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Hybrid membrane using polyethersulfone-modification of multiwalled carbon nanotubes with silane agent to enhance high performance oxygen separation

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Abstract - Mixed matrix membrane comprising carbon nanotubes embedded in polymer matrix have become one of the emerging technologies. This study was investigated in order to study the effect of silane agent modification towards carbon nanotubes (CNT) surface at different concentration on oxygen enrichment performances of asymmetric mixed matrix membrane. 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. Sieve-in-a-cage' morphology observed shows the poor adhesion between polymer and unmodified CNT. The gas separation performance of the asymmetric flat sheet mixed matrix membranes with modified CNT were relatively higher compared to the unmodified CNT. Hence, coated hollow fiber mixed matrix membrane with chemical modification on CNT surface using (3-aminopropyl)-triethoxy methyl silane agent can potentially enhance the gas separation performance of O₂ and N₂.

Keywords — mixed matrix membrane, carbon nanotubes, oxygen enrichment, gas separation

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I. INTRODUCTION

Membrane separation technology is currently one of the most innovative and rapidly growing fields across science and engineering. The preparation of asymmetric cellulose acetate membranes in the early 1960s by Loeb and Sourirajan is generally recognized as a pivotal moment for membrane technology. Gas separation is one of application of the rapidly developing membrane technology. The production of a gas at a specific purity from a multi-component gas mixture can be achieved using gas separation techniques such as adsorption, absorption and cryogenic distillation. In gas separation by membranes, the gases are separated based on differences in their solubility and diffusivity in the membrane. The

important factors affected application of membrane in gas separation such as feed composition, membrane materials, membrane configuration, plant capacity and operating costs. Currently, many researchers have focused studies on mixed matrix membrane to enhance gas separation performance. Hybrid membrane materials, or mixed matrix membranes, are a new class of membrane materials that offer the potential of significantly advancing the current technology. This concept involves the incorporation of highly selective molecular sieves within a polymeric matrix, resulting in a hybrid membrane material with superior selectivity over that of polymer matrix alone, while maintaining processability under current membrane formation technology (Zimmerman et al., 1997). Nevertheless, many

researchers (Duval et al., 1994; Vankelecom et al., 1996 and Kusworo et al., 2008) have identified difficulties in obtaining good polymer-sieve contact with rigid, glassy polymers, such as polyimides. Such glassy polymer mixed matrix membranes often demonstrated poor polymer-sieve adhesion, resulting in macroscopic voids and no selectivity enhancement. Thus, appropriate selection of the sieve and matrix phases is an important consideration to match the fast-gas permeability (Mahajan and Koros, 2000).

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 (Ismail et al., 2008). There are two basic types of CNT: single-wall carbon nanotubes (SWNT) and multiwall carbon nanotubes (MWNT) (Kim et al., 2006). 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. (2006) 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 of helium and hindering the diffusion of nitrogen due to the impermeable properties of CNTs. However, it is important to point out that for intractable polymers; this potential has not been realized, mainly because of the difficulties in the solubility. In addition, CNTs also tend to form into aggregates due to its high surface energy, which lead to inhomogeneous dispersion in the polymer matrix. This factor can reduce the separation performance of polymer composite carbon nanotubes.

In order to improve the dispersion of CNTs in solvents or polymers in order to fabricate good composite mixed matrix carbon nanotubes membrane different approaches have been reported recently. One of the approaches is used surfactants to disperse CNTs in solvents and polymers. Islam et al. (2003) studied the solubilization of CNTs in the presence of surfactants such as sodium dodecylbenzene sulphate (SDS), polyaryleneethynylene and polyvinylpyrrolidone (PVP). However, the preparation of CNTs-polymer composites using the surfactant dispersion is limited to water-soluble polymers (Zhang et al., 2006). The second method is direct mixing of CNT into the polymer with a twin-screw melt mixer. However, this method is limited for low viscous polymer materials.

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 (Ma et al., 2007). 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 (Shanmugaraj et al., 2007).

