

Mixed Matrix Membranes Incorporating of Polyethersulfone-Functionalized Multi-Walled Carbon Nanotubes to Enhance High Performance CO₂ Separation

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Abstract: Mixed matrix membrane comprising carbon nanotubes embedded in polymer matrix have become one of the emerging technologies and have been actively discussed in contemporary membrane separation literature. The mechanical strength of conventional membranes is one of the limitations in their applications. In other hand, the resulting carbon nanotube-mixed matrix membrane offers a viable route to overcome the limitations demonstrated by the conventional polymeric and inorganic membranes. A new type of mixed matrix membrane consisting of functionalized carbon nanotubes and polyethersulfone is prepared for biogas purification application. PES mixed matrix membrane with and without modification of carbon nanotubes were prepared by a dry/wet phase inversion technique using a pneumatically flat sheet membrane casting machine system. The modified carbon nanotubes were prepared by treating the carbon nanotubes with chemical modification using Dynasylan Ameo (DA) silane agent to allow PES chains to be grafted on carbon nanotubes surface. The results from the FESEM, DSC and FTIR analysis confirmed that chemical modification on carbon nanotubes surface had taken place. Meanwhile, the nanogaps in the interface of polymer and carbon nanotubes were appeared in the PES mixed matrix membrane with unmodified of carbon nanotubes. The modified carbon nanotubes mixed matrix membrane increases the mechanical properties and the permeability of methane gas. For PES-modified carbon nanotubes mixed matrix membrane the maximum selectivity achieved for CO₂/CH₄ is 34.21.

Key words: Mixed matrix membrane • Carbon nanotubes • Gas separation

INTRODUCTION

One of the most important challenges that our world will face in the twenty-first century will be continuing to meet the ever increasing energy needs of its citizen. Along with the need to find a renewable long term energy source is the need to find a more environmental friendly one. One of the promising candidates as a power source solution for the future world energy problem is biomass. Biomass includes trees, crops, plants, agricultural and forest residue, wastes from food and beverage manufacturing effluents, animal waste, animal manure, sludge from waste water treatment plants and the organic

fraction of domestic waste [1]. Common terminology to describe the biological origin of a product includes terms such as biofuel, bioenergy and biogas. There are three major categories of biochemical technologies developed for biomass or biogas production; ethanol fermentation, biodiesel production and anaerobic digestion [2]. The biogas is composed of methane (50-70%), carbon dioxide, water vapour and trace gases such as ammonia and hydrogen sulphide.

The utilization of biogas as an efficient energy source depends strongly on its methane concentration. Therefore, biogas purified and enriched in methane can be used for household applications, automobile fuel

(liquefied) or electricity generation. This can be done by compressing the gas in cylinders, what is possible only after removing CO₂, H₂S and water vapour. There is a lot of potential if biogas could be made viable as a transport vehicle fuel like CNG, by compressing and filling the cylinders in it after scrubbing and drying. Enrichment of methane in biogas to have fuel of higher calorific value can be achieved by removal of carbon dioxide. Current technologies to purify off-gas and increase its caloric value have been primarily limited to physicochemical methods such as chemical separation, membrane separation, cryogenic separation as well as adsorption.

Currently, membrane separation of gases has emerged into an important unit operations technique offering specific advantages over more conventional separation procedures such as absorption, distillation, scrubbing and amine treatment [3]. At the present, polymeric membranes dominate the membrane separation field due to the fact that they are well developed and quite competitive in separation performance and economics. The choice of membrane material will be dictated by the nature of the gases mixture to be separated. Glassy polymers such as polysulfone, polyethersulfone, polyimide and ethyl cellulose which are known to have high mechanical stability and desirable inherent transport properties at high temperature are more commonly used [3]. Despite concentrated efforts to tailor polymer structure to affect separation properties; current polymeric membrane materials have seemingly reached a limit in the trade-off between productivity and selectivity [4]. Pure polymer membranes are oftentimes shows several limitations as low selectivity, high temperature instability and swelling and decomposition in organic solvents. Hybrid membranes composed organic- inorganic has attracted attention as the future membrane material. Hybrid membranes or mixed matrix membrane concept combines the advantages of high separation capabilities of the molecular sieves and the desirable mechanical properties and economical processing capabilities of polymers [3-5]. Many studies have reported that the separation performance of mixed matrix membrane could be improved by integrating porous or nonporous inorganic filler such as zeolite, silica, carbon molecular sieve and activated carbon. Currently, significant efforts have been devoted in fabrication of mixed matrix membrane by use carbon nanotubes as great potential filler [6]. There are two basic types of CNT: single-wall carbon nanotubes (SWNT) and multiwall carbon nanotubes (MWNT) [7]. In this respect more attention of researchers is devoted towards for fabrication of the

mixed matrix membranes by dispersing either single walled (SWNT) or multi walled (MWNT) carbon nanotubes into various polymer matrices. The properties of polymer nanocomposites containing carbon nanotubes depend on several factors in addition to the polymer: synthetic process used to produce nanotubes; nanotube purification process (if any); amount and type of impurities in the nanotubes; diameter, length and aspect ratio of the nanotubes objects in the composite (isolated, ropes and/or bundles); nanotubes orientation in the polymer matrix. Kim *et al.* [8] studied the effect of incorporating of CNTs on polyimidesiloxane matrix on gas separation performance. They observed that the addition of small CNTs to the copolymer matrix will be reducing the permeability helium and hindering the diffusion of nitrogen due to the impermeable properties of CNTs.

