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Effect of surface-etched modification on halloysite nanotubes (HNTs) for polysulfone mixed matrix membrane in CO₂/CH₄ separation

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Abstract. Mixed matrix membranes (MMMs) were fabricated from a 25 wt% of polysulfone (PSf) with halloysite nanotubes (HNTs) selected as the inorganic filler. The incorporation of 1 wt% to 5 wt% of HNTs in the membrane is promising in improving the performance of the membrane for gas separation due to its barrier properties. HNTs was modified by surface-etched method before it is embedded into the membrane in order to reduce the interfacial defects as well as the agglomeration in the membrane. This study further investigated the improvement of the polymer-clay interface interaction, characterize the functional groups, structure and surface area of the newly modified clay and also mechanical properties of the membrane. From the FTIR spectra, it can be seen that the functional group of surface-etched HNTs reduced in intensities compared to the unmodified HNTs. There are no distinct changes in XRD pattern for both unmodified and modified HNTs and tensile strength shows an increment in MMMs embedded with modified clay compared to unmodified clays. The incorporation of surface-etched HNTs was able to improve the membrane properties to a desired membrane that can be applied in the CO₂ and CH₄ separation.

1. Introduction

Gas separation is one of the important steps in order to provide a healthy pipeline system. Carbon dioxide as it generally known is an acidic gas which its presence in the pipeline stream may cause damage to the pipeline itself. Existence of CO₂ in the stream would give a more acidic gas stream as well as giving a corrosion effect on the pipeline [1]. In the recent years, separating gases via mixed matrix membranes has caught the attention of researchers. The process of CO₂ capture specifically, by using membrane separation is promising as it involving high energy efficient, simplicity in operation and also environmentally sustainable according to [2]. It is not only help to provide a healthy gas stream but also promising a long-lasting usage of the pipeline and equipment. Mixed matrix membranes consist of two phases which are continuous phase and dispersed phase. These phases represent organic polymer and also inorganic fillers respectively. Nine types of polymers used in about 80% of gas separation [3]. However, this polymeric membrane did have some drawbacks as it resulting in different behavior for the permeability and selectivity of the membrane. Therefore, few researchers came out with a type of membrane with the incorporation of inorganic fillers. It is proven that by dispersing fillers which will act as molecular sieves, in the membrane,



could help to improve the performance of the membrane especially for its permeability and gas selectivity [2, 3].

Polysulfone is a glassy polymer that is often used in membrane separation. Glassy polymer has a rigid chain structures with a restricted segmental motion [4]. Many researchers have been using polysulfone as the polymer in continuous phase as it possesses good permeability and selectivity in gas separation [5, 6, 7, 8]. It is also a good polymer to be used for gas separation due to its mechanical, thermal and chemical stabilities [9]. HNTs generally possess 13.8 ± 1.4 nm of average lumen internal diameter and 30 to 70 nm of external diameter [10]. Previous studies show a better performance of membranes by using various types of inorganic fillers such as zeolites, carbon molecular sieves, metal organic frameworks (MOFs), carbon nanotubes and many more different kinds of fillers. However, the use of HNTs provide is favorable due to it is naturally abundant and can be purchased in a low cost. It is also proven to be environmentally safe upon operation.

Modification of the inorganic filler surface have proved to be able to help in the improvement of the membrane's performance. By modifying the outer surface of the nanotubes could help in improving the affinity of the HNTs towards the non-polar media [11]. CO₂ adsorption and selectivity can be improved by increasing the alkalinity via chemical modification of the HNTs [12]. Surface-etching modification of the HNTs supposedly resulting in increasing roughness of its surface which can help in tuning the supports properties of the HNTs as well as act as adsorption sites and active centres chemical reaction directly [13]. An increment occurred in term of loading capacity and surface area from 9 to 35% and 200-300 m²/g respectively, after the HNTs underwent etching process with sulphuric acid [14]. This increment is important since the HNTs depends on its loading capacity and lumen size to function well [11]. On the other hand, selective etching by acidic treatment of the alumina sheets may results in enlarged cavity of the clay nanotubes [15].

Various methods have been done to increase the inorganic filler dispersion in the membranes as well as reducing the interfacial defects of the MMMs. For example, the sed in-situ growth of filler particles in a polymer particle suspension for the membrane preparation [16, 17]. Other than that, the surface inorganic filler also has been introduced with functional groups and metal nanoparticles which help to increase solubility of penetrant in the nanocomposite membranes [4, 18]. Besides, there are also studies done on incorporating MMMs with reduced inorganic filler size such as [19], which reduced the particle size of the graphene oxide and ZIF/80 and [20], with reduced crystal sized of Cu-BTC that has shown the increment in permeability and solubility of the MMMs.

