Reaktor, Vol. 12 No. 4, Desember 2009, Hal. 245-252

SYNTHESIS AND CHARACTERIZATION OF POLYIMIDE-ZEOLITE MIXED MATRIX MEMBRANE FOR BIOGAS PURIFICATION

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Abstract

Biogas has become an attractive alternative energy source due to the limitation of energy from fossil. In this study, a new type of mixed matrix membrane (MMM) consisting of polyimide-zeolite was synthesized and characterized for biogas purification. The MMM consists of medium concentration of polymer (20% wt polyimide), 80% N-Methyl-2-pyrrolidone (NMP) and 25% zeolite 4A in total solid were prepared by a dry/wet phase inversion technique. The fabricated MMM was characterized using SEM, DSC, TGA and gas permeation. Post treatment coating procedure was also conducted. The research showed that surface coating by 3% silicone rubber toward MMM PI 20% gave the significant effect to improve membrane selectivity. The ideal selectivity for CO_2/CH_4 separation increased from 0.99 for before coating to 7.9 after coating for PI-Zeolite MMM, respectively. The results suggest that PI-Zeolite MMM with good post treatment procedure will increase the membrane selectivity and permeability with more saver polymer requirement as well as energy saving due to low energy for mixing.

Keywords: *biogas purification, mixed matrix membrane, polyimide, zeolite*

Abstrak

Biogas telah menjadi sumber energi alternatif yang semakin menarik sehubungan dengan keterbatasan energi fosil di dunia akhir-akhir ini. Dalam penelitiani ini, mixed matrix membrane (MMM) yang terdiri dari polyimide-zeolit telah disintesa dan dikarakterisasi untuk pemurnian biogas. MMM dengan konsentrasi polimer medium (20% wt polyimide), 80% N-Metil-2-pyrrolidone (NMP) dan 25% zeolit 4A (dalam padatan total) dibuat dengan teknik inversi fasa. MMM yang terbentuk dikarakterisasi dengan menggunakan SEM, DSC, TGA dan permeasi gas. Perlakuan paska pembuatan membran dengan pelapisan permukaan (surface coating) juga dilakukan pada penelitian. Hasil penelitian menunjukkan bahwa pelapisan permukaan membran MMM Polyimide-Zeolite 20% menggunakan larutan 3% silicon rubber memberikan efek signifikan terhadap peningkatan selektivitas membran. Selektivitas ideal untuk CO_2/CH_4 meningkat dari 0,99 menjadi 7,9 setelah pelapisan. Hasil penelitian ini dapat disimpulkan bahwa pelapisan permukaan membran MMM Polyimide-Zoelite dengan konsentrasi medium (20%) dapat meningkatkan selektifitas dan permeabilitas membrane dengan keunggulan yang menyertainya yaitu lebih hemat kebutuhan polymer dan energi untuk pengadukan.

Kata kunci: *pemurnian biogas, mixed matrix membrane, polyimide, zeolit*

INTRODUCTION

Biogas has become an attractive alternative energy source due to the limitation of energy from fossil. This is due to its characteristics i.e. renewable source, environment friendly, clean, cheap and versatile fuel. However, the use of biogas is limited by its low quality. Except the main component of CH_4 (55-80% vol), biogas contains substantial amount of CO_2 (20-45% vol) and H_2S (0-1% vol) (Kapdi *et al.*, 2005). In addition, biogases are also frequently saturated by water vapor. The presence of CO_2 as an incombustible gas reduces its calorific value and makes it uneconomical to compress and transport to longer distances. The H_2S content poses serious problems of odor, toxicity for human and animal health, and corrosion (Truong and Abatzoglou, 2005). Nevertheless, if biogas is cleaned up sufficiently, biogas has the same characteristics as natural gas (NG) (Esteves *et al.*, 2008). There is a lot of potential if biogas could be made viable as a transport vehicle fuel like Compressed Natural Gas (CNG). Besides the use of biogas as a vehicular fuel, small scale or bulk biogas storage for domestic consumption is also potential large market. Therefore, biogas purification before compression at high pressure for storage in cylinders is essential.

