HNTs

In Figure 5, the typical asymmetric membrane consists of two distinct layers; which are active skin layer and porous structure. Ideally, there are two sub-structure in the porous layer of a membrane, which are spongy type and finger-like sub-structure. Hence, the sub-structure should serve as good mechanical support for the skin layer. Previous research by Rezaee et al. (2015) proves that with the addition of fillers, a morphological structure of finger-shaped pores tapering towards the skin and oblong shape image also visible throughout the cross-section can be obtained [22].
Figure 5. SEM cross-sectional images at (Magnification of ×500) (a) neat membrane, (b) MMMs-AC (c) MMMs-HNTs

In Figure 5(a), the prepared neat PSf membrane shows two distinctive morphologies, namely few separated closed-end drop-like pores and sponge structure exist as a significant part of the membrane at the bottom of a membrane [23]. In Figure 5(c), there is no sponge layer; hence it can be seen some of the closed-end drop like pores replaced by finger-like pores with closed ends. Hence, the formation of a finger-like structure, caused by the presence of high concentrated nascent layer, which inhibits the solvent exchange rate from the top layer [24]. Hence, the finger-like pores in HNT cross-sectional area promote the gas permeances, as shown in the results of this study for the gas permeation test.

Membrane with 1 wt% of AC loading as depicted in Figure 5(b), shows that the spongy part of the membrane is diminished and the closed-end drop like pores turn into large and open-end macro-voids which expose to the bottom surface [10]. Furthermore, as can be seen for the MMMs-AC, the number of open-end macro-voids increased. Through a simultaneous exchange of solvent, when the membrane placed in the non-solvent (water), these causes the NMP molecules to merge together and forms large macro-voids [25].

The thickness of the skin layer and partial dense layer of the membrane is decreasing from neat membrane < MMMs-HNTs < MMMs-AC with 28.6 μm, 19.8 μm, and 11.9 μm (Figure 5). Hence, the thickness of MMMs-HNTs decreased by 30.8% compared to the neat membrane, while MMMs-AC decreases by about 58.4% respectively. But, the thickness of MMMs-HNTs increases by 66.39% from MMMs-AC. On the other hand, the thickness of the neat membrane is greater, and it should be another way around, and is postulated that the reason behind this phenomenon may be due to time taken for demixing. Moreover, the thickness of the skin layer reduces because of the faster de-mixing process between non-solvent and solvent. The thickness of the MMMs-AC skin layer decreased compared to the neat PSF membrane and MMMs-HNTs. Since activated carbon is a greater hydrophilic filler, it causes non-solvent which is water to diffuse into PSF polymer matrix and replaced by solvent easily; hence quick de-mixing occurs between non-solvent and solvent, reduces the skin layer thickness [30].
Hence, from here, can be conclude that for thicker skin layer like MMMs-HNTs, it has have greater selectivity but lower permeability and vice-versa for thinner skin layer [26].

Under circumstance where higher pressure was used, the thin skin layer could rupture due to finger-like pores formed, which act as weak points under pressure facilitating membrane failure [27]. From the results of SEM analysis, an image in Figure 5(b) consists of a larger number of finger-like pores compared to Figure 5(c), which probably can damage the membrane if higher pressure was used. From this analysis, it can be concluded that the incorporation of halloysite nanotubes into the polymer matrix gives a better morphology structure of the membrane as compared to MMMs-AC and neat membrane. Therefore, since there are some changes in the thickness of the skin layer and overall morphological properties, these may affect the gas transport properties of different membranes.

3.1.3 Energy Dispersive X-Ray. EDX used to identify the elements present in sample membranes in order to prove the even distribution of activated carbon and halloysite nanotubes in MMMs. In this study, elemental analysis carried out for two membranes, which are MMMs-AC, and MMMs-HNTs. Hence, the incorporation of 1 wt% of activated carbon and halloysite nanotubes further analyzed by Energy Dispersed X-ray spectrometer (EDX) analysis.