Therefore, it is the focus of this study to introduce silane agent to the multiwalled carbon nanotubes surface. The carbon nanotubes were functionalized using Dynasylan Ameo silane coupling agent. A Thermal Catalytic Chemical Vapour Deposition (CCVD) has been used to synthesize carbon nanotubes. The modified of carbon nanotubes with Dynasylan Ameo silane coupling agent will be used as a selective inorganic filler for fabrication of hybrid mixed matrix membrane for oxygen separation.

II. Experimental

2.1 Material selection

Polyethersulfone (Radel A300) supplied by Amoco Chemicals, was used as a membrane material. N-Methyl-2-pyrrolidone (NMP) and polyvinylpyrrolidone (PVP K30) purchased from Merck, Darmstadt, Germany, had been used as a solvent and nonsolvent, respectively, while distilled water was used as a nonsolvent. Water was used as a coagulation medium. Sodium chloride (NaCl) of analytical purity grade supplied by Merck was used as received.

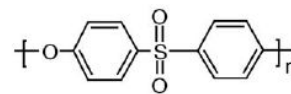


Figure 1: Chemical Structure of PES

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 (C₂H₂) and nitrogen (N₂). Each gas tank was connected to a regulator. The amount of the gas was measured with a flow meter. Both of the gas streams were passed through a moisture trap to make sure the gas was dry. The moisture trap contained silica gel. The gas streams were controlled by an on-off valve

before mixing up. The function of the gas mixing chamber is to mix the gas uniformly prior to the reaction. 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. A Carbolite CTF 12/65/550 model tube furnace was used. In the furnace, the acetylene was heated up and reacted to the supported catalyst to synthesize CNTs. The particle size of MWNTs was about 25.76 nm.

2.2. 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. This solution was further agitated by stirring at high speed for at least 2 days. 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. The solution was poured onto a clear, flat and smooth glass plate that was placed on the trolley. Stainless steel support casting knife was used to spread the solution to a uniform thickness by pneumatic force.

2.3. 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 H2SO4. 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 oC 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 oC 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.

2.4. 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 oC to allow curing before permeation testing.

2.5. 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 2 illustrates the gas permeation cell set up. The cross-membrane pressure difference was maintained 1 bar.

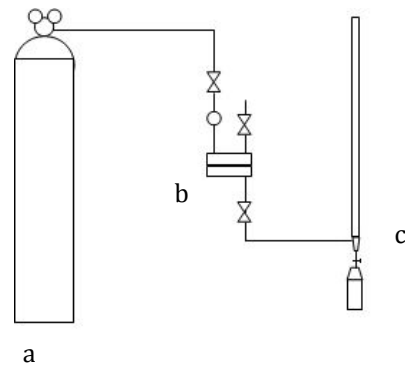


Figure 2: Gas permeation test cell; (a) gas silinder, (b) membrane cell, (c) buble soap

Pressure normalized gas permeation flux or permeance for gas I, (P/l)I, in (GPU), can be calculated as follows:

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

where Qi is the volumetric flow rate of gas i, is pressure difference across membrane (cmHg), A is membrane affective surface area (cm2) and l is membrane skin thickness (cm). The ideal separation factor can be calculated by using equation below:

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

III. Results and Discussion

3.1. 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 hybrid mixed matrix membrane PES-CNTs. Therefore, unmodified and modified CNTs mixed matrix membranes were characterized using Field Emission Scanning Electron Microscopy (FESEM), Fourier Transform Infrared Spectroscopy FTIR and Gas Permeation Test.