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 compared to the conventional separation processes (Lin and Chung, 2001). In addition, advantages of membrane technology are its simplicity, i.e. no absorbent, which has to be regenerated; it can be easily retrofitted, modularized and scaled-up for several applications (Baker, 2000).

Commercial membrane systems for gas separation were available since the mid-1970s, but the most important innovation for large-scale commercialization of polymeric membranes for gas separation was achieved by Permea (now Air Products) in 1980 (Baker, 2002). Currently, the main challenge in application of the membrane technology for gas separation is how to get the materials with higher permeability and selectivity as well as good thermal stability (Lin and Freeman, 2004). Generally, better selectivity is obtained with glassy polymers. The glassy state offers a more structured sieving matrix than the rubbery state as well as higher load bearing properties allowing for high pressure drop across the membrane. Typical glassy polymers used in membranes for commercial gas separation are polysulphone, cellulose acetate and polyimide (Stern, 1994; Robeson, 1999). Among them, aromatic polyimide is well known having excellent properties, e.g. high thermal stability, chemical resistance, mechanical strength, and low dielectric constant (Lin and Chung, 2001). Due to high glass transition temperature and low solubility of polymer, it is possible to apply polyimide in a wide range of temperatures and pressures. Moreover, the polymer is characterized by high selectivity and permeability to the gases in comparison to the others. According to Harasimowicz *et al.* (2007), polyimide have permeability higher than 400 Barrers for CO_2 and their CO_2/CH_4 selectivity is higher than 15. Morever, according to Hao *et al.* (1996), polyimide made from 6FDA-HAB has CO_2/CH_4 selectivity up to 60. However, PI polymer still has some limitation i.e relatively expensive and high viscosity cause the high energy requirement for mixing during membrane preparation.

Kusworo *et al.* (2007) has made an effort to decrease polymer cost of polyimide and increase processability by mixing PI with the cheaper polymer (polyether sulphone, PES) with ratio 20:80 by 25% wt of total polymer in N-Methyl-2-pyrrolidone (NMP). These composite membranes offer relatively low cost of polymer besides easy to cast the polymer solution so it will reduce the mixing power. However, Kusworo *at al.* (2007) is still use polymer in 25% concentration. In effort to decrease the polymer requirement, in this study, the MMM consists of medium concentration of polymer (20% wt PI) were synthesized and characterized for biogas purification. The effect of coating on the separation performance of fabricated membrane was also examined.

EXPERIMENTAL

Material Selection

The selection of polymers and fillers in this research is to obtain a MMM having high permeability and selectivity of CO_2/CH_4. The polyimide polymer is selected due to it's characteristics that polyimide polymer has aromatic rings and functional groups of big volume, which act like molecular sieves, as a material for membranes used for gas separation is reasonable. Due to high glass transition temperature and low solubility of polymer, it is possible to apply polyimide in a wide range of temperatures and pressures. Moreover, the polymer is characterized by high selectivity and permeability to the gases in comparison to the others. According to Hao *et al.* (1996), polyimide made from 6FDA-HAB has CO_2/CH_4 selectivity up to 60. Polyimide polymers used in this research was matrimide resin. Matrimide was obtained from Alfa Aesar Johnson Matthey Company USA. The matrimide polymers were dried overnight in a vacuum oven at 120◦C before used for dope preparation. *N*-methyl-pyrrolidinone (NMP) was from Merck. The chemical structure of the polyimide is shown in Fig. 1.

Zeolite molecular sieve was selected due to their high selectivity and compatibility towards polar compounds, such as H_2S (Hao *et al*, 1996). The zeolite 4A was purchased from Aldrich and the particle size was 2 μm. In order to remove the adsorbed water vapor or other organic vapors, all zeolite particles were dehydrated at 300^{o}C for 3 h before use.