Based on Figure 6 shows the EDX mapping for the neat membrane. An intensity of carbon, oxygen, and sulphur elements with a percentage of 60.72%, 7.97%, and 10.74% shown for a neat membrane. The polysulfone element was detected in the neat membrane and also supported by previous research [28][29].

![EDX mapping](image)

**Figure 1.** Elemental spectrum and elemental composition of the neat membrane

Figure 7 displays elemental analysis for MMMs-AC. The presence of activated carbon in the polymer matrix was only verified by carbon, and oxygen with a percentage of 36.21%, and 5.17%. The results show that there is an absence of some elements of activated carbon. This phenomenon occurs may be due to agglomeration of activated carbon in the membrane.
Hence, in Figure 8, the EDX analysis for MMMs-HNTs shows a peak for oxygen, aluminium, and silicon with a weight percentage of 18.55%, 4.77%, and 5.66%. The present elements corresponding to the chemical structure of raw HNTs of $\text{Al}_2\text{Si}_2(\text{OH})_4 \cdot n\text{H}_2\text{O}$ with a molar ratio of 1:1 Al to Si ratio [30][31]. Meanwhile, due to the sputtering of the gold coating during SEM application, traces of gold found in all of the three membranes.

Furthermore, in Table 3 shows the EDX elemental composition of the neat membrane, MMMs-AC, and MMMs-HNTs. It can be concluded that the elemental analysis results prove that halloysite nanotubes are scattered throughout the polymeric matrix regardless of the loadings of fillers in the membrane with uniform distribution. Thus, the EDX analysis revealed the presence of halloysite nanotubes, and no agglomeration was observed.

| Elements  | Neat membrane | MMMs-AC | MMMs-HNTs |
|-----------|---------------|---------|-----------|
| Carbon, C | 60.72         | 36.21   | 41.29     |
| Oxygen    |               |         |           |
| Aluminum  |               |         |           |
| Silicon   |               |         |           |
| Gold      |               |         |           |

Figure 2. Elemental spectrum and elemental composition of MMMs-AC

Figure 3. Elemental spectrum and elemental composition of MMMs-HNTs

Table 3. EDX Elemental Composition of Neat membrane, MMMs-AC and MMMs-HNTs
Oxygen, O  &  7.97  &  5.17  &  18.55  \\  
Sulphur, S  &  10.74  &  0.00  &  0.00  \\  
Aluminium, Al  &  0.00  &  0.00  &  4.77  \\  
Silicon, Si  &  0.00  &  0.00  &  5.66  \\

3.1.4 Mechanical strength of different membrane by using tensile test. Mechanical properties such as tensile strength and elongation at break were analyzed for PSF neat membrane and mixed matrix membrane. Since the incorporation of fillers affects the morphology structure, consequently it will have an effect on the mechanical properties of MMMs. The fundamental reason for the addition of inorganic particles into the polymer matrix is to modify the structure of the membrane by improving the mechanical properties such as tensile strength, and elongation at break. Conversely, non-homogenous dispersion of fillers causing the formation of the defective structure of the membrane and weakens the mechanical properties of such membrane. Figure 9 shows the overall stress-strain curve using data in Table 4.

![Figure 4. Overall stress-strain curve of the neat membrane, MMMs-HNTs and MMMs-AC](image)

Another key factor that affects the mechanical strength is the interfacial interaction between inorganic fillers and the polymeric matrix. Figure 10 and Table 4 show the average tensile strength and the elongation at break for the neat membrane, MMMs with activated carbon and halloysite nanotubes. Among three types of membrane, MMMs-HNTs displays the highest tensile strength followed by the neat membrane and MMMs-AC of 8.09 MPa, 7.99 MPa, and 7.62 MPa respectively. Similar results by Nagla et al. (2020), where the mechanical strength for MMMs-HNTs increased at a low loading of HNTs in the polymer matrix [32]. This is most probably is due to the cylindrical tube-like structure of HNTs, which increases the surface area of interaction between the polymer matrix and HNTs. Besides that, the higher mechanical strength of MMMs-HNTs also because of the enriched hydroxyl groups found at HNTs, which improves the molecular force of attraction and hydrogen bonding between HNTs and PSF membrane [30].
Figure 5. Tensile strength and elongation at break for membranes