This study was conducted to modify the HNTs by increasing the surface roughness via surface-etching process and thus help in reducing interfacial defects as well as improving the polymer-clay interaction. HNTs underwent the modification were incorporated into the PSf membrane and characterized by using FTIR, XRD and also tensile strength. Based on these analyses, the membranes have improved properties that are desirable for better gas separation.

2.0 Experimental

2.1. Materials

The polymer used in this research is polysulfone supplied by Sigma Aldrich in the form of pellets while HNTs used are also purchased from the same supplier under the same trade which is Sigma-Aldrich. Solvent used to dissolve the PSf is N-methylpyrrolidone (NMP) under the trade of Merck. For surface-etching process of the HNTs, sodium carbonate (Na₂CO₃) supplied by HmBG Chemicals and sodium nitrate (NaNO₃) supplied by Merck were used.

2.2. Modification of HNTs

Surface-etched HNTs were prepared by grounding 0.6 g of Na_2CO_3 , 10.0 g of NaNO_3 and 2.0 g of raw HNTs powders in a mortar. After that, the mixture was put into a ceramic crucible and heated up for 1 hour at 350°C with heating rate of $5^\circ\text{C}/\text{min}$. The mixture was let to cool down before washing with diluted nitric acid and deionised water to remove soluble salts and impurities from the mixture. Lastly, the mixture was dried overnight in a vacuum oven at 80°C [21].

2.3 Membrane fabrication

Neat membrane preparation started with the PSf being dried in an oven at 60°C for 24 hours to ensure that the moisture in the PSf is fully dried. Then the PSf were mixed with N-methylpyrrolidone (NMP) with the ratio of 25:75 wt%. This mixture was stirred by using overhead stirrer at 215 rpm until the PSf fully dissolved. For MMMs, the HNTs were mixed in the NMP prior to the addition of PSf.

After mixing, the solution was sonicated in a water bath for 40 minutes with loosened cap to release air bubbles formed during the stirring process. Followed by this process, the solution was left overnight to further remove bubbles trapped in the solution. The next step was casting the solution to form a membrane by pouring a small amount of the solution were poured onto clean glass plate and casted. Then the membrane formed was soaked in water bath overnight and then transferred and immersed in methanol solution for 4 hours to further remove the solvent in the membrane. The membranes were then dried for 3 days before characterization [22].

Table 1. Mixed matrix membranes preparation formulation.

Membranes	PSf (wt%)	NMP (wt%)	HNTs (wt%)
U1	25	75	1 wt% unmodified
U2	25	75	2 wt% unmodified
U3	25	75	3 wt% unmodified
U4	25	75	4 wt% unmodified
U5	25	75	5 wt% unmodified
SE1	25	75	1 wt% surface-etched
SE2	25	75	2 wt% surface-etched
SE3	25	75	3 wt% surface-etched
SE4	25	75	4 wt% surface-etched
SE5	25	75	5 wt% surface-etched

2.4 Membrane Characterization

The spectra from FTIR that obtained by using fourier transform infrared (FTIR) with the attenuated total reflection (ATR) accessory conducted by Perkin Elmer Spectrum 100 with wavelength ranging from 400 to 4000 cm^{-1} . This analysis was used to determine the successfulness of the etching process of the HNTs by studying the functional group of the HNTs as well as the MMMs. X-ray diffraction (XRD) data were obtained by using X Pert Pro XRD with generator voltage and tube current at 40 kV and 230 mA respectively with Cu $\text{K}\alpha_1$ at 0.154056 nm and $\text{K}\alpha_2$ at 0.154439 nm . The tensile strength was done by using a tensile test machine, Shimadzu Trapezium Lite X Version 1.1.2. Prior to the test, membranes were cut into a rectangular

with the dimension of 25 x 50 mm². The membranes were tested with 5 mm/min of cross head speed. The tensile strength and elongation at break of the membranes were obtained.