At present, different approaches are reported to improve the dispersion of CNTs in solvents or polymers in order to fabricate the composite mixed matrix nanotubes membrane. Recent reports on the chemical compatibility and dissolution properties of CNTs have promoted a great deal of interests in developing modification and functionalization of their surface. The chemical functionalization of multiwall CNT can be done by using novel silane coupling agents which helps to covalently link polymers. Besides that, treatment by carboxylic acid groups also can be used in this modification but for the strong acid used it can defects on CNTs sidewalls and decrease the aspect ratio of CNTs and other possible surface modification techniques included plasma, thermal and laser ablation [9]. By using silane agents, the coupling process can be accomplished via the chemical reaction between the trialkoxy groups of silane molecules and the hydroxyl groups of silane molecules and the hydroxyl groups on the glass substrates, whereas other functional group of silane molecules, which are generally ethylene, amine, epoxy and thiohydroxy can be remained [10].

In the present study, the feasibility fabrication and characterization result of mixed matrix membrane films using carbon nanotubes particles as selective inorganic fillers was investigated. A Thermal Catalytic Chemical Vapour Deposition (CCVD) has been used to synthesize carbon nanotubes. The carbon nanotubes were functionalized using Dynasylan Ameo silane coupling agent. The aim is to get a CNTs linked with the coupling agent having a functional group such as a double bond which can be utilized further for copolymerization. Hence, this reaction product (CNTs silanization) can be chemically explored for improving their compatibility with polymer matrix.

MATERIALS AND METHODS

Material Selection: Polyethersulfone was supplied by Solvay Advanced Material (USA). The polymers were dried in a vacuum oven at 120°C overnight before dope preparation; N-methyl-pyrrolidinone (NMP) from Merck was used as the solvent due to its low toxicity. The multi-wall nanotubes (MWNTs) were produced using Thermal Catalytic Chemical Vapour Deposition (CCVD). The CCVD system is simple and includes a cost effective fixed bed flow reactor. It is easy to handle and does not require expensive power supply or high pressure reaction chamber. The system can be divided into three major components: the gas sources, the gas mixing component and the tube furnace. There are two types of gases used, acetylene (C_2H_2) and nitrogen (N_2). Each gas tank was connected to a regulator. The amount of the gas was measured with a flow meter. The gas mixture was measured again before it flown into the furnace. The custom built reactor is a fixed bed flow reactor where the solid form catalyst has been placed stationary in the high temperature zone within the furnace to react with the gas source. The carbon deposition yield will deposit on the active catalyst and the CNTs can be collected upon cooling of the system after the reaction. The particle size of MWNTs was about 25.76 nm.

Fabrication of Asymmetric Polyethersulfone-carbon Nanotubes Mixed Matrix Membrane: In this study, the polymer solution consists of 25 wt% polymer, 75% NMP and 0.5 wt% nanotubes in the total solid. The homogeneous polyethersulfone was prepared according to the following procedure; the unmodified or modified carbon nanotubes were dispersed into the solvent and stirred for 24 hours followed by the addition of a desired amount of polyethersulfone. The solution was agitated with a stirrer at least 24 hours to ensure complete dissolution of the polymer. Before casting, the homogeneously prepared solution was degassed under vacuums for 3 hours. Flat sheet membrane was prepared according to the dry/wet phase inversion technique.

Chemical Modification Method of Carbon Nanotubes Surface: Carbon nanotubes samples were additionally modified by a silane coupling agent. First, the CNTs were again dried and pre-treated in H_2SO_4 . Double bonds present in the aromatic nanotube structure were oxidized with a sulfuric acid. This pre-treatment is necessary to create carboxylic acid moieties on nanotubes sidewalls that can react with the silane and also to remove impurities from the supported catalyst. For this purpose, the CNTs were dispersed in the sulfuric acid solution at

50°C and stirred for 20 h. The solution of oxidized of CNTs are filtered and the filtrate is washed thoroughly with ultra-pure water until a pH close to 5 is reached. The black mixture is dried overnight under vacuum. Then, the pre-treated CNTs were sonicated in a solution of the silane coupling agent using Dynasylan Ameo (DA) in ethanol/toulene in order to avoid agglomerates of CNTs and to evaporate the solvent. Ethanol was chosen in this study due to its strong interaction with water and its relatively benign nature. The mixture of modification nanotubes was then filtered through a filter paper and the residue was washed thoroughly with ethanol to remove the unreacted silane. Finally, the modified carbon nanotubes was dehydrated at 110 °C for 5 hours in a vacuum oven to remove the adsorbed water vapor or other organic vapors before it was ready to be used in preparation of dope solution.