Table 4. Tensile Test Results for the Membranes

| Type of membrane       | Neat PSF membrane | MMMs with HNTs | MMMs with AC |
|------------------------|-------------------|----------------|--------------|
| Average tensile strength (MPa) | 7.99             | 8.09           | 7.62         |
| Elongation at break (%) | 16.70            | 14.8           | 14.58        |
| Elastic modulus (MPa)   | 231.95           | 246.78         | 217.35       |
| Maximum load (N)        | 45.06            | 46.78          | 56.88        |

Based on Setiawan et al. (2019), the elongation at break of the membrane depends on the ability of inorganic filler to restrict polymer chain movement and circumvent the phenomena of large macroscale extension. Lower elongation at break in MMMs-HNTs is due to its strong interfacial interaction between PSF polymer matrix and evenly distributed HNTs and also because of the brittleness of membrane in the presence of clay, which known as nanocomposites [4]. Moreover, Mohamed et al. (2020) also found that the elongation at break for MMMs-HNTs decreases compared to the neat membrane, which is due to the incorporation of nano-sized inorganic materials into the polymeric membrane [30].

The neat PSF membrane exhibited the largest elongation of 16.70%, which proves that the polymer chain is more flexible, where it can be stretched to a greater extent because of the weak interfacial interaction between the molecules of the polymer. Meanwhile, the mixed matrix membrane sample with 1 wt% of activated carbon content showed the second least elongation at break than MMMs-HNTs with 14.58%. MMMs-HNTs composite membrane displays significant increment in both tensile strength as well as in elongation at break with 8.09 MPa and 14.80% compared to MMMs-AC. Therefore, the mechanical strength of the membrane was much better when halloysite nanotubes are added into the PSF polymer matrix.

3.2 Gas Separation Performance

The gas permeation test is carried out in order to study the gas separation performance of neat and mixed matrix membrane when CO₂ and CH₄ gas flow through it. Hence, the parameters studied are (1) effect of the addition of fillers on gas separation performance on the membrane, (2) effect of different pressure on gas separation performance on the membrane, and (3) effect of coating of the membrane using PDMS on gas separation performance on the membrane.
3.2.1 Effect of Addition of Fillers on Gas Separation Performance on Different Types of Membranes. Neat membrane, MMMs-AC, and MMMs-HNTs membranes are tested in order to evaluate its selectivity and permeability for the separation of CO$_2$/CH$_4$ gas at a fixed pressure of 2, 4, 6, 8, 10 bar which carried out at 25°C room temperature. The permeance and selectivity values of CO$_2$ and CH$_4$ for neat and mixed matrix membrane are tabulated as a function on the effect of filler in Figure 11 and Figure 12.

![Figure 6. CO$_2$ and CH$_4$ permeance of different uncoated membranes at a pressure of 2 bar](image)

![Figure 7. CO$_2$ and CH$_4$ selectivity of the uncoated membrane at a pressure of 2 bar](image)

At the pressure of 2 bar, the overall results exhibit a decrease in CO$_2$ and CH$_4$ permeance from the neat membrane to MMMs with activated carbon; which is 12.43 and 18.2 to 4.46 and 4.11, showing that there is a decrease of 64.1% for CO$_2$ permeance and 77.4% for CH$_4$ permeance respectively. Nevertheless, the selectivity of the membrane increased for MMMs-AC and MMMs-HNTs compared to the neat membrane. This is because the addition of the porous fillers selectively permits the gas through the pores. Thus, the incorporation of fillers into the polymeric membrane also increases the selectivity of CO$_2$ gas relative to CH$_4$ gas.