3.0 Results and Discussion

3.1 FTIR

3.1.1 Unmodified and Surface-etched HNTs

The modified powder HNTs were sent for FTIR in order to identify the changes in the composition of the modified and unmodified HNTs. Figure 1 shows the FTIR spectra of the unmodified (**U**) and surface-etched (**SE**) HNTs powder. From the spectrum of surface-etched HNTs, it can be seen that there is a significant reduction of the intensity of the stretching vibration at the wavelength of 3963 and also 3620 cm⁻¹ if compared to the unmodified HNTs. These reductions are due to the loss of O-H group during the etching process that occur on the chemical bonds of the silica and alumina sheet [13]. Other than these peaks, surface-etched HNTs show almost similar composition characteristics as the unmodified HNTs. However, peak at 1347 cm⁻¹ of surface-etched HNTs shows the significant difference of these spectra. It might be due to the hydroxyl vibration which contribute to the presence of adsorbed water molecules [23]. The bending vibrations peak of Si-O group can be found at wavelength 519 and 522 cm⁻¹ for unmodified and surface-etched HNTs respectively. At frequencies 441 and 449 cm⁻¹ shows the presence of Al-O group and peaks at frequencies 725 and 745 cm⁻¹ shows the presence of the Si-O-Al for both surface-etched and unmodified HNTs respectively. From this modification, it can be seen that the intensity of bending vibration of the Al-OH group is reduced at the frequency of 906 cm⁻¹ of unmodified HNTs and 910 cm⁻¹ of surface etched HNTs. The weakening of these stretching vibrations was due to the breakage of the Si-O bond on the etching site [21].

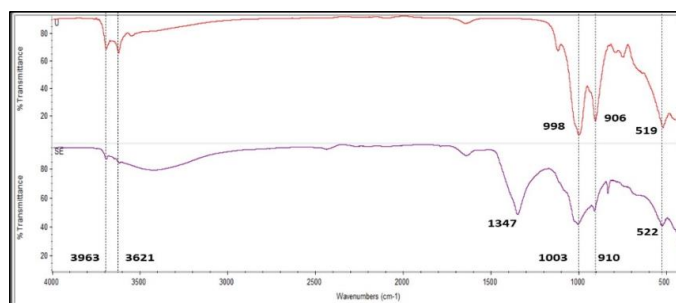
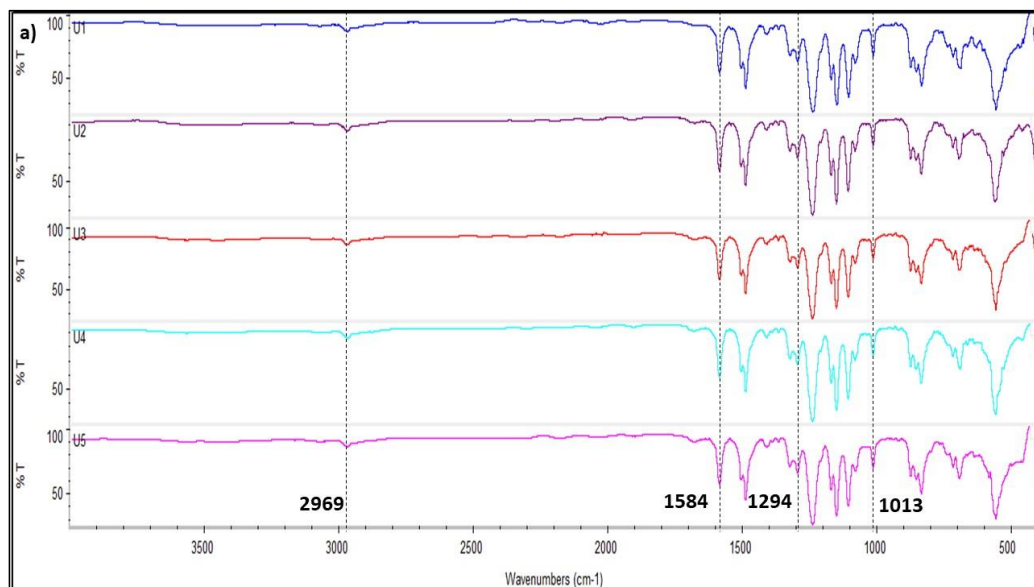


Figure 1. FTIR spectra of unmodified and surface-etched HNTs.