Post-Treatment Procedure: The membrane sheets were coated with highly permeable elastomeric silicone polymer (Sylgard 184 Dow Corning). The membrane coating was done after the uncoated membranes were tested. The intention of coating is to fill any surface pinholes or defects on membrane surface. Membranes were submerged in the 3% w/w solution of silicone in n-hexane for 24 hours and subsequently placed in oven for 3 days at 120°C to allow curing before permeation testing.

Characterization of Blend Hollow Fiber Mixed Matrix Membrane: A Supra 35 VP Field Emission Scanning Electron Microscopy (FESEM) was used to ensure the asymmetric structure and to determine the dimension of the fibers. Membrane samples were fractured in liquid nitrogen. The membranes were mounted on an aluminium disk with a double surface tape and then the sample holder was placed and evacuated in a sputter-coater with gold. The changes in the chemical structure caused by silane treatment were identified using Fourier transform infrared spectroscopy (FTIR). The IR absorption spectra were obtained at room temperature in a range from 4000 to 500 cm^{-1} with a spectral resolution of 8 cm^{-1} and averaged over 16 scans. The glass transition temperature of each cast film was determined using differential scanning calorimetry (Mettler Toledo DSC 822e). A small piece of membrane or pure polymer sample was first stored under vacuum at 100°C for 24 hours to remove adsorbed water; then weighed and placed into aluminium DSC pans. The scanning range was 50- 320°C with scanning rate of 10°C min^{-1} in the first DSC cycle to remove thermal history and then cooled from 320 to 25°C at the rate of 10°C min^{-1} ; finally the second cycle was carried out with the same procedure.

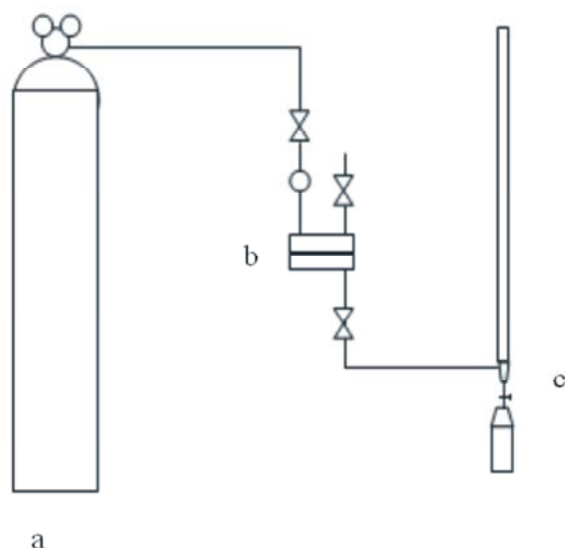


Fig. 1: Gas permeation test cell; (a) gas tank, (b) membrane cell, (c) bubble soap

Module Fabrication and Gas Permeation Experiment:

The permeation test involved the use of gas permeation cell in which the membrane was placed on a sintered metal plate and pressurized at the feed side. Gas permeation rates were measured by a constant pressure system using a soap bubble flow meter. Figure 1 illustrates the gas permeation cell set up. The cross-membrane pressure difference was maintained 1 bar. Pressure normalized gas permeation flux or permeance for gas i , $(P/l)_i$, in (GPU), can be calculated as follows:

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

where Q_i is the volumetric flow rate of gas i , Δp is pressure difference across membrane (cmHg), A is membrane effective surface area (cm^2) and l is membrane skin thickness (cm). The ideal separation factor $\alpha_{i/j}$ can be calculated by using equation below:

$$\alpha_{i/j} = \frac{(P/l)_i}{(P/l)_j} \quad (2)$$

RESULTS AND DISCUSSION

Morphology of Asymmetric Polyethersulfone-nanotubes Mixed Matrix Membranes: Primarily, this study was conducted to examine the effect of chemical modification on carbon nanotubes surface using (3-aminopropyl)-triethoxy methyl silane for fabricated mixed matrix

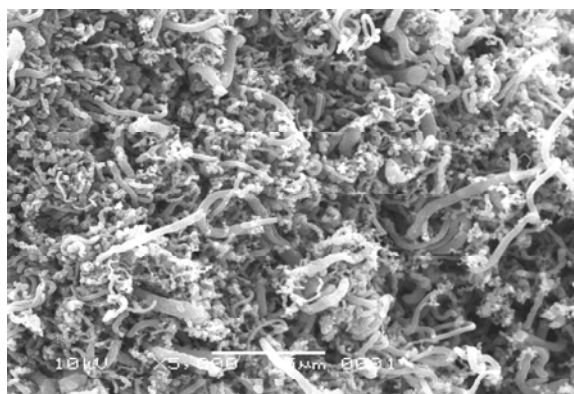


Fig. 2: FESEM image of unmodified CNTs



Fig. 3: FESEM image of CNTs after silanization using Dynasylan Ameo coupling agent