According to Koros et al. (2003), porous inorganic fillers with specific pores usually have higher selectivity and permeability that surpasses Robeson Upper bound [33]. Consequently, when such types of fillers are added to the polymeric matrix, this improves the sieving properties, and the mixed matrix membrane tends to have higher selectivity compared to the neat membrane [34]. The fillers inside the PSf polymer matrix possess molecular sieving effect and forms a permeable channel, which allows for the better separation of gas compared to the neat membrane.
Through micro-mesoporous activated carbon in PSf polymeric matrix, more adsorbable gas (CO$_2$ transported against less adsorbable gas CH$_4$) which is by surface diffusion [35]. In the surface diffusion, the highly adsorbable gas molecule (CO$_2$) adsorbed on the membrane surface, and then move along to the permeate side on the pore surface until desorbing the gas. In this type of mechanism, the highly adsorbable gas molecules (CO$_2$) have greater permeability compared to less adsorbable gas molecules (CH$_4$) with lower permeability. This causes the selectivity to be higher compared to the neat membrane. Meanwhile, in MMMs-HNTs smaller gas (CO$_2$) transported through molecular sieving filler, whereby diffusion of larger molecules (CH$_4$) hindered by HNTs.

Although the results at 2 bar seem to be satisfactory, but the selectivity of MMMs-HNTs shows a slight decline as compared to MMMs-AC from 1.086 to 0.82. This is probably due to the formation of surface defects in MMMs-HNTs where CH$_4$ gas molecules pass through the non-selective voids, which results in poor MMMs selectivity. Thus, this section can conclude that the addition of fillers increases the selectivity of CO$_2$/CH$_4$ of the membrane. Hence, the results show that the MMMs with the incorporation of molecular sieving effect porous fillers, selectively separate the gases.

3.2.2 Effect of Different Pressure on Gas Separation Performance. The effect of different and increase of feed pressure, which is 2, 4, 6, 8 and 10 bar on gas permeability and CO$_2$/CH$_4$ selectivity, investigated for neat membrane and MMMs displayed in Figure 13, Figure 14, and Figure 15.

![Figure 8. CO$_2$ permeance at different pressure](image)

For all the MMMs in Figure 13, CO$_2$ permeance starts to decrease with increasing the feed pressure from 2 bar to 10 bar. The declining trend shows that for all fabricated MMMs, indicates there is no plasticisation occurred since no noticeable increase in CO$_2$ permeance at pressure up to 10 bar. Similar results by Shafie et al. (2019) also showed that both the CO$_2$ and CH$_4$ permeance shows a decline trend with increasing pressure that could be due to the fact of the strong interaction between polymer and fillers which induced the absorption of CO$_2$ without any formation of swelling in the membrane [36]. Hence, this proves that incorporation of HNTs and AC in the polymer phase restricts the mobility of the polymer chain and does not induced plasticization in MMMs.

Figure 14 shows the CH$_4$ permeance for pressure at 2 to 10 bar. At 2 bar, the results show a decrease of CH$_4$ permeance for MMMs-HNT of 42.16 % compared to the neat membrane at the same pressure. This proves that by adding HNTs the CH$_4$ permeance decrease, thus increasing the gas separation performance of the membrane. Moreover, this also can be explained through the structure of HNTs where the inner surface of cylindrical HNTs allows the additional transport channel for CO$_2$ gas molecules. However, HNTs does not supply any additional transport channel for CH$_4$ gas, because it is barely to be adsorbed to HNTs and also due to weak interaction between HNTs and CH$_4$ gas molecules.
Thus, this is also in agreement by the increase in separation factor, where the selectivity of MMMs-HNTs with 15.83 at 2 bar pressure compared to the neat membrane and MMMs-AC. This result also supported by SEM image, where on the MMMs-HNT, there is an absence of interfacial gaps between HNTs and polymer matrix and proper distribution of particles on the polymer matrix.

