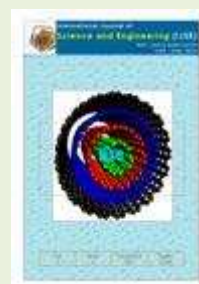




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Fabrication and Characterization of Polyimide-CNTs hybrid membrane to enhance high performance CO₂ separation

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Abstract - This study investigates the CO₂ separation performance of a hybrid membranes flat sheet based on polyimide incorporated with carbon nanotubes (CNTs) particles. CNTs was selected and its loading were a 1 wt% in total solid. The hybrid composite membranes were fabricated in order to increase their separation performance for the gaseous mixture of CO₂ and CH₄. Hybrid Composite membrane incorporated carbon nanotubes were manufactured by the dry-wet phase inversion technique using flat sheet membrane casting machine system, in which the CNTs were embedded into the polyimide membrane and the resulting membranes were characterized. 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 results revealed that the good multi-wall carbon nanotubes dispersion leads to enhanced gas permeation properties. It is also concluded that addition of carbon nanotubes particles into the matrix of Polyimide polymer has significant effect on the membrane structure and properties.

Keywords — Hybrid composite membrane, carbon nanotubes, carbon dioxide separation, gas separation

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I. INTRODUCTION

Membrane processes have encompassed a wide range of application in gas separation where by gas separation via selective permeation through polymer membranes has become one of the fastest growing branches of the separation technology (Kim et al., 2004; Ismail et al., 2008; Kusworo et al., 2008 and Kusworo et al., 2014). In particular, separation of CO₂/CH₄ has received high attention due to the great significance on industrial applications such as natural gas purification and CH₄ recovery from landfill gas. However, membrane separation needs to compete directly with traditional gas separation processes such as scrubbing using chemical solvent, cryogenic distillation and pressure swing adsorption (PSA) process. Carbon dioxide need to be removed from the

natural gas because it has reducing the heating value and it causes corrosion in the gas pipe lines when in the presence of water due to the formation of corrosive carbonic acid. Hence, removal of CO₂ is necessary in this process. Advantages of membranes are low capital investment, ease of operation, low energy consumption cost effectiveness even at low gas volume and good weight and space efficiency (Spillman, 1989). However, to extend membranes application and compete successfully with those traditional CO₂/CH₄ gas separation processes, great attention has been made in the fabrication of high performance membrane. Modifications on the physical and chemical structures of polymer films have been carried out in order to achieve better separation characteristics. Currently, membranologist concentrates their efforts in

developing new membrane materials capable of operating beyond the upper bound has focused on hybrid composite membranes (Kusworo et al., 2008; Ismail et al., 2008; Kusworo et al. 2013 and Kusworo et al., 2014). This membrane combine polymer with an inorganic filler, usually zeolite or molecular sieve. Results obtained using hybrid composite membranes showed very promising and encouraging trends however, they normally accompanied by losses or reduction in selectivity.

A potential filler which has not yet received widespread attention for use in hybrid composite for gas separation is carbon nanotubes (CNTs). Carbon nanotubes are graphite sheets rolled into circular bundles having diameter of several angstroms or tens of nanometers, and their lengths can be up to several micrometers. The CNTs can be synthesized as a single walled or multiwalled nanotubes or nanotubes. Some of the attractive characteristics of CNTs are their outstanding mechanical properties, their high strength-to-weight ratio and their excellent thermal stability.

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).

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. The common method to modify of the CNT surface is through chemical functionalization at defect sites. In this method, active sites are introduced onto the surface of CNT by chemical oxidation, via adding concentrated H₂SO₄ and/or HNO₃ (Shaffer et al., 1998). Generally, the chemical modification is used to enhance the carbon nanotubes-polymer interface.

Kusworo et al. (2014) investigated the effect of silane agent to the multiwalled carbon nanotubes surface. The carbon nanotubes were functionalized using Dynasylan Ameo silane coupling agent. The modified of carbon nanotubes with Dynasylan Ameo silane coupling agent will be used as a selective inorganic filler for fabrication of hybrid composite polyethersulfone membrane for oxygen separation.

Therefore, this study was focused to fabricate hybrid composite membrane using polyimide as polymer matrix and CNTs as inorganic filler for CO₂ separation in CH₄

mixture. A Thermal Catalytic Chemical Vapour Deposition (CCVD) has been used to synthesize carbon nanotubes.