membrane PES-CNTs. Figure 2 shows the field emission scanning electron microscopy (FESEM) micrographs of carbon nanotubes synthesized in Catalytic Chemical Vapour Deposition (CCVD) system using $\text{CoFeAl}_2\text{O}_3$ catalyst. In Figure 2, the growth of CNTs can be clearly observed. The entangled and sinuous nanotubes are grown from the catalyst particles. The average diameter of the diameter of the as grown CNTs on the catalyst is 30 nm. The CNTs can be seen as bundles of tubes with fluffy and spongy texture. The aggregation of CNTs in fabrication of polymer-nanotubes composites membranes can also be affected by the length and aspect ratio of CNTs [11]. Obviously, the as-grown nanotubes bundles are pure without purification, as no amorphous carbon and carbonaceous particles deposited on the catalyst. However, the impurities of metallic catalyst can be clearly showed on the surface of the ropes. Moreover, the gas flow through the mixed matrix membrane produced from CNTs without purification can be blocked with the metallic impurities.

The FESEM micrograph of CNTs after silanization is presented in Figure 3. From Figure 3 can be obtained that a clear distribution of bunches of CNTs is observed after

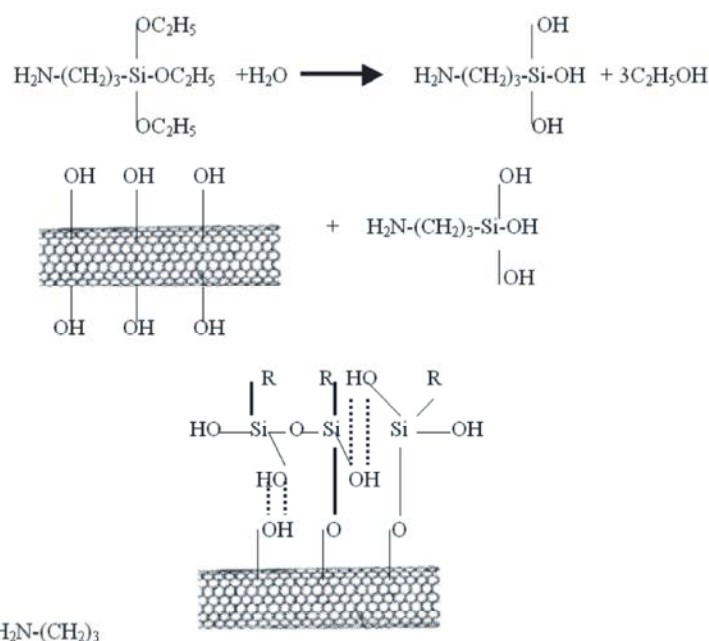


Fig. 4: Sequence of the silanization reactions on the nanotubes surface

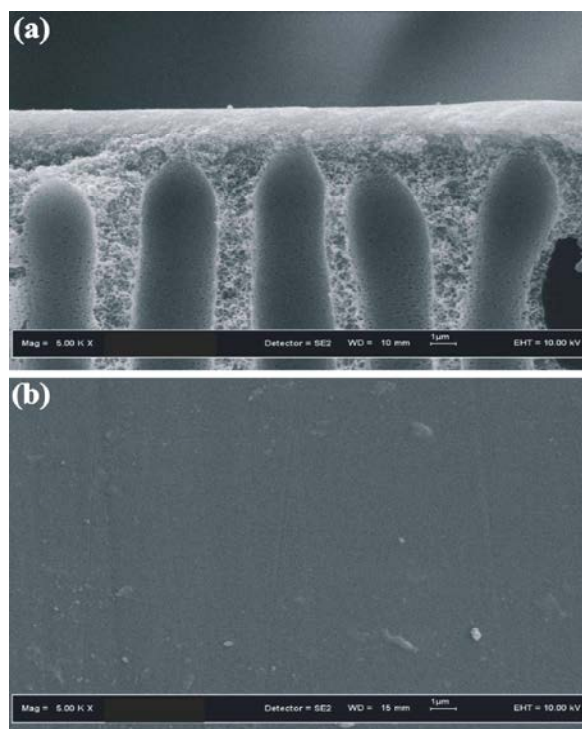


Fig. 5: SEM picture of asymmetric polyethersulfone membrane at the: (a) cross section and (b) outer surface image layer.

pre-treatment using sulfuric acid and follows by chemical modification using Dynasylan Ameo (DA) silane agent. As shown in Figure 3, the CNTs modified, the longer

structure becomes shorter. The molecular formula for Dynasylan Ameo is H₂N-(CH₂)₃-Si(OC₂H₅)₃. The silicon at the centre is connected to two different functional group; the organophilic amino group (NH₂) and the ethoxy group (C₂H₅O). Surface treatment of carbon nanotubes with Dynasylan Ameo silane coupling agent was carried out to produce silanol groups through hydrolysis reaction. Generally, the hydrolysis reaction occurs in the present of water molecules. Silanol groups formed as a product of a hydrolysis reaction react with hydroxyl groups found on nanotubes surfaces to form siloxane bonds (-Si-O-carbon nanotubes) through a condensation reaction. The DA silane agent consists of three ethoxy groups that are three reactive centres which can be used for the formation siloxane bonds with the nanotubes channel. These -Si-O-carbon nanotubes bonds were formed as a stable structure on surface of nanotubes. Upon the hydrolysis ethanol was released. On the other hand, the organophilic amino group reacted with the polymer chain. The schema of hydrolysis and condensation reaction and the chemical modification on nanotubes surface are shown in Figure 4.

In order to further investigate the effect of silanization of CNTs on the dispersion of CNTs in mixed matrix membrane, careful FESEM inspections were carried out. The FESEM micrographs of the cross-sectional and the surface of the neat PES, PES-unmodified nanotubes and PES-modified nanotubes mixed matrix membranes are shown in Figures 5-7. As shown in Figures 6-7, structure of nanotubes composite membranes showing finger like

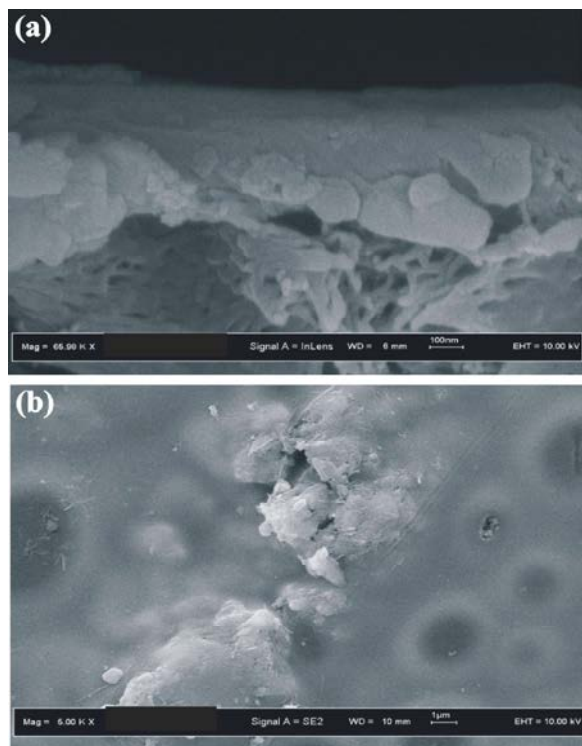


Fig. 6: SEM picture of asymmetric polyethersulfone-unmodified CNTs membrane at the: (a) cross section and (b) outer surface image layer.

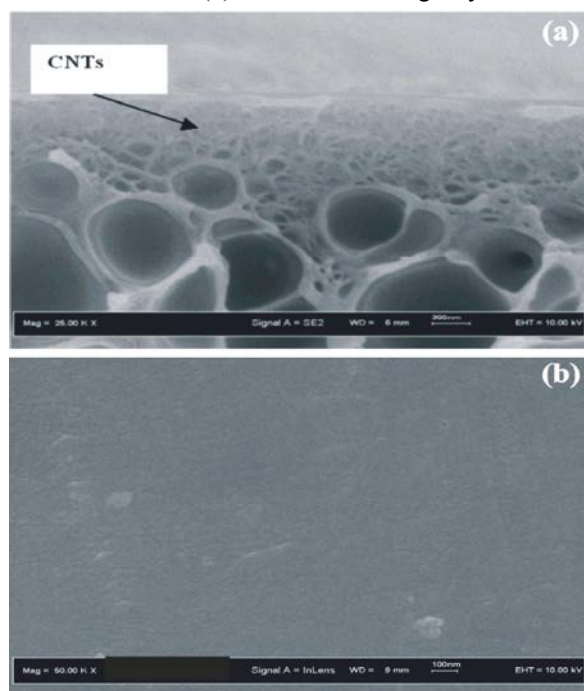


Fig. 7: SEM picture of asymmetric polyethersulfone-modified CNTs membrane at the: (a) cross section and (b) outer surface image layer.

structure which consisted of a dense skin layer supported by a spongy porous substructure. The unmodified carbon nanotubes particle seemed to good adhere with polymer matrix as shown in Figure 6. The smooth surface of the unmodified nanotubes-PES mixed matrix membrane might be due to the shape of the carbon nanotubes particles appeared to be oblong, therefore no sharp edges that could easily perforated the active surface skin. However, in the case of unmodified carbon nanotubes, the unselective voids appeared indicated that the carbon nanotubes did not completely adhered on the surface of polymer matrix. The small surface ruptures and aggregation are also occurred on the mixed matrix membrane with unmodified carbon nanotubes as shown in Figure 6b.