3.1.2 MMMs Embedded with Unmodified and Surface-etched HNTs

From the figure 2a, the spectra of MMMs with unmodified HNTs can be seen from 1 wt%, 2 wt%, 3 wt%, 4 wt% and 5 wt%, while figure 2b shows the spectra for MMMs with surface-etched HNTs from 1wt%, 2wt%, 3wt%, 4wt% and 5wt%. As can be seen from the figure, the spectra show that there is no significant

difference between the different of the unmodified HNTs embedded into the membrane. Almost all of the same spectra can be seen from 1 wt% to 5 wt% of HNTs in the membrane. Peak ranging at 2966 to 2969 cm^{-1} from **U1** to **U5** represent the stretching vibration of the C-H bond in polysulfone. All of these membranes show the peak of 1584 cm^{-1} and 1294 cm^{-1} which contribute to the stretching vibration of the C=C benzene ring and O=S=O bond of the polysulfone respectively. Si-O and Al-O peak of the HNTs can be observed at the peak ranging from 1013 to 1080 cm^{-1} . By comparing both of these spectra it can be seen that no distinct changes can be seen as both consist of the same materials and chemicals used during membrane fabrication. However, the intensity of the peak representing the Si-O bond seems to be weakened for MMMs incorporated with surface-etched MMMs due to the etching process that took place at the etching site of the HNTs as explained in 3.1.1.



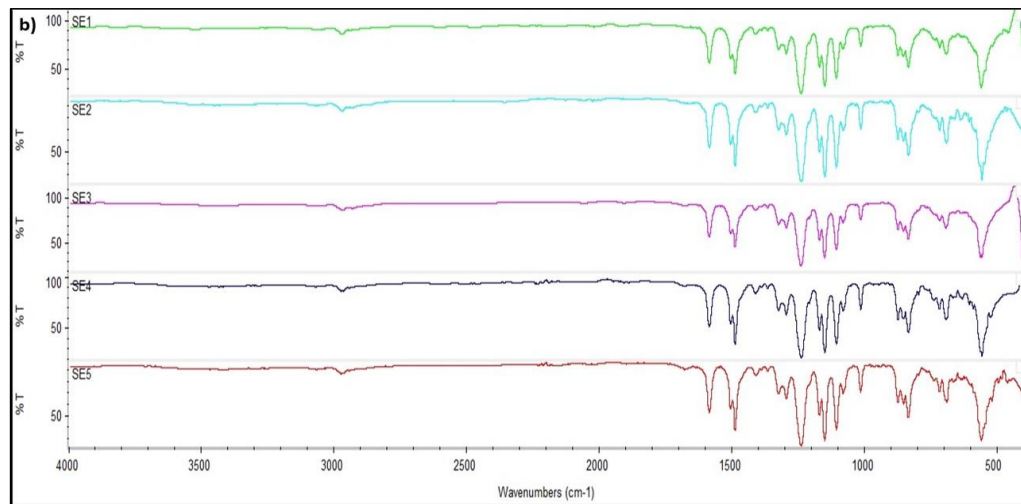


Figure 2. FTIR spectra for MMMs with (a) unmodified HNTs and (b) surface-etched HNTs

3.2 XRD patterns for unmodified and surface-etched HNTs

Figure 3(a) and (b) shows the comparison in XRD pattern of both unmodified and surface-etched HNTs. From both of these figures, there is no significant difference could be found. This has proved that surface treatment does not give a huge effect on the phase structure of the HNTs [21]. According to the figure, peak $2\theta=11.8$ contribute to the d_{001} diffraction plane with a basal spacing of 0.74nm can be seen in both XRD pattern of MMMs. Peak at $2\theta=24.8$ can be observed in both patterns shown as the d_{002} diffraction plane with 0.358nm basal spacing. Both of these peaks are attributed to the dehydrated halloysite structure [10]. Tubular structure of the HNTs can be confirmed by the presence of intense diffraction at $2\theta=19.87$. This peak which has 0.446nm basal spacing is attributed to the d_{002} plane. SiO_2 can be seen at the diffraction peak at $2\theta=26.6$ with basal spacing 0.334nm and attributed to the d_{020} plane [24].

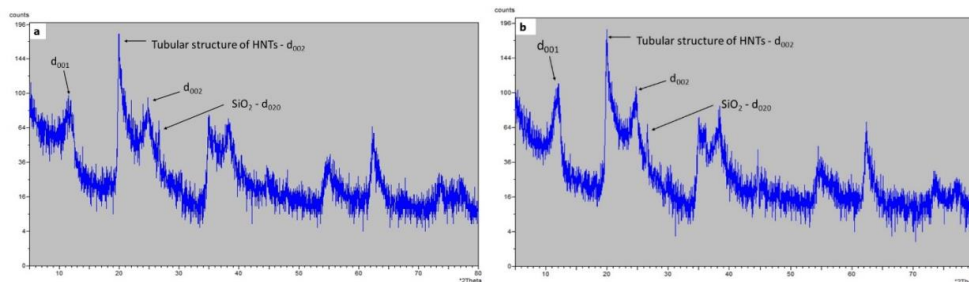


Figure 3. XRD pattern for (a) unmodified and (b) surface-etched HNTs

3.3 Tensile strength of the membrane

From the data obtained, tensile strength of the membrane can be calculated and thus shown in graphs below with membranes embedded with unmodified HNTs (**MU**) versus membranes incorporated with surface-etched HNTs (**MSE**). As can be seen in the graph from figure 4a, for the MMMs with unmodified HNTs, the tensile strengths are slightly increase from 1wt% to 5wt% of HNTs embedded. While for MMMs with surface-etched HNTs, the tensile strength fluctuated as the weight loadings of the HNTs increases. This fluctuating phenomenon could be due to the agglomerated HNTs in the membrane. There is an increment in MMMs with surface-etched HNTs compared to unmodified HNTs. According to the graph in figure 4b, it can be seen that the elastic modulus of the MMMs increases as the weight percentage of the HNTs embedded increases for both types of membranes. This could be attributed to the better dispersion and good interaction of the HNTs in the polymer matrix. However, at 5wt% of HNTs in both types of the MMMs seems to be decreases which might be due to poor dispersion of the HNTs since the filler has the highest probability to be agglomerated at this concentration [25]. The elongation at break for both types of MMMs is shown in figure 4c. From this chart, it can be seen that the elongation at break of both MMMs were fluctuated as the HNTs loadings increases. However, the flexibility of MMMs did increases as the surface-etched HNTs were added into the polymeric membrane.

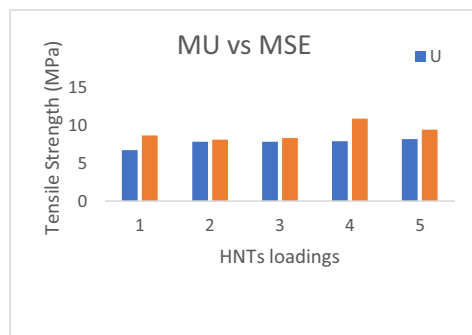


Figure 4a. Tensile strength of MMMs incorporated with unmodified vs surface-etched HNTs

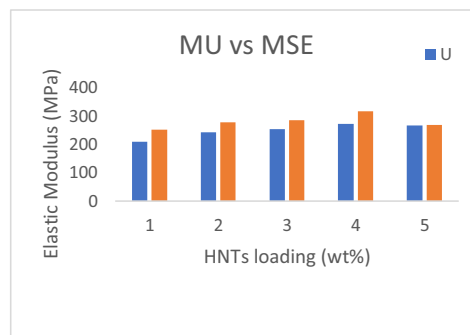


Figure 4b. Elastic modulus of MMMs incorporated with unmodified vs surface-etched HNTs

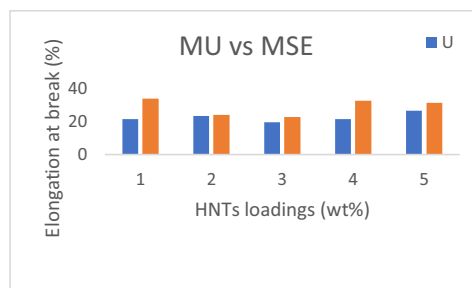


Figure 4c. Elongation at break of MMMs incorporated with unmodified vs surface-etched HNTs

4.0 Conclusion

Surface-etched HNTs were prepared through alkali-etching process by using sodium carbonate (Na_2CO_3) and sodium nitrate (NaNO_3) as the main chemicals. Mixed matrix membranes were applied with this modified HNTs starting from 1 wt% to 5 wt%. FTIR shows a desirable spectrum of surface-etched HNTs compared to unmodified HNTs. Modified HNTs shows a similar peak pattern to the unmodified HNTs which shows that the modification did not alter the phase structure of the HNTs. While mechanical strength of the membranes was improved with the incorporation of the surface-etched HNTs. From this analysis, it is envisaged that surface-etched HNTs could help to improve the MMMs performance in separating gases.

5.0 Reference

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