![Figure 9. CH₄ permeance at different pressure](image)

From the bar chart in Figure 15, it can be seen that the MMMs-HNTs show better selectivity towards gas as compared to MMMs-AC. At a pressure of 2 bar, the selectivity is increased to 15.83 compared to MMMs-AC with only 7.06 respectively. Hence, these results show that the incorporation of HNTs into PSF polymer matrix increases the selectivity by 10 times as compared to MMMs-AC. This is due to the fact of the unique hollow tubular structure of HNTs, which contributes to the rapid flow of gases through cylindrical of HNTs and enhance the selectivity of the membrane. In another way around, the selectivity of the neat membrane is higher, which is from 11.93 to 7.06 compared to MMMs-AC. This may be due to improper mixing of casting solution or sedimentation of activated carbon during the formation of membrane solution. Other than that, this can be supported by SEM results, which shows that MMMs-AC is not suitable to be used for gas because of a greater number of finger-like pores that probably can damage the membrane if high pressure is used.

![Figure 10. Selectivity of the membrane at different pressure](image)

From the results shows that the selectivity is higher and decreases in permeability, it is mostly attributed due to the presence of a rigidified polymer layer around the fillers. This is probably due to the incorporation of porous fillers into the polymeric matrix. In this case, the free volume decreases; however, there is no gap formed in the interface, thus allowing stronger contact between the fillers and...
polymeric matrix and also restrict the movement of polymer chains [37]. Here the selectivity CO\textsubscript{2}/CH\textsubscript{4} increases in polymer layer rigidification case because the membrane has greater resistance in transporting larger kinetic diameter of gas molecules. Thus, this analysis proves there is no plasticization occurs as pressure increases due to the stronger interaction between polymer and filler. Therefore, improvement in selectivity indicates that incorporation of halloysite nanotubes at 1 wt% is noteworthy for the CO\textsubscript{2} separation.

3.2.3 Effect of Coating on the Performance of Different Membrane. Usually, the permeability of CO\textsubscript{2} is higher compared to CH\textsubscript{4}, for all the coated membrane. This is because the kinetic diameter of CO\textsubscript{2} is smaller than CH\textsubscript{4}; however, the condensability of CO\textsubscript{2} is higher than CH\textsubscript{4} that exhibits higher permeability as compared to CH\textsubscript{4}. MMMs and the neat membrane was further modified in order to investigate the effects of PDMS coating on gas separation performance.

As depicted in Table 5, both CO\textsubscript{2} and CH\textsubscript{4} permeance for uncoated membranes is higher when compared to the modified membrane with PDMS. Thus, the difference in permeance causes both the gas penetrant to be more permeable by the formation of unselective defects in the uncoated membrane. This is the main reason why the selectivity of all uncoated membrane is lower than the coated membrane. As can be seen, the surface defects and pinholes formed on the surface layer of the membrane can be repaired through PDMS coating by forming a selective layer on the surface of the membrane and intended to reduce the blockage of gases permeation which causes a drop of both gas permeability [38].

The bar chart shows the selectivity of coated and uncoated for different membranes in Figure 16. Meanwhile, the selectivity of coated MMMs-HNTs membrane shows a tremendous improvement from 0.82 to 15.83 as compared to uncoated MMMs-HNTs. The result is also supported by previous studies done by Zulhairun et al., (2015), that shows an increment in the selectivity of gas when the MMMs are coated with PDMS [39]. The PDMS coating on membrane increases the selectivity of gas by decreasing the permeance of both CO\textsubscript{2} and CH\textsubscript{4}. Moreover, a high increment in selectivity could also be related when the membrane is fully coated; there is high solubility of gases in PDMS. Although, the result for selectivity for MMMs-HNTs is acceptable but the MMMs-AC has lower selectivity compared to the neat membrane. This is maybe due to incomplete drying of the coating layer on MMMs-AC. In conclusion, it is found that the PDMS coating was able to improve the separation performances of the membrane for all the three membrane samples.