The cross-section and surface of PES-modified CNTs using 25 wt% of silane are shown in Figure 7(a)-(b). The porous substrate of the fabricated membrane and the active skin layer can be seen in Figure 7. Cross-section of porous substrate region for PES modified CNT clearly show the compatibility between modified CNT loading with PES. Moreover, from the cross section can be seen that CNTs clearly act as the filler to in the PES polymer host. Due to the chemical and physical properties of amino silane could be able to enhance the bond strength which provides a stable and strong bond between the modified CNT with PES matrix and finally reduced the presence of voids surrounded on CNT surface. The strong bonding was produced by the adsorption of functional groups of curing agent into amino-functionalized CNTs because of strong interfacial bond, which may lead to the non-stoichiometric balance between epoxy prepolymer and curing agent, thus leading to the inhibition of cross-linking reaction between them and when the content of CNTs is higher, congregation of CNTs because of intrinsic van der Waals forces possibly occurs, leading to bubbles and small aggregates [7]. Therefore, the good compatibility between polymer matrix and carbon nanotubes would finally lead to diminish gas penetrants via unselective voids of carbon nanotubes and simultaneously high gas separation performance of membrane is able to be achieved. Figure 7 had also revealed the presence of some CNT under the skin layer due to the cutting in nitrogen. The smooth surface of carbon nanotubes might also induce to enhance the adhesion between the nanotubes and the host of polymer.

FTIR Characterization: These characterizations were carried out on each of the fabricated mixed matrix membrane to analyse the infrared spectrum measurement

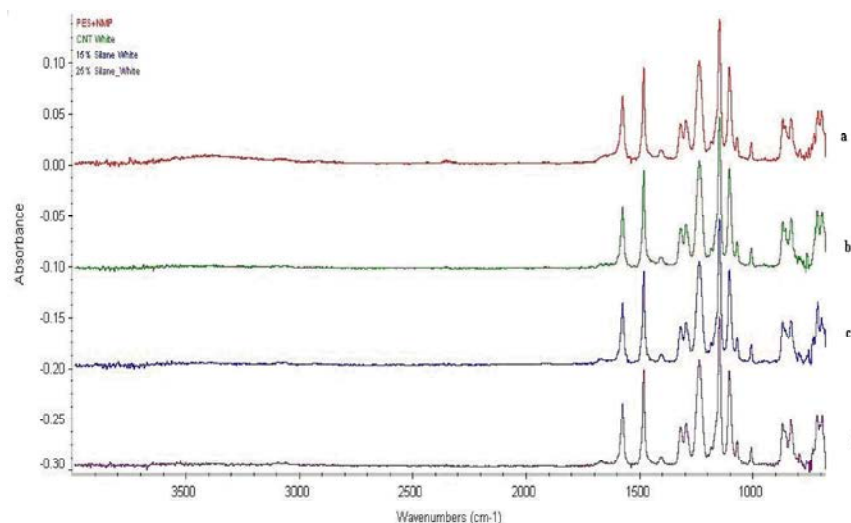


Fig. 8: FTIR spectra recorded in the region of 2000 cm^{-1} to 400 cm^{-1} for (a) neat PES, (b) Pure silane, (c) PES-CNTs 25 wt% silane, (d) CNTs, (e) PES-CNTs 15 wt% silane.

based on adsorption band changes of functional group in mixed matrix membrane. Through this analysis, it can be determined the presence of chemical bonding from the functional group which attach to the membrane structure. Theoretically, the reactions as described in Figure 4 can be proven through these differential spectra. Therefore, the change of vibration band position of neat PES (0 wt% silane), PES-modified CNTs (15 wt% silane) and PES-modified CNTs (25 wt% silane) has been examined throughout FTIR analysis. Figure 8 presents the FTIR spectroscopy of PES-CNTs mixed matrix membrane with untreated CNTs and modified surface of carbon nanotubes with different concentration of silane agent in the region of the 2000 cm^{-1} to 400 cm^{-1} , respectively. Through this analysis, chemical modification on CNT surface is quite clear in 25 wt% of concentration of silane that been used for modification. So, vibration band position of this sample was taken as a representative for all PES-modified CNT (15 wt% and 25 wt% silane) to be analyzed since the band position has only a slight different.

The free silanol groups on the CNT surface are the most reactive groups and may provide the side for the physical and chemical adsorption of the silane coupling agent. From Figure 8 (c) and (e), the weak absorption peak at near 955 cm^{-1} are the overlapping bond of the asymmetric stretching of Si–O–Si with Si–O–C stretching vibration and they are originate from the bond between the OH bonded to the Si atom on the CNT surface and the OH bonded to the Si atom of the silane molecule (OH–OH interaction). Through the samples, the band detected at

1008 cm^{-1} is attribute to nonbridging OH stretching vibration representing the H-bonding that occurred between the H atom of OH group bonded to the Si atom of (3-aminopropyl)-triethoxy methyl silane and oxygen atoms bonded to Si atoms on the CNT surface (O–OH interaction). The peak located at near $1120\text{--}1050\text{ cm}^{-1}$ that is described to N–H bond exists in PES- modified CNT 15 wt% silane and PES-modified CNT 25 wt%, while the peak around 1650 cm^{-1} is assigned to the C=C stretching vibration in Figure 8 (c) and (e). A weak absorption peak located at near 2950 cm^{-1} that is described to N–H₂ bonding were found in Figure 8 (c) which by mean the silane group exist in those membrane. Consequently, these bands were considered as evidence of the modification by chemical bonding of (3-aminopropyl)-triethoxy methyl silane molecules to the CNT surface. In other words the chemical modification on carbon nanotubes surface had successfully taken place.

