Enhanced biogas separation performance of nanocomposite polyethersulfone membranes using carbon nanotubes

T.D. Kusworo* and Budiyono

Faculty of Engineering, University of Diponegoro, Jl. Prof. Sudharto Tembalang, Semarang, Indonesia.
tutukjoko@yahoo.com
*Corresponding Author: tutukjoko@yahoo.com

Abstract - This study is performed primarily to investigate the effect of chemical modification on carbon nanotubes surface towards biogas purification performance of mixed matrix membrane. In this study, polyethersulfone (PES)-carbon nanotubes mixed matrix hollow fiber membrane for modified and unmodified carbon nanotubese were spun using dry/wet spinning technique. The modified carbon nanotubes were prepared by treating the carbon nanotubes with acid treatment to allow PES chains to be attached 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, the productivity and purity of biogas compare to neat PES and unmodified carbon nanotubes mixed matrix membrane. For PES-modified carbon nanotubes mixed matrix membrane the maximum selectivity achieved for CO_2/CH_4 is 32.59.

Keywords - mixed matrix membrane; carbon nanotubes; biogas; gas separation.

Introduction

Off-gas from anaerobic digestion or biogas has being become significant potential as an alternative energy due to the limitation of energy source from fossil. This is due to its characteristics i.e. renewable source, environment friendly, clean, cheap and versatile fuel. However, the use of biogas still has limitation due to low-quality of biogas containing substantial amounts of CO_2 (20-45 vol%) and H_2S (0-1 vol%) in addition to main component CH_4 (55-80 vol%). However, the use of biogas still has limitation due to low-quality of biogas containing substantial amounts of CO_2 (20-45 vol%) and H_2S (0-1 vol%) in addition to main component CH_4 (55-80 vol%). In addition, biogases are also frequently saturated by water vapour. The presence of CO_2 as an incombustible gas reduce its calorific value and make it uneconomical to compress and transport to longer distances [1]. Biogas purified and enriched in methane can be used for household applications, automobile fuel (liquefied) or electricity generation. There is a great need to make biogas transportable. This can be done by compressing the gas in cylinders, what is possible only after removing CO2, H_2S 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. Elimination of carbon dioxide from the flue gas helps to increase its calorific value as well as to eliminate the greenhouse gas. The carbon dioxide thus generated can be utilised as an effective refrigerant.

A variety of processes are being used for removing CO_2 and H_2S from NG in petrochemical industries. Several basic mechanisms are involved to achieve selective separation of gas constituents. These may include physical or chemical absorption, adsorption on a solid surface, membrane separation, cryogenic separation and chemical conversion. However, membrane separation processes have emerged during the last two decades. This is due to the fact that membrane separation processes may offer more capital and energy efficiency when compared to the conventional separation processes [4]. In addition, advantage of membrane technology is its simplicity, i.e. no absorbent, which has to be regenerated; it can be easily retrofitted, modularized and scaled-up for several applications [5].

At the present, polymeric membranes dominate the membrane separation field due to the fact that they are well developed and quite competitive in separation

10

performance and economics. 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. 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 [4-6]. Mixed matrix composite membranes have received world-wide attention in the field of material science in the last 2 decades [2-7]. As the consequence, it has been proposed as an alternative approach to obtain the high selectivity benefits of molecular sieve materials (e.g. carbon molecular sieves (CMS), silica and zeolites) and to counter the costly processing of purely homogeneous molecular sieving membranes through incorporating these sieves into a process able polymeric matrix. This heterogeneous or hybrid membrane concept combines the advantages of each medium: high separation capabilities of the molecular sieves, the desirable mechanical properties and economical processing capabilities of the polymers.

Currently, significant efforts have been devoted in fabrication of mixed matrix membrane by use carbon nanotubes as great potential filler. 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 [7] 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.

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. The carbon nanotubes were functionalized using acid treatment technique. 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.