![Figure 11](image-url)

**Figure 11.** Selectivity of uncoated and coated membranes at pressure of 2 bar

| Membrane Type | Selectivity |
|---------------|-------------|
| NEAT          | 0.829       |
| MMMs-AC       | 1.087       |
| MMMs-HNT      | 0.898       |

| Membrane Type | Selectivity |
|---------------|-------------|
| UNCOATED      | 11.958      |
| COATED        | 15.813      |

**Table 5:** Selectivity and permeance results for coated and uncoated membranes
Membrane | Pressure | Coated membrane | Uncoated membrane
|-----------|-----------|-----------------|-----------------|
|           | $P_{CO_2}$ | $P_{CH_4}$ | Selectivity, $\alpha$ ($CO_2/CH_4$) | $P_{CO_2}$ | $P_{CH_4}$ | Selectivity, $\alpha$ ($CO_2/CH_4$) |
| Neat      | 2          | 0.99        | 0.0830          | 11.93        | 12.43      | 18.20          | 0.68 |
| MMMs-HNTs | 0.76       | 0.048       | 15.83           | 6.12         | 7.47       | 0.82           |
| MMMs-AC   | 0.60       | 0.085       | 7.06            | 4.46         | 4.11       | 1.086          |
| Neat      | 4          | 0.35        | 0.042           | 8.33         | 6.98       | 10.29          | 0.68 |
| MMMs-HNTs | 0.43       | 0.036       | 11.94           | 3.05         | 4.71       | 0.65           |
| MMMs-AC   | 0.21       | 0.049       | 4.29            | 2.40         | 3.016      | 0.81           |
| Neat      | 6          | 0.15        | 0.052           | 2.88         | 4.55       | 6.94           | 0.65 |
| MMMs-HNTs | 0.19       | 0.026       | 7.31            | 1.81         | 3.51       | 0.52           |
| MMMs-AC   | 0.092      | 0.029       | 3.17            | 1.68         | 2.20       | 0.76           |
| Neat      | 8          | 0.096       | 0.046           | 2.087        | 3.16       | 5.11           | 0.62 |
| MMMs-HNTs | 0.11       | 0.022       | 5.00            | 1.38         | 2.78       | 0.51           |
| MMMs-AC   | 0.051      | 0.022       | 2.32            | 1.14         | 1.68       | 0.68           |
| Neat      | 10         | 0.054       | 0.067           | 0.81         | 2.26       | 3.59           | 0.63 |
| MMMs-HNTs | 0.075      | 0.017       | 4.41            | 0.90         | 1.76       | 0.51           |
| MMMs-AC   | 0.035      | 0.025       | 1.40            | 0.76         | 1.19       | 0.64           |

4. Conclusions
In this work, FTIR results prove the presence of elements of activated carbon and halloysite nanotubes compared to the neat membrane and therefore these shows that we have successfully fabricated all the mixed matrix membranes, namely MMMs-HNTs and MMMs-AC. Moreover, in addition to inorganic fillers changes the morphological structure from end drop like pores to closed finger-like pores and reduced the sponge-like structure along with the decrease of the thickness of the skin layer. The mechanical strength demonstrated an enhancement in tensile strength and elongation at break for MMMs-HNTs at a low loading of HNTs in PSF polymeric matrix compared to neat membrane and MMMs-AC. The results revealed that it is due to increase in surface area of interaction between polymer matrix and HNTs and owing to its feature of enriched hydroxyl groups at HNTs improve the molecular force and hydrogen bonding between PSF polymeric matrix and HNTs.

Gas permeation results revealed that rigidification of polymer chain layer caused a decrease in permeability and an increase in selectivity. For the gas separation performance, the results showed an overall increase in the mixed matrix membrane with HNTs over the neat membrane and MMMs-AC. The addition of halloysite nanotubes into polymeric matrix increases the selectivity to 15.83 compared to the neat membrane with only 11.93 and MMMs-AC with a selectivity of 7.06, at 2 bar. This claim supported by SEM results where finger-like pores formed in the cross-sectional area of MMMs-HNTs, promotes the gas permeance. In conclusion, incorporation of HNTs into PSf polymeric matrix not only improve the tensile strength and morphological properties of the membrane but also improves CO$_2$/CH$_4$ gas separation performance compared to activated carbon.

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