Differential Scanning Calorimetry Analysis: The Differential Scanning Calorimetry has been done to indicate whether the CNT-PES blends were indeed miscible by observing the glass transition temperatures of the blend composition. The T_g for each membranes was determined from the heat flow versus temperature curve using an onset method. The influence of silane modification on the glass transition temperature of PES-carbon nanotubes mixed matrix membranes are tabulated in Table 1. As shown in Table 1, the glass transition value, the amino-functionalized CNT have increased the glass transition temperature T_g . This can be

Table 1: Effect of functionalization of CNTs on the glass transition temperature of PES-CNTs mixed matrix membrane

Membrane	T_g (°C)
Neat PES	219.05
Untreated CNTs	220.58
15 wt% DA silane	222.45
25 wt% DA silane	228.10

Table 2: Effect of silane concentration on the gas separation performance of polyethersulfone-CNTs mixed matrix membranes at room temperature and 4 bars.

Membrane	Single gas permeance (GPU)		Selectivity
	CO ₂	CH ₄	CO ₂ /CH ₄
Neat PES	26.52	4.86	5.46
Untreated membrane	35.18	7.08	4.97
15 wt% DA silane	29.74	1.44	20.67
25 wt% DA silane	27.13	1.14	23.89

seen in the effect of T_g for CNT modification with 25 wt% silane. The increasing of T_g in amino-functionalized CNTs MMM is because of the strong interaction between the PES matrix and amino-functionalized membrane which reduce the matrix mobility which will express itself in a shift of T_g [12] and beside that the diffusion of small molecules can be retarded under high temperature. It can also be seen that compared with neat PES polymer, the T_g of the mixed matrix membranes increased about 9°C with the incorporating only 1 wt% modified carbon nanotubes using 25 wt% silane treatment into the matrix. This phenomenon indicates that the mobility of polymer chains is reduced due to the restriction effect of carbon nanotubes. This result is in agreement with the previous study [13]. Based on Table 1, it can be concluded that the carbon nanotubes surface modification using Dynasylan Ameo silane coupling agent could induced the adherence between polymer matrix and carbon nanotubes particles. Therefore, it can be concluded that modified carbon nanotubes using chemical modification included into PES matrix will be made the composite film stiffer and stronger due to strong interfacial interaction between the nanotubes and PES host matrix. Moreover, with addition the nanotubes the movement of polymer chain in polymer host matrix will be restricted and this phenomenon likes physical cross-linking.

Gas Separation Performance of PES-Carbon Nanotubes Mixed Matrix Membrane: In the gas separation performance, the criteria which is important in determining whether the membrane are classified as good or not was determined by the ability of the membrane to give the high enhancement in gas separation performance than others

membrane. Thus, this testing was carried out in order to study the membrane effectiveness due to the effect of chemical modification on carbon nanotubes surface. The membrane effectiveness in the gas separation performance was determined by the membrane permeability and selectivity for tested biogas purification. In this study, we were used gas sample of CO₂ and CH₄ to represent the biogas product. The gas permeation properties for each flat sheet carbon nanotubes mixed matrix membrane were measured by using variable pressure constant volume method. The permeability and selectivity for tested gases CO₂/CH₄ obtained were presented in Table 2. The Table 2 summarize the permeability and selectivity data of neat PES, PES unmodified and PES-modified CNT at various silane concentrations. Generally, the idea to put inorganic filler into organic polymer was enhanced gas permeability of polymer nanocomposites membranes was due to the disturbed polymer chain packing by the nanofillers [14]. Therefore, the well dispersed and good adherence of carbon nanotubes will be effectively increased the gas permeability due to more effectively insert between polymer chains of the matrix. The addition of 1 wt% of modified carbon nanotubes loading to PES resulted in about 45.60% increases in permeability of CH₄. However, for the small gas molecules such as CO₂ permeability slightly increased with the addition of carbon nanotubes in the PES host matrix. The main pathways of gas transport through the mixed matrix membranes are through dense layer of PES matrix, highly selective carbon nanotubes and non-selective gaps or voids between the matrix and sieve particles. From FESEM data in Figure 6-7, the carbon nanotubes are well dispersed in polymer matrix and serve as channels to transport gas molecules. The permeability of CH₄ exhibits the higher increasing of permeability compared to CO₂ gas. The results are consistent with the previous study done by Chen and Sholl [15]. They observed that the main factor affecting the increase of CH₄ permeability with addition of carbon nanotubes into polymer host is due to the extremely fast diffusion of gas molecules adsorbed inside carbon nanotubes. They also reported that the MWNT membranes should be strongly selective for CH₄ and would produce very large fluxes of CH₄. Therefore, as presented in Table 3, the ideal selectivity for CO₂/CH₄ of the PES-1 wt% carbon nanotubes was slightly increased due to preferential sorption of CH₄ in the carbon nanotubes. Moreover, the permeability for unmodified carbon nanotubes for all gases also increases compared to neat PES membrane. However, the CO₂/CH₄ selectivity