II. EXPERIMENTAL

2.1 Material selection

Polyimide (PI) was supplied by Alfa Aesar Johnson Mattew Mexico and used as a membrane material. N-Methyl-2-pyrrolidone (NMP) purchased from Merck, Darmstadt, Germany, had been used as a solvent, respectively. Water was used as a coagulation medium. 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. The particle size of CNTs was about 25.76 nm.

2.2. Fabrication of asymmetric polyimide-carbon nanotubes mixed matrix membrane

In this study, the polymer solution consists of 25 wt % polymer (Polyimide), 75 % NMP and 0.5-1 wt% nanotubes in the total solid. The homogeneous polyimide was prepared according to the following procedure; the inorganic carbon nanotubes particles were dispersed into the solvent and stirred for 24 hours followed by the addition of a desired amount of polyimide. 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. 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.

2.4. 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.

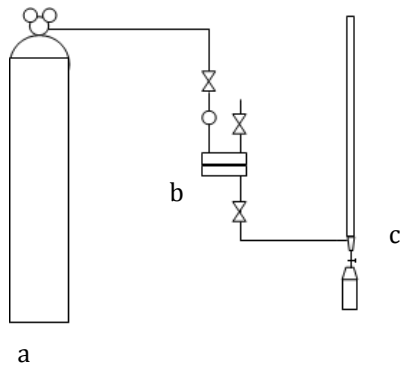


Figure 1: Gas permeation test cell; (a) gas silinder, (b) membrane cell, (c) bubble soap

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

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

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

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

III. RESULTS AND DISCUSSIONS

3.1. Morphology of asymmetric polyimide-nanotubes mixed matrix membranes

Figure 2 shows the scanning electron microscopy (SEM) micrographs of carbon nanotubes synthesized in Catalytic Chemical Vapour Deposition (CCVD) system using $Fe_2Al_2O_3$ catalyst. In Figure 2, the growth of CNTs can be clearly observed. The entangled and sinuous nanotubes are grown from the catalyst particles. The 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 3. From Figure 3 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 $H_2N-(CH_2)_3-Si(OC_2H_5)_3$ (Kusworo et al., 2014).

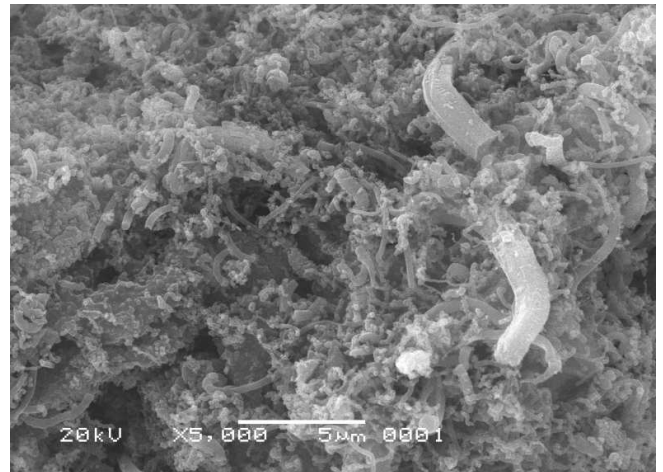


Figure 2: Carbon nanotubes surface with no modification

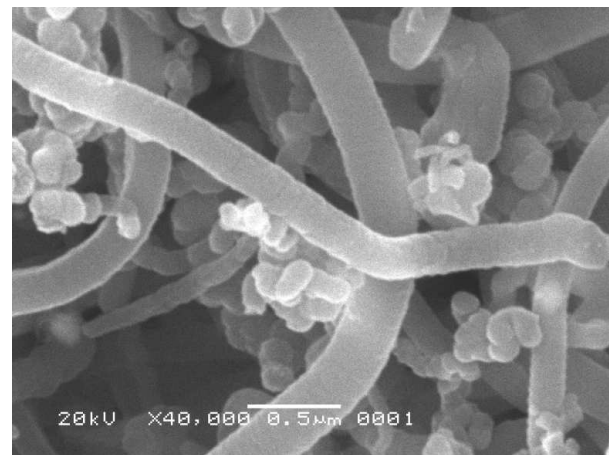
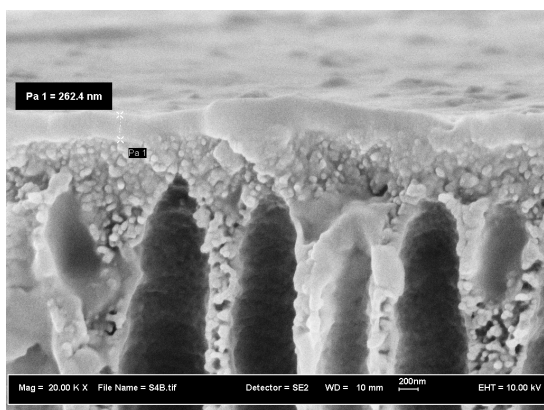
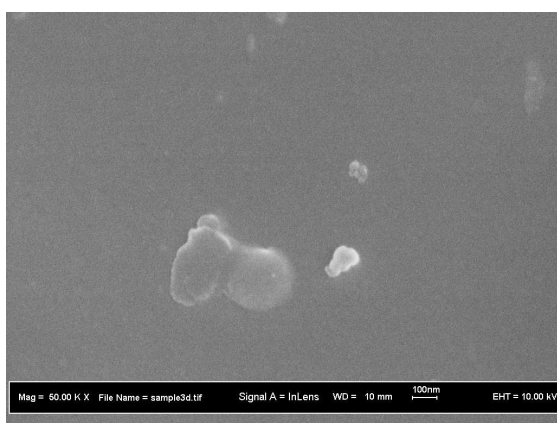