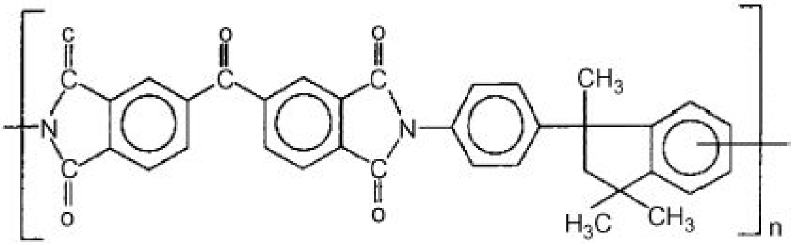

Figure 1. Chemical structure of polyimide

Fabrication of Asymmetric Flat Sheet MMM

In this study, the polymer solution consists of 20% wt PI polymer 80% NMP and 25% wt zeolite in the total of solid. The homogeneous polyimide were prepared according to the following procedure; the inorganic molecular sieve particles were dispersed into the solvent and stirred for 24 h followed by the addition of a desired amount of polyimide. The solution was agitated with a stirrer at least 24 h to ensure complete dissolution of the polymer. Before casting, the homogeneously prepared solution was degassed under vacuums for 3 h. 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. Membranes were cast at different shear rates by varying the speed of the trolley (casting speed). The glass plate with the membrane film was then immersed into the coagulant bath or water bath. During this process, solvent exchange occurred and solidified the membrane film to a complete membrane structure.

To ensure all of the solvent in the membrane structure is removed, membranes were immersed in an aqueous bath for 1 day, followed by immersion in methanol for 4 h and air-dried for 24 h at room temperature. The mixed matrix membranes were finally dried in oven at 120◦C for 4 h to remove all the residual solvents.

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^{o}C to allow curing before permeation testing.

Membrane Characterization

A Supra 35 VP Field Emission Scanning Electron Microscopy (FESEM) was used to observe the membrane structure and to determine the dimension of the fibers. Membrane samples were fractured in liquid nitrogen. The membranes were mounted on an aluminum 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 of 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^{o}C for 24 hours to remove adsorbed water; then weighed and placed into aluminum DSC pans. The scanning range was 50-320^{o}C with scanning rate of 10^{o}C min^{-1} in the first DSC cycle to remove thermal history and then cooled from 320 to 25^{o}C at the rate of 10^{o}C min^{-1}; finally the second cycle was carried out with the same procedure.

Module Fabrication and Gas Permeation Experiment

Membranes formed were exposed to two different gases CH_4 and CO_2 and were measured its permeabilities. 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. Fig. 2 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), was 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 the membrane (cmHg), *A* is membrane affective 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:

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

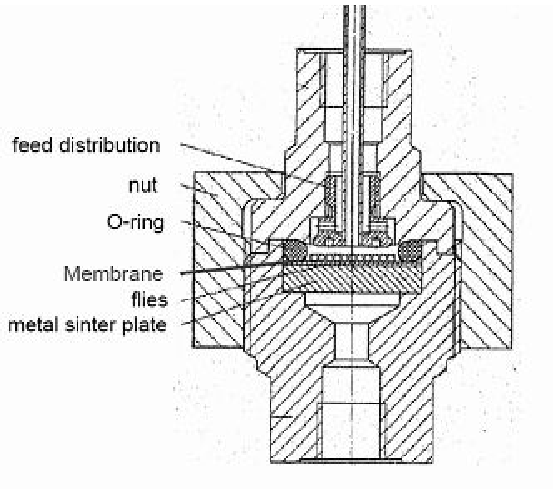

Figure 2. Gas permeation test cell

For biogas separation testing, in this study we were used gas sample of CO_2 and CH_4 to represent the biogas product. The gas permeation properties for each flat sheet polyimide-zeolite mixed matrix membrane were measured by using variable pressure constant volume method.

RