

# FABRICATION AND CHARACTERIZATION OF POLYIMIDE/POLYETHERSULFONE-FUMED SILICA MIXED MATRIX MEMBRANE FOR GAS SEPARATION

A.F. Ismail<sup>1\*)</sup> and T.D. Kusworo<sup>1,2)</sup>

## Abstract

*This study is performed primarily to investigate the feasibility of fumed silica as inorganic material towards gas separation performance of mixed matrix membrane. In this study, polyimide/polyethersulfone (PES)-fumed silica mixed matrix membranes were casted using dry/wet technique. The results from the FESEM, DSC and FTIR analysis confirmed that the structure and physical properties of membrane is influenced by inorganic filler. FESEM's cross-section view indicated good compatibility between polymer and fumed silica for all of range fumed silica used in this study. The gas separation performance of the mixed matrix membranes with fumed silica were relatively higher compared to that of the neat PI/PES membrane. PI/PES-fumed silica 5 wt% yielded significant selectivity enhancement of 7.21 and 40.47 for O<sub>2</sub>/N<sub>2</sub>, and CO<sub>2</sub>/CH<sub>4</sub>, respectively.*

**Keywords:** gas separation membrane, mixed matrix membrane, silica

## 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). Membrane separation of gases technology offers a number of significant advantages such as membrane devices are almost always compact and modular, membrane system can be operated in mild conditions with simple equipment and membrane systems are energy efficient owing to a large reduction in power electricity and fuel consumption. In order to extend membranes application and compete successfully with those traditional gas separation processes, great attention has been made in fabricating high separation performance membrane. Modifications on the physical and chemical structures of polymer films have been carried out in order to achieve better separation characteristics.

For the last two decades, the possibility of using synthetic membranes for industrial gas separations has attracted considerable interest since membrane separation technologies have the advantages of energy efficiency, simplicity and low cost. However, for wider commercial utilization, there is still a need to develop membranes with higher permeate fluxes and higher transport selectivities. Conductive polymers, due to their high gas transport selectivities, give rise to a new class of polymeric materials for membrane based gas separation though poor mechanical properties obstruct

the applications for this purpose. This problem leads to the exploration of a new idea of combining the conducting polymers with insulating polymers forming mixed matrix composite membranes.

Mixed matrix composite membranes have received world-wide attention in the field of material science in the last 2 decades (Kusworo et al.; Rafizah and Ismail, 2008; Suer et al., 1994; Tantekin-Ersolmaz et al., 2000; Mahajan and Koros, 2000; Li et al., 2006). There are two types of polymer that can be use as membrane matrix in mixed matrix membrane which is rubber polymer and glassy polymer. It has been generally observed that when using rubbery polymers as membrane matrix there exist an adequate contact between the disperse phase of the molecular sieve and the polymeric phase. However, the high gas fluxes of these polymeric rubber matrixes can lead to low improvement in the mixed matrix membrane selectivity. Duval et al. prepared carbon molecular sieve and zeolite filled membranes. Their result showed that zeolites such as silicate-1, 13X and KY improve, to a large extent, the separation properties of otherwise poorly selective rubber polymers towards a mixture of CO<sub>2</sub>/CH<sub>4</sub> while the carbon molecular sieves did not improve the separation performances.

The adhesion between the polymer phase and the external surface of the particles appeared to be a major problem when glassy polymers are used in the preparation of such membranes. It seems that the weak polymer-filled interaction makes the filler tend

<sup>1)</sup> Membrane Research Unit, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 UTM, Skudai, Johor Bahru, Malaysia

<sup>\*</sup> Corresponding author: Tel.:+60-7-5535592; Fax:+60-7-5581463

E-mail address: afauzi@utm.my

<sup>2)</sup> Department of Chemical Engineering

University of Diponegoro, Jl. Prof. Sudharto, Tembalang, Indonesia

to form voids in the interface between the polymer and the filler. Various techniques have been employed to improve the polymer-filler contact. For examples Duval et al. in their preparation of zeolite filled glassy polymer membranes, found a poor adhesion between the polymer phase and the external surface of the particles. To overcome this problem various methods were investigated to improve the internal membrane structure, such as, surface modification of the zeolite external surface, preparation above the glass transition temperature and heat treatment.

Therefore, the present work proposes an alternative preparation of mixed matrix membranes for gas separation by using inorganic filler materials that differ substantially from those molecular sieves normally used. The employed material was fumed silica and then investigating its effects on the separation performance of mixed matrix membranes. The fumed silica had been surface treated with silane during its commercial production, hence expected to enhance the adherence between the polymer matrix and fumed silica. Since fumed silica particles are nonporous, they do not permeate penetrant as a zeolite might. They presumably alter PI/PES chain packing to effect substantial changes in transport properties. To our knowledge, there is no documentation on the use of fumed silica for PI/PES mixed matrix membrane.

### Experimental

#### Material selection

Polyimide resin was supplied by Alfa Aesar Johnson Matthey Mexico and polyethersulfone 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 fumed silica was supplied by Degussa and namely Aerosil® R380.

#### Fabrication of asymmetric mixed matrix membrane

In this study, the polymer solution consists of 25 wt % polymer (blend PI/PES, 20/80), 75 % NMP and 5-20 wt% fumed silica in the total solid. The homogeneous polyimide and polyethersulfone were prepared according to the following procedure; the inorganic molecular sieve 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. Then, a desired amount of polyethersulfone was added to the homogenous solution. 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.

#### Characterization of asymmetric mixed matrix membrane

A Supra 35 VP Field Emission Scanning Electron Microscopy (FESEM) was used to investigate the asymmetric structure and to determine the dimension of the fibres. 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 addition of fumed silica 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<sup>-1</sup> with a spectral resolution of 8 cm<sup>-1</sup> and averaged over 16 scans.

#### Module fabrication and gas permeation experiment

The gas permeation properties of the flat mixed matrix membrane and pure polymer film were measured by the variable volume method, using an upstream pressure up to 8 bars, while the downstream pressure was effectively atmospheric. The high pressure gas controlled by a line regulator was fed into the test cell. Permeation experiments were carried out at room temperature. The experiments were performed after a period of equilibrium of 15 min. A schematic of the gas permeability equipment is shown in Figure 1. The material used for the construction was stainless steel 316 and double walled permeation cells. The permeate volumetric flow rate was measured by means of a soap bubble meter reading to 0.05 cm<sup>3</sup>. The effective area inside the cell was 14.5 cm<sup>2</sup>. Two O-rings were used as the sealing agent. The downstream side was always purged with the test prior to the permeation test. The permeance or pressure-normalized flux, ( $P/L$ ), is calculated by:

$$(P/L) = \frac{Q_i}{(\Delta p)(n\pi D_l)} \quad (1)$$

where  $Q_i$  is the volumetric flow rate of gas 'i' at standard temperature and pressure,  $\Delta p$  is the trans-membrane pressure drop (cmHg),  $n$  = number of tested fibers;  $D$  = outer diameter of the fibers (cm);  $l$  = effective length of the fibers (cm). Permeances are expressed in gas permeation units, GPU, (1GPU =  $1 \times 10^{-6} \text{ cm}^3 \text{ (STP) cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$ )