Figure 3: Carbon nanotubes surface with modification

In order to further investigate the effect of silanization of CNTs on the dispersion of CNTs in hybrid composite polyimide membrane, careful FESEM inspections were carried out. The FESEM micrographs of the cross-sectional and the surface of the PI-CNTs modified nanotubes mixed matrix membranes are shown in Figures 4. As shown in Figure 4, structure of carbon nanotubes composite membranes showing finger like structure which consisted of a dense skin layer supported by a spongy porous substructure. Due to the stable structure of $-Si-O-$ bonds on the surface of carbon nanotubes, the presence of voids surrounded on carbon nanotubes surface finally reduced as shown in Figure 4. Hence, this 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. The smooth surface of carbon nanotubes might also be induced to enhance the adhesion between the carbon nanotubes and the host polymer.



(a)



(b)

Figure 4: SEM picture of asymmetric polyimide-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.

Table 1: Summary results for TGA testing.

Membranes	Weight Lost (mg)	% weight lost
PI	2.967	57.82
Unmodified CNTs	2.925	51.25
Modified CNTs with 15 % Silane	2.657	46.15
Modified CNTs with 25% Silane	2.572	44.43

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 polyimide (PI) 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 25% 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 PI matrix and silane-functionalized CNTs, so the diffusion of small molecules was retarded although under the high temperature.

3.3. Gas Separation Performance of PI-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. The transport of gases in a asymmetric membrane is usually governed by the solution diffusion mechanism. The permeance for 1 wt% carbon nanotubes in total solid for different pure gases, CO₂ and CH₄ is reported as in Table 2. The permeation rate is in the order of CO₂ > CH₄, respectively. The high permeation rate observed for CO₂, is a result of the more strongly adsorbing properties of CO₂ through the channels of CNTs when compared to CH₄. The presence of functional groups such as the hydroxyl groups has also contributed towards the enhancement of the permeance of the hybrid composite membrane. The increase in the solubility of CO₂ in the hybrid composite membrane was the result of the strong interaction between the CO₂ molecules. The addition of open ended and shortened CNTs has also resulted unfavorable permeability increase for CO₂ as compared to the CH₄ gas. On the other hand, the slower diffusing CO₂ molecules reduced the mobility of the adsorbed CH₄ which has resulted in an increase in the selectivity for CO₂ as presented in Table 2. The selectivity of the neat PI and different silane concentrations is also tabulated in Table 2.

Table 2: Gas Permeabilities of neat PI, PI-CNTs and PI - modified CNTs

Membrane	Single gas permeance (GPU)		Selectivity CO ₂ /CH ₄
	CO ₂	CH ₄	
Neat PI	38.52	1.86	20.70
Untreated membrane	42.90	3.56	12.05
15 wt % DA silane	48.86	1.92	25.44
25 wt % DA silane	54.42	1.94	28.05

*GPU = 1 x 10⁻⁶ cm³ (STP)/cm² s cmHg

IV. CONCLUSIONS

Successful hybrid composite membranes production are depended on the bonding of the carbon nanotubes particle can be achieved with the polymer matrix. Generally, carbon nanotubes with hydrophilic surfaces do not interact well with hydrophobic polymers used in flat sheet casting. Therefore, the surface of the carbon nanotubes particles must be modified to change the level of interaction between polymer and the carbon nanotubes. The FESEM for the cross-sectional and surface area images of hybrid composite membrane indicated that the modified of carbon nanotubes dispersed well in the polymer matrix. The smooth surface of carbon nanotubes might also help to enhance the adherence between the nanotubes and the host polymer.

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