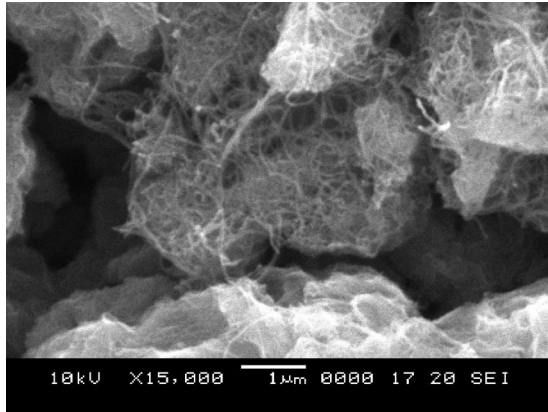


Figure 3: Carbon nanotubes surface with no modification

In Figure 3, the growth of CNTs can be clearly observed. The entangled and sinuous nanotubes are grown from the catalyst particles. The nanotubes have narrow diameter and length up to 100 micrometers. The average diameter of the diameter of the as grown CNTs on the catalyst is 25.76 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 (Zhu et al., 2006). 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 4. From Figure 4 can be concluded that a clear distribution of bunches of CNTs is observed after chemical modification using Dynasylan Ameo. The molecular formula for Dynasylan Ameo is $H_2N-(CH_2)_3-Si(OC_2H_5)_3$. The silicon at the centre is connected to two different functional group; the organophilic amino group (NH_2) and the ethoxy group (C_2H_5O). 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.

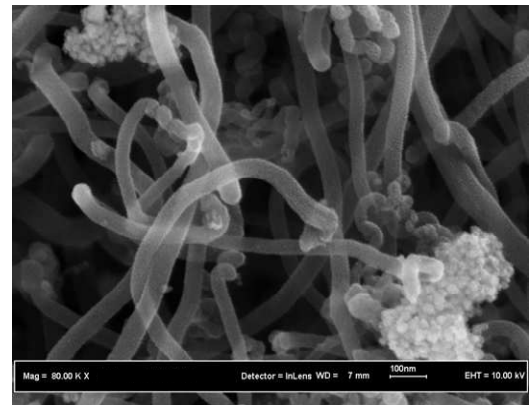
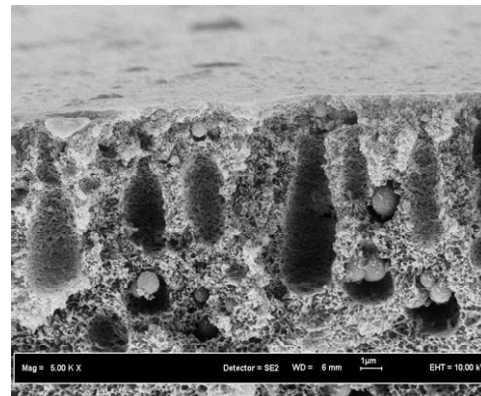
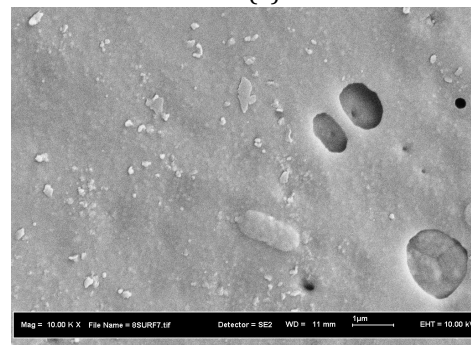


Figure 4: Carbon nanotubes surface with modification

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 PI/PES blend, PI/PES-unmodified nanotubes and PI/PES-modified nanotubes mixed matrix membranes are shown in Figures 5 to 6.



(a)

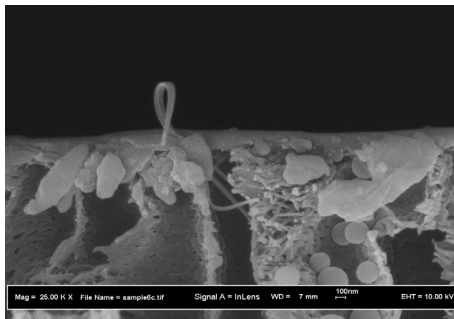


(b)