The ideal separation factor (gas A over gas B) of the hollow fiber membrane was determined by

$$\alpha = \frac{(P/L)_A}{(P/L)_B} \quad (2)$$

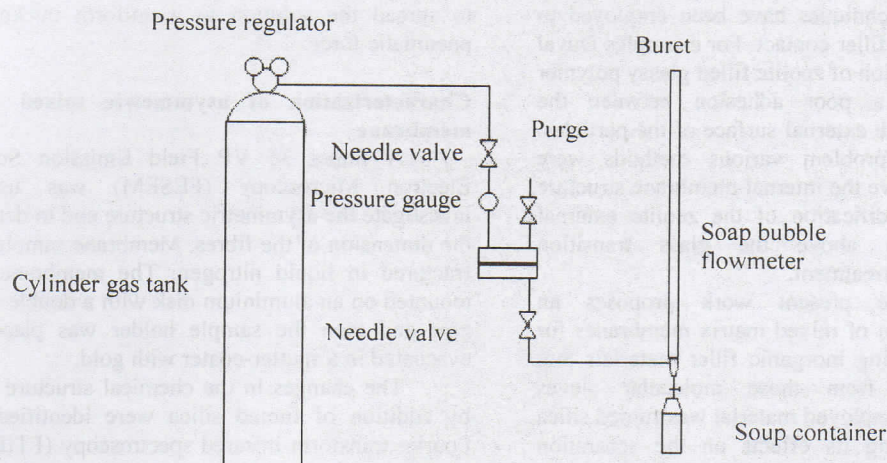


Figure 1. Flat sheet membrane gas permeation measurement set up

## Results and Discussion

### Characterization and gas separation performance of polyimide/polyethersulfone-fumed silica mixed matrix membrane

Figures 2(a)-(c) show FESEM micrographs of the cross-sectional and the surface of the PI/PES-20 wt% silica and 5 wt %, respectively. As depicted in Figure 2, the silica particles appear to be well dispersed throughout the PI/PES matrix. Figure 2 (b) shows that the polymer adheres well to the fumed silica and does not show any unselective voids around fumed silica suggesting better wetting properties with the polymer matrix. This phenomenon can be explained by the properties of commercial fumed silica used in this study. The fumed silica (Aerosil R812) had been surface treated with silane as a commercial product; hence the silica particles are covered with acidic surface silanol groups which could reacted with organic molecules leading to the formation of interfacial layer between silica filler and PI/PES matrix. However, the small agglomeration of silica particles appeared in the mixed matrix membrane with 20 wt% loading and forms a small domain in polymer matrix as shown in Figure 2a. Although some silica particles aggregate and form silica domains, higher magnification of the FESEM image in Figure 2b show that the silica particles are well adhered with polymer.

In this case, small agglomeration might be due to high loading of silica particles in the mixed matrix membrane. Careful inspection of the surface image reveals that silica particles aggregation observed on the outside surface of membrane as depicted in Figure 2c. The aggregation of silica could be deformed the active skin layer resulting in low selectivity and high permeability. The aggregation of silica particles might

be due to the present of too many tiny particles at high loading (20 wt% in the total solid). To eliminate the effect of particles agglomeration, the number of particle had to be reduced by lowering the filler loading. The FESEM cross-sectional images of 5 wt % fumed silica-PI/PES mixed matrix membrane are shown in Figures 3 (a)-(c). Figures 3 (a)-(c) show the successfully formation of PI/PES-silica mixed matrix membrane and indicates no sign of aggregation. It observed that the silica particles are well dispersed throughout in the polymer matrix. Figure 3a also shows that the silica particles are well placed within the active skin layer.

Figure 4 display the FTIR spectra of PI/PES-zeolite without silane treatment and PI/PES-fumed silica in the region of  $4000\text{ cm}^{-1}$  to  $400\text{ cm}^{-1}$ , respectively. In the spectra of the PI/PES-fumed silica a broad band at  $3432\text{ cm}^{-1}$  can be ascribed to  $\text{-OH}$  stretching vibration in the hydroxyl groups. The increase in the relative intensities of this bands compared to PI/PES-zeolite suggested that there are more  $\text{-OH}$  groups on the PI/PES-fumed silica. Based on the FTIR spectra, it is confirmed that the surfaces of silica possess the polar group of hydroxyl group. Therefore, the PI/PES mixed matrix membrane used fumed silica could induced the adhesion between filler and polymer matrix as shown in Figure 3. The gas permeation properties of PI/PES-20 wt % fumed silica and 5 wt % mixed matrix membranes were measured using a variable-pressure constant volume method. The permeability of each gas through each cast membrane was measured at least for 3 runs. The permeabilities for pure gases  $\text{O}_2$ ,  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  and the calculated ideal separation factor for  $\text{O}_2/\text{N}_2$ ,  $\text{CO}_2/\text{CH}_4$  gas pairs are tabulated in Table 1.

For all gases tested, the permeability values increased in proportion to the amount of fumed silica in the polymer matrix. The addition of 5 wt % fumed silica to PI/PES resulted in a ~ 54 % and ~ 43 % increase in the CO<sub>2</sub> and O<sub>2</sub> permeability, respectively. However, the selectivity slightly increased or constant as shown in Table 1. At high fumed silica loading (20 wt %), the permeability is increased dramatically by ~ 96 %. Despite these increases, the separation factor decreased only slightly (23 %). Since the fumed silica particles were non porous for molecular sieving to take effect, this improvement in selectivity and permeability could be contributed to the fumed silica-gas penetrant

interaction. The increase in permeability might be due to the disruption of polymer chain packing in the presence of silica particles. The increases in O<sub>2</sub>/N<sub>2</sub> selectivity and oxygen permeability as compared to those in neat polymer were also reported for polymer/silica composites by Koros and Moaddeb (1997). At high fumed silica loading, CO<sub>2</sub> permeability in the PI/PES-fumed silica mixed matrix membrane is approximately 95 % higher than that in the neat PI/PES membrane. The higher increase in permeability suggested that some permeation might be also occurred through the nano gaps in the interface of polymer and filler.

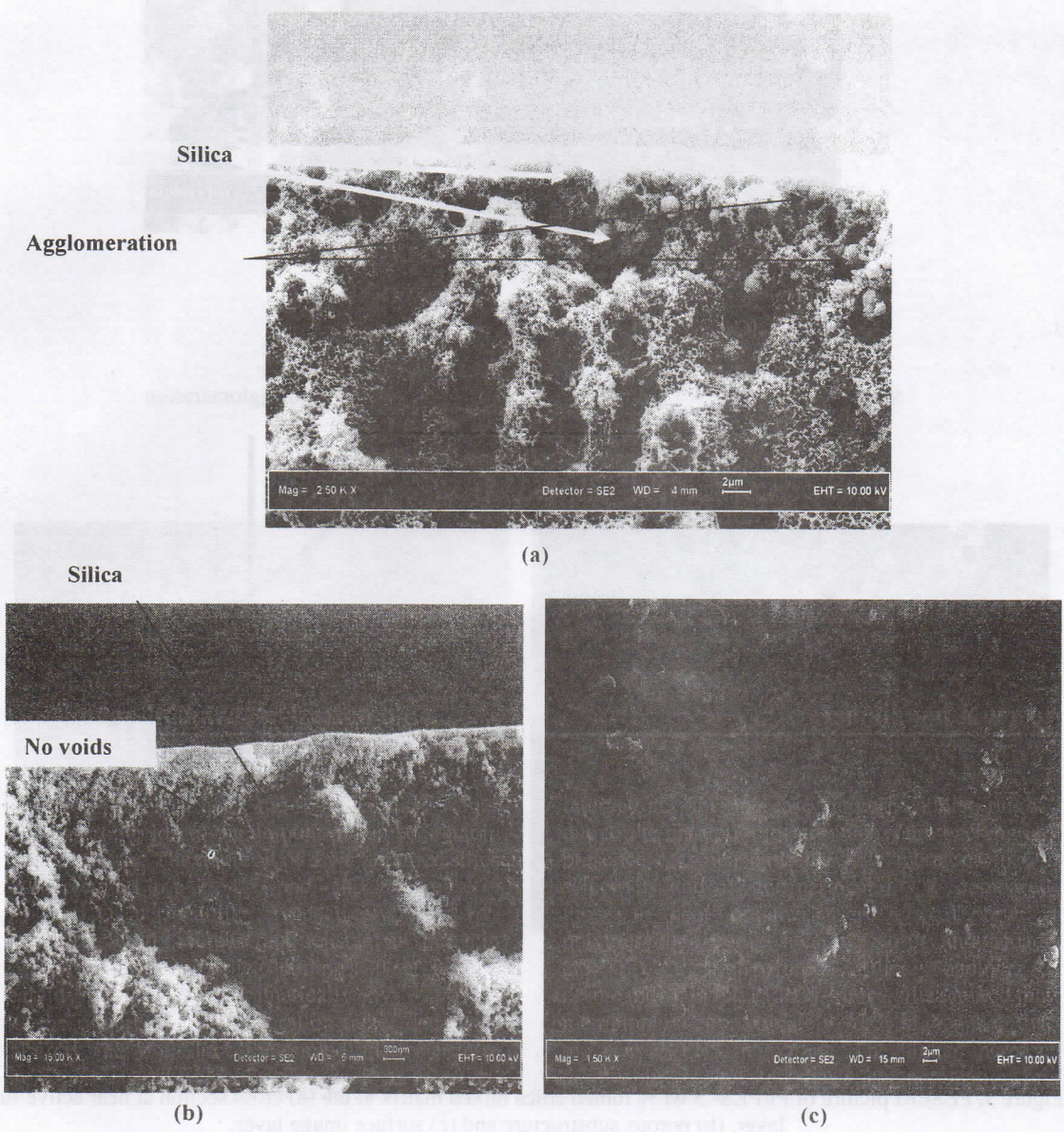
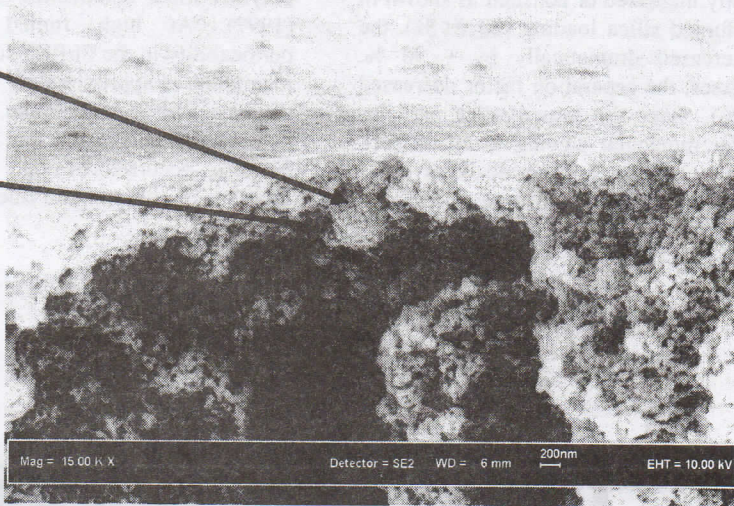


Figure 2. FESEM picture of PI/PES- 20 wt % fumed silica mixed matrix at the (a) cross section, (b) high magnification at near active surface layer and (c) surface image layer

interaction. The increase in porosity might be due to the dispersion of polymer chains leading to the presence of silica particles. The increase in O<sub>2</sub> selectivity and oxygen permeability as compared to the neat PES membrane was also reported for silica loaded PES membranes by Kwon and Mochizuki [10].

For all cases tested, the permeability values increased in proportion to the amount of fumed silica in the polymer matrix. The addition of 5 wt % fumed silica to PES resulted in a 20% increase in oxygen permeability. The CO<sub>2</sub> and O<sub>2</sub> permeability values increased slightly with the addition of silica. Table 1. A high level silica loading (5 wt %) in the membrane is not recommended. Despite the high oxygen permeability, the membrane is not recommended for use in gas separation.