Table 3: Effect of silicone rubber coating on gas permeation properties of Polyethersulfone-modified CNTs (25wt% silane) mixed matrix membrane at room temperature and 4 bars

Membrane	Single gas permeance (GPU)		Selectivity
	CO ₂	CH ₄	
Coated neat PES	20.36	0.70	28.75
Uncoated PES-silane	27.13	1.14	23.89
Coated PES- silane	24.78	0.73	34.21

was decreased for unmodified carbon nanotubes mixed matrix membrane. Therefore, the increase of permeability in the PES-unmodified carbon nanotubes was not due to the gas transportation inside the nanotubes. As shown in Figure 6, the PES- unmodified carbon nanotubes are not well distributed in polymer matrix and the severe unselective voids between carbon nano-particles and polymer matrix was appeared. Hence, the PES chains could not fall onto the carbon nanotubes walls tightly and forming a narrow gaps surrounding the carbon nanotubes. Therefore, gas molecules can easily passed through the unselective voids or the gaps. The unselective voids would be functioned as pinholes that allow all gases molecules pass rapidly without any selectivity. Thus, the permeability of all gases is increased thus reducing the gas selectivity. As can be seen in Table 3, the silane treated of modified carbon nanotubes filled PES polymer host mixed matrix membrane improved the CO₂/CH₄ selectivities or biogas purification. However, the improved selectivities were still lower compared to neat PES polymer membrane. The results indicated that the silane treatment induced to enhance the adherence but this improvement did not completely reduce the interface void between polymer and carbon nanotubes particles.

Effect of Silicone Coating and Thermal Curing on Gas Separation Performances: As discussed in section 3.4, the unselective voids were not completely eliminated in the PES-modified carbon nanotubes. Therefore, the influence of silicone rubber coating and thermal curing on the gas transport and gas separation properties of fabricated PES- 1 wt% modified carbon nanotubes mixed matrix membrane was studied. Gas separation performance of coated membrane fibers was also influenced by thermal curing time. In this study the coated membrane fibers was dried in a vacuum oven at temperature 120 °C for 72 hours. These fabricated membranes were selected due to their better separation properties compared to other silane concentration. Gas separation performance of this fabricated membrane was improved and comparison between coated and uncoated membrane was made.

Table 3 shows the comparison of permeability and selectivity for tested biogas purification between coated and uncoated PES-modified carbon nanotubes. From the tabulated data obtained, it can be observed that the PES- 1 wt% carbon nanotubes mixed matrix membrane coated with silicon rubber yield low permeability and high selectivity in the separation of CO₂/CH₄ compared to the uncoated membranes. As shown in Table 4, the highest membrane selectivity observed from the PES-1 wt% modified carbon nanotubes mixed matrix membrane achieved that is 34.21 for CO₂/CH₄, respectively. From the highest selectivity yield of 34.21 for CO₂/CH₄, it can be concluded that this silicone rubber coating can successfully suppress gas transport of Knudsen diffusion mechanism. This is probably due to the defects at the outermost skin layer have been sealed by the silicone coating. The surface structure of the membrane was improved by reducing the defects on the fiber surface, hence resulting in high selectivity and low permeability. Therefore, the gas transport mechanism that dominated this coated fibers are a combination of molecular sieving and solution diffusion. This phenomenon indicated that the voids generated by the unfavourable interaction between polymer and carbon nanotubes phases can be eliminated by combination of silane surface treatment and silicon coating. Due to the well-dispersed and without unselective voids, the carbon nanotubes would more effectively serve as channels to transport gas molecules.

CONCLUSION

In this study, the polyethersulfone (PES) with silanization of carbon nanotubes using Dynasylan Ameo silane coupling agent for the use of fabricating mixed matrix membrane for biogas purification. Based on the experimental results and analysis, the following conclusions can be made.

- The FESEM for the cross-sectional and surface area images of mixed matrix membrane films indicated that the modified of carbon nanotubes dispersed well in the polymer matrix. The surface ruptures are not occurred on the carbon nanotubes mixed matrix membrane might be due to the shape of carbon nanotubes appeared to be oblong. The smooth surface of carbon nanotubes might also help to enhance the adherence between the nanotubes and the host polymer.
- The PES-modified carbon nanotubes membranes had increased the permeability of methane gas and the CO₂/CH₄ selectivity.

- The carbon nanotubes have been potentially as in organic filler for mixed matrix membrane for the future biogas purification membrane.

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