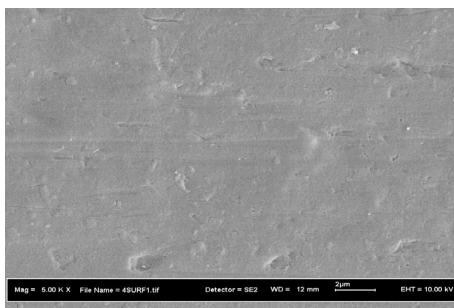
Figure 5: SEM picture of asymmetric polyethersulfone-unmodified CNTs membrane at the: (a) cross section and (b) outer surface image layer

As shown in Figures 5 and 6, structure of carbon nanotubes composite membranes showing finger like structure which consisted of a dense skin layer supported by a spongy porous substructure. The unmodified carbon nanotubes particle seemed to have a good adhesion with polymer matrix as shown in Figure 5. 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.



(a)



(b)

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

3.2. Thermogravimetric Analysis (TGA)

Thermal stability is one of the most important properties of CNT/polymer nanocomposites for potential applications as functional or structural components at elevated temperatures. Decomposition temperatures, varied differently depending on the CNT surface functionalization for the samples containing silane- CNT, increased with increasing CNT content, indicating that the thermal decomposition of silane- CNT was retarded by the presence of silane-CNT. This characterization is conducted to study the relationship between the thermal decomposition temperatures with the weight loss of the composition. The weight loss of the composition is shown in Table 1.

The same thermal decomposing temperature is used in identifying the rate of each composition to diffuse as already shown in Table 1. The amino-functionalized CNT have a great effect on the onset decomposing temperature. Introducing different amino-functionalized CNT to the PES matrix can increase the initial decomposing temperature of neat matrix more or less. This can be seen when the increasing of the composition of amino functional, the weight losses of the composition retarded. It is proven when 15% of silane for CNT surface modification gives the smallest percent of weight loss among others. In this condition, the compositions become stable which was affected from the strong interaction between PES matrix and silane-functionalized CNTs, so

the diffusion of small molecules was retarded although under the high temperature.

Table 1: Weight loss of thermal decomposing of PES-CNT-silane

Onset thermal decomposing temperature at 550 °C			
Composition	Weight before Decomposing , mg	Weight loss, mg	% weight loss
Neat PES	5.57	3.39	60.86
PES-unmodified CNT	5.45	2.85	52.29
PES-CNT (15 wt% silane)	5.34	2.77	51.76

3.3. Gas Separation Performance of PES-Carbon nanotubes mixed matrix membrane

Although the improvement on adhesion between carbon nanotubes and polymer surface was clearly observed by FESEM, one of the most important criteria required by a good membrane was the ability to show high gas separation performance. Thus, in this study the effect of chemical modification on carbon nanotubes surface towards gas separation performance was studied. The membrane effectiveness in the gas separation performance was determined by the membrane permeability and selectivity for tested gas O₂/N₂. 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 O₂/N₂ obtained were tabulated in Table 2. Table 2 summarize the permeability and selectivity data of neat PES, PES unmodified and PES-modified CNT.

Table 2: Gas permeabilities of neat PES, PES-CNTs and PES-modified CNTs

Membrane	Single gas permeance (GPU*)		Selectivity O ₂ /N ₂
	O ₂	N ₂	
PES Neat	7.25± 0.45	1.33± 0.01	5.45
PES-unmodified CNT	10.56± 0.03	3.35±0.15	3.15
PES-modified CNT	12.07±0.12	1.84±0.13	6.54

*GPU = 1 x 10⁻⁶ cm³ (STP)/cm² s cmHg

IV. Conclusion

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

- i. The FESEM for the cross-sectional and surface area images of hybrid 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.
- ii. The PES-modified carbon nanotubes membranes had increased the permeability of oxygen gas and the O₂/N₂ selectivity.
 - iii. The carbon nanotubes have been potentially as inorganic filler for hybrid mixed matrix membrane for the future oxygen purification from the air.

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