Silica  
No voids

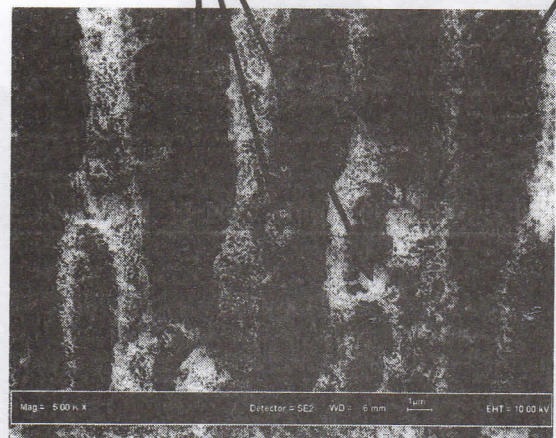


(a)

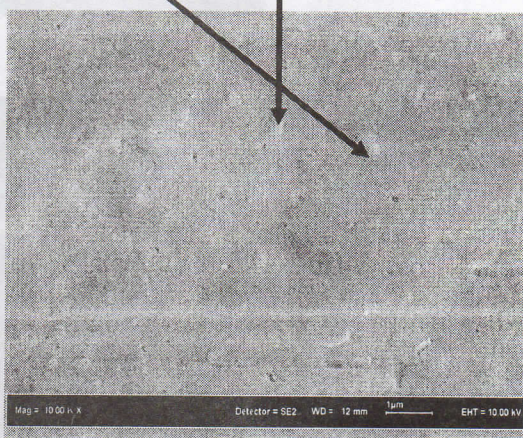
Silica

No voids

No agglomeration



(b)



(c)

Figure 3. FESEM picture of PI/PES- 5 wt % fumed silica mixed matrix at the (a) cross section at near active surface layer, (b) porous substructure and (c) surface image layer.

Table 1. Gas permeabilities of various gases in the PI/PES-fumed silica mixed matrix membranes

PI/PES-fumed silica	Single gas permeance (GPU)*				Selectivity	
	CO <sub>2</sub>	CH <sub>4</sub>	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	O <sub>2</sub> /N <sub>2</sub>
PI/PES neat	43.68	1.23	9.35	1.45	35.67	6.45
5 wt %	67.53	1.89	13.05	2.08	35.73	6.57
20 wt %	85.48	3.45	14.24	2.88	24.77	4.94

\*GPU =  $1 \times 10^{-6} \text{ cm}^3 \text{ (STP)/cm}^2 \text{ s cmHg}$

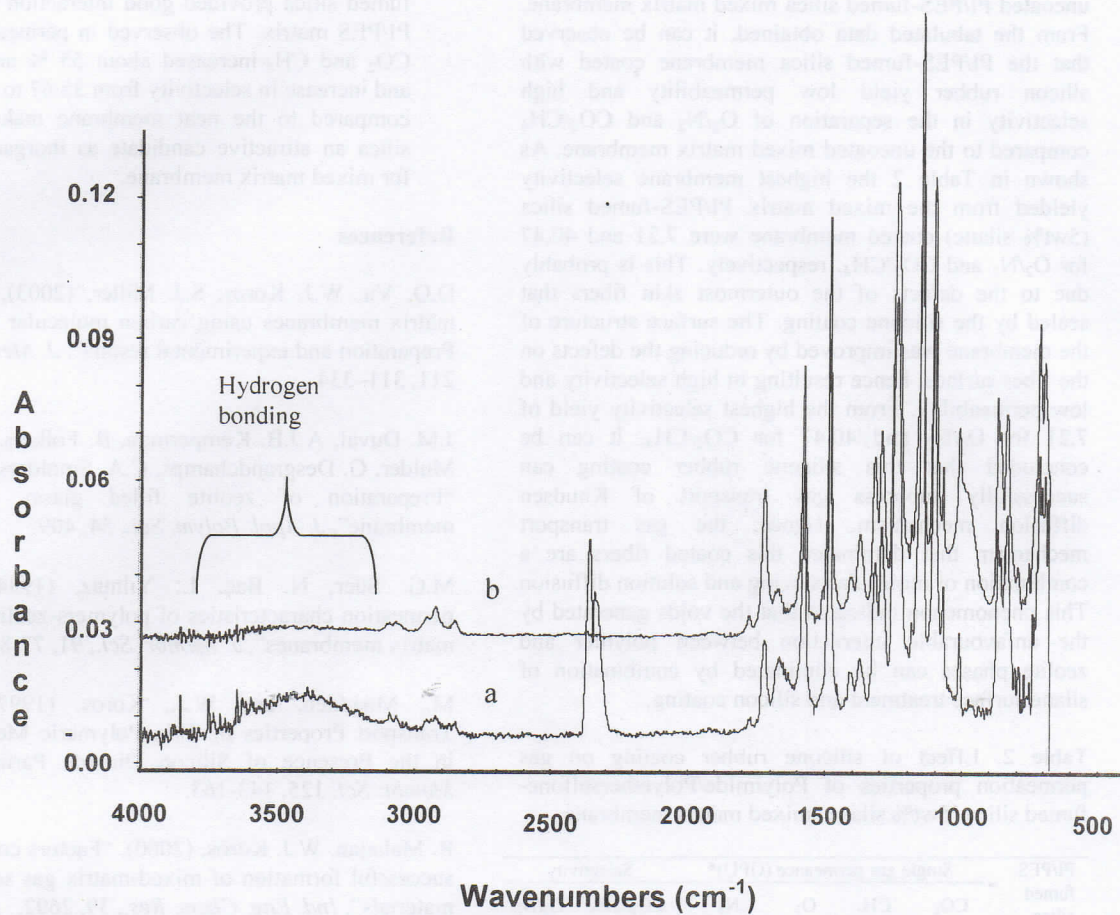


Figure 4. FTIR spectra recorded in the region of  $4000 \text{ cm}^{-1}$  to  $400 \text{ cm}^{-1}$  for (a) PI/PES-zeolite without silane treatment, (b) PI/PES-fumed silica.

**Effect of silicone coating and thermal curing on gas separation performances**

As discussed in section 3.1, the unselective voids were not completely eliminated in the PI/PES-fumed silica. Therefore, the influence of silicone rubber coating and thermal curing on the gas transport and gas separation properties of fabricated mixed matrix membrane PI/PES-fumed silica (5 wt% silica) 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 60 °C for 2 days. 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 2 shows the comparison of permeability and selectivity for tested gases between coated and uncoated PI/PES-fumed silica mixed matrix membrane. From the tabulated data obtained, it can be observed that the PI/PES-fumed silica membrane coated with silicon rubber yield low permeability and high selectivity in the separation of O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub> compared to the uncoated mixed matrix membrane. As shown in Table 2 the highest membrane selectivity yielded from the mixed matrix PI/PES-fumed silica (5wt% silane) coated membrane were 7.21 and 40.47 for O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/CH<sub>4</sub>, respectively. This is probably due to the defects of the outermost skin fibers that 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. From the highest selectivity yield of 7.21 for O<sub>2</sub>/N<sub>2</sub> and 40.47 for CO<sub>2</sub>/CH<sub>4</sub>, it can be concluded that this silicone rubber coating can successfully suppress gas transport of Knudsen diffusion mechanism. Hence, 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 zeolite phases can be eliminated by combination of silane surface treatment and silicon coating.

Table 2. Effect of silicone rubber coating on gas permeation properties of Polyimide/Polyethersulfone-fumed silica (5wt% silane) mixed matrix membrane

PI/PES-fumed silica	Single gas permeance (GPU)*				Selectivity	
	CO <sub>2</sub>	CH <sub>4</sub>	O <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub> /CH <sub>4</sub>	O <sub>2</sub> /N <sub>2</sub>
Coated	35.68	0.882	7.69	1.067	40.47	7.21
Uncoated	67.53	1.89	13.05	2.08	35.73	6.57

\*GPU = 1 x 10<sup>-6</sup> cm<sup>3</sup> (STP)/cm<sup>2</sup> s cmHg

**Conclusions**

In this study, the possibility of fabrication of the polyimide (PI)-polyethersulfone (PES) blending with new inorganic filler fumed silica was investigated. Based on the experimental results and analysis, the following conclusions can be made.

- (i) The uniformly dispersed fumed silica in PI/PES matrix was successfully fabricated. The stability of the surface modified fumed silica in NMP solvent was found to be good enough to be used for the formation of blend membrane.
- (ii) From the FESEM analysis, the surface ruptures are not occurred on the fumed silica mixed matrix membrane. The phenomenon might be due to the shape of fumed silica appeared to be oblong. The smooth surface of fumed silica might also help to enhance the adherence between the silica and the host polymer.
- (iii) The high surface coverage of silanol group on fumed silica provided good interaction with the PI/PES matrix. The observed in permeability of CO<sub>2</sub> and CH<sub>4</sub> increased about 55 % and 53 % and increase in selectivity from 35.67 to 40.47 as compared to the neat membrane make fumed silica an attractive candidate as inorganic filler for mixed matrix membrane.

**References**

D.Q. Vu, W.J. Koros, S.J. Miller, (2003), "Mixed matrix membranes using carbon molecular sieves I. Preparation and experimental results", *J. Membr. Sci.* 211, 311-334

J.M. Duval, A.J.B. Kemperman, B. Folkers, M.H.V. Mulder, G. Desgrandchamps, C.A. Smolders, (1994), "Preparation of zeolite filled glassy polymer membrane", *J. Appl. Polym. Sci.*, 54, 409.

M.G. Süer, N. Baç, L. Yılmaz, (1994), "Gas permeation characteristics of polymers-zeolite mixed matrix membranes", *J. Membr. Sci.*, 91, 77-86.

M., Moaddeb, and W.J., Koros, (1997), "Gas Transport Properties of Thin Polymeric Membranes in the Presence of Silicon Dioxide Particles", *J. Membr. Sci.* 125, 143-163.

R. Mahajan, W.J. Koros, (2000), "Factors controlling successful formation of mixed-matrix gas separation materials", *Ind. Eng. Chem. Res.*, 39, 2692.

S.B.Tantekin-Ersolmaz, C. Atalay-Oral, M. Tather, A. Erdem-Senatarlar, B. Schoeman, J. Sterte, (2000), "Effect of zeolite particle size on the performance of polymer-zeolite mixed matrix membranes", *J. Membr. Sci.*, 175, 285.

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*. In Press, Accepted Manuscript.

W.A.W. Rafizah and A.F. Ismail, (2008). "Effect of carbon molecular sieve sizing with poly(vinyl pyrrolidone) K-15 on carbon molecular sieve-polysulfone mixed matrix membrane". *J. Membr. Sci.* 307, 53-61

Y.K. Kim, H.B. Park, Y.M. Lee. (2004). "Carbon molecular sieve membranes derived from thermally labile polymer containing blend polymers and their gas separation properties". *J. Membr. Sci.*, 243, 9-17.

Y. Li, H. M. Guana, T. S. Chung, S. Kulprathipanja, (2006). "Effects of novel silane modification of zeolite surface on polymer chain rigidification and partial pore blockage in polyethersulfone (PES)-zeolite A mixed matrix membranes". *J. Membr. Sci.* 275, 17-28.

... yang dilakukan dengan cara ...

... yang dilakukan dengan cara ...