Methods

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 carbon nanotubes (CNTs) were produced using Thermal Catalytic Chemical Vapour Deposition (CCVD. The particle size of CNTs was about 25.76 nm. In this study, the polymer solution consists of 25 wt % polymer, 75 % NMP and 1 wt% carbon nanotubes in the total solid. 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. Carbon nanotubes samples were additionally modified by a acid treatment. 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 remove impurities from the supported catalyst. 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.

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. 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. 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.

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

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

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

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

Results and Discussions

Primarily, in this study the effect of chemical modification on carbon nanotubes using sulfuric acid for fabricated flat sheet mixed matrix membrane PES-carbon nanotubes were examined. There were some differences between unmodified and modified carbon nanotubes. Field Emission Scanning Electron Microscopy (FESEM) characterization was used in order to determine the qualitative analysis of flat sheet mixed matrix membrane. In order to further investigate the dispersion of the functionalized MWNTs (multi walled carbon nanotubes) in MMMs (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 1-3. As shown in Figures 1-3, structure of 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 good adhere with polymer matrix as shown in Figure 2. 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 Figures 2a-b.
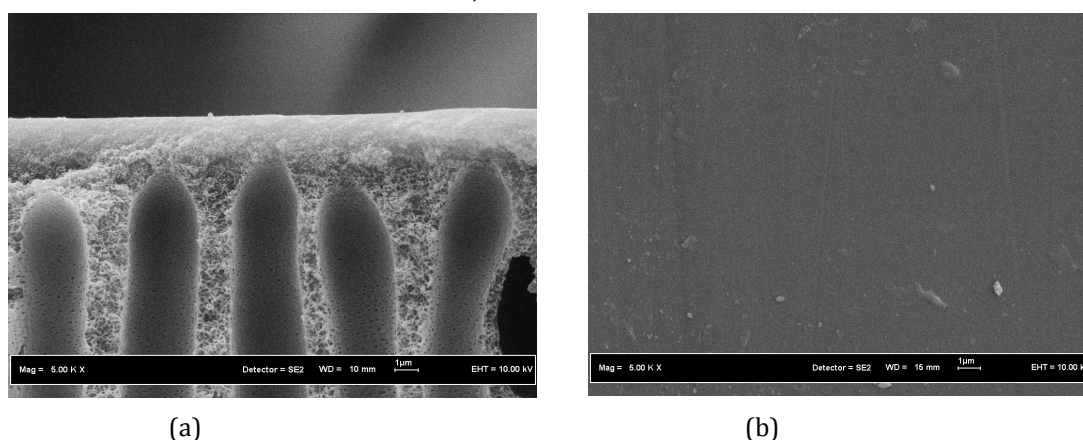

(a)   (b)

Figure 1: SEM picture of asymmetric polyethersulfone membrane at the: (a) cross section and (b) outer surface image layer.

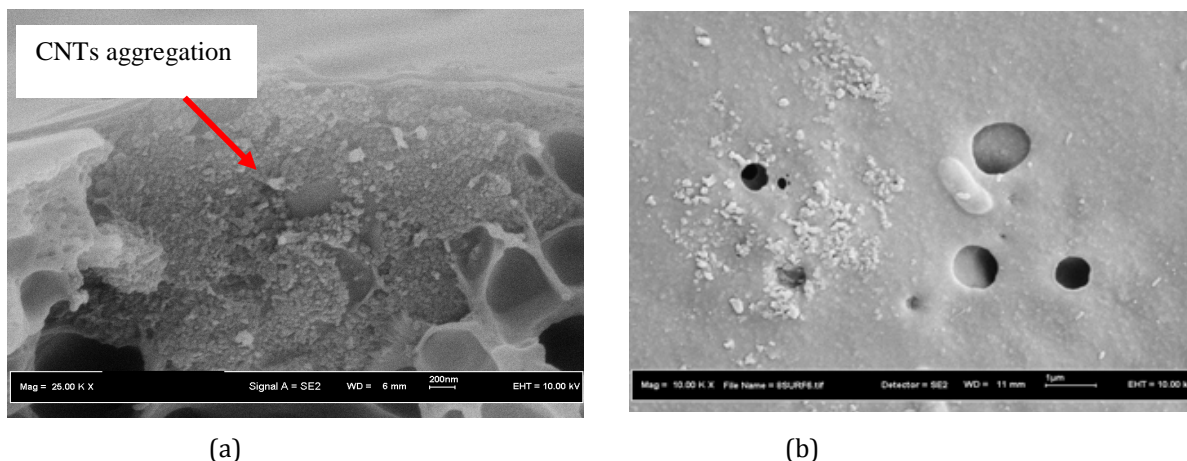(a)   (b)

Figure 2: SEM picture of asymmetric polyethersulfone-unmodified CNTs membrane at the: (a) cross section and (b) outer surface image layer.

The cross-section and surface of PES-modified CNTs using 2.5 M of sulfuric acid are shown in Figures 3(a)-(b). The porous substrate of the fabricated membrane and the active skin layer can be seen in Figure 3. 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 sulfuric acid 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. Therefore, the good compatibility between polymer matrix and carbon nanotubes would finally lead to diminish gas penetrants via unselective voids of carbon

12

nanotubes and simultaneously high gas separation performance of membrane is able to be achieved [7]. The smooth surface of carbon nanotubes might also induce to

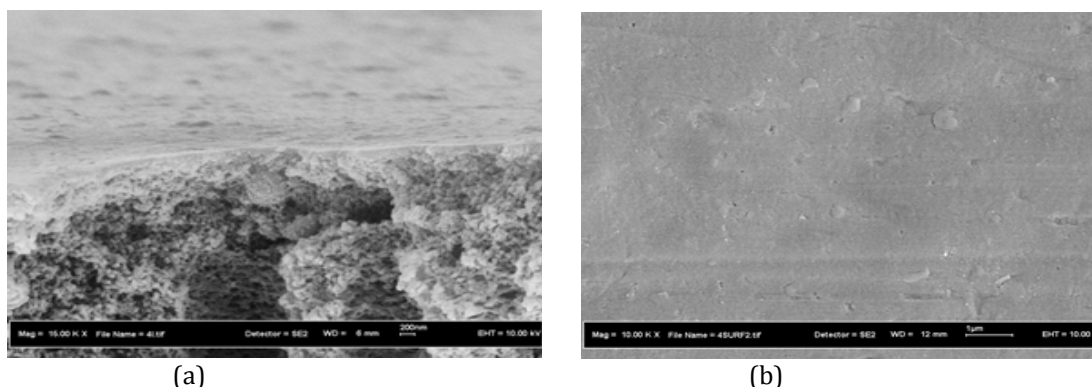enhance the adhesion between the nanotubes and the host of polymer.

Figure 3: SEM picture of asymmetric polyethersulfone-modified CNTs membrane at the: (a) cross section and (b) outer surface image layer.

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 acid treatment modification on the glass transition temperature of PES-carbon nanotubes mixed matrix membranes are tabulated in Table 1. In the thermo gravimetric and differential thermo gravimetric results of pure and functionalized CNTs, it should be reports on thermal degradation of MWNTs reveal that the on set of degradation starts at around certain temperature, which is attributed to the degradation of grapheme walls with complete degradation at around related temperature [10-11]. As shown in Table 1, the glass transition value, the acid treatment of functionalized CNT have increased the glass transition temperature T_g. This can be seen in the effect of T_g for CNT modification with acid treatment. Increase in temperature leads to the condensation reaction between the adsorbed sulfuric acid and –OH groups present in the functionalized CNT surface and thereby eliminates water and methanol. The second and third transitions are attributed to the break down of hydrogen bonds and the bonds that present in grafted sulfuric acid leading to a major weight loss.

It can also be seen that compared with neat PES polymer, the T_g of the mixed matrix membranes increased about 5 $^\circ$C with the incorporating only 1 wt% modified carbon nanotubes using 2.5 M acid 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 [11]. Based on Table 1, it can be concluded that the carbon nanotubes surface modification using acid treatment 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.

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

Membranes	Tg (^{0}C)
PES	218.8
Unmodified CNTs	220.27
Modified CNTs with 2.5 M H_2SO_4	223.65

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 CO_2 removal. In this study, we were used gas sample of CO_2 and CH_4. 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 CO_2/CH_4 obtained were presented in Table 2. The Table 2 summarizes the permeability and selectivity data of neat PES, PES unmodified and PES-modified CNT.

Table 2: Effect of sulfuric acid treatment on the gas separation performance of polyethersulfone-CNTs mixed matrix membranes at room temperature and 10 bars.

Membrane	Single gas permeance (GPU)		Selectivity
	CO_2	CH_4	CO_2/CH_4
Neat PES	20.36	0.70	28.75
Untreated membrane	25.18	1.96	12.84
Modified membrane	27.05	0.83	32.59

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. 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 32.85 % increases in permeability of CO_2. 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 Figures 3a-b, the carbon nanotubes are well dispersed in polymer matrix and serve as channels to transport gas molecules. The results are consistent with the previous study done by Chen and Sholl [12]. Moreover, the permeability for unmodified carbon nanotubes for all gases also increases compared to neat PES membrane. However, the CO_2/CH_4 selectivity 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 2, 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 2, the acid treatment could modify carbon nanotubes filled PES polymer host mixed matrix membrane which can improved the CO_2/CH_4 selectivities.

Conclusion

In this study, the polyethersulfone (PES) with acid treatment of carbon nanotubes for the use of fabricating mixed matrix membrane for CO2 removal. 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 CO_2/CH_4 selectivity.
❖ The carbon nanotubes have been potentially as in organic filler for mixed matrix membrane for the future CO_2 removal membrane application ie., biogas purification, natural gas and flue gas purification membrane.

References

[1] Kapdi, S.S., V.K. Vijay, S.K. Rajesh, R. Prasad., Biogas scrubbing, compression and storage: perspective and prospectus in Indian context, Renew. Energy 30 (2005) 1195–1202.

[2] Lin, W.H., and T.S.Chung.. Gas permeability, diffusivity, solubility, and aging characteristics of 6FDA-durene polyimide membranes, Journal of Membrane Science, 186 (2001), 183–193

[3] Baker, R.W., Membrane Technology and Applications, McGraw-Hill, New York,

[4] Hacarlioglu, P., L. Toppare, L. Yilmaz, Polycarbonate–polypyrrole mixed matrix gas separation membranes. J. Membr. Sci., 225. (2003). 51-62.

[5] C.M. Zimmerman, A. Singh., W.J. Koros, Tailoring mixed matrix composite membranes for gas separations. J. Membr. Sci., 137. (1997). 145-154.

[6] T.D. Kusworo, A.F. Ismail, A. Mustafa and T. Matsuura, Dependence of Membrane Morphology and Performance on Preparation Conditions: The Shear Rate Effect in Membrane Casting, Separation and Purification Technology, 61. (2007) 249-257.

[7] S. Kim, T.W. Pechar, E. Marand, Poly(imide siloxane) and carbon nanotube mixed matrix membranes for gas separation, Desalination, 192 (2006) 330-339.

[8] P.M. Ajayan, O. Stephen, C. Colliex, D. Trauth, Science, 265, (1994) 1212-14.

[9] K.-T. Lau and D. Hui, The revolutionary creation of new advanced materials-carbon nanotubes composites, Composites: Part B, 33 (2002) 263-277.

[10] P. C. Ma, J.-K. Kim, B. Z. Tang, Effects of silane functionalization on the properties of carbon nanotube/epoxy nanocomposites, Composites Science and Technology, 67, (2007) 2965-2972.

[11] B.-K. Zhu, S.-H. Xie, Z.-K. Xu, Y.-Y. Xu, Preparation and properties of the polyimide/multi-walled carbon nanotubes (MWNTs) nanocomposites, Comp. Sci. Technol. 66 (2006) 548-554.

[12] H. Chen, D.S. Sholl, Prediction of selectivity and flux for CH4/H2 separations using single walled carbon nanotubes as membranes, J. Membr. Sci., 269 (2006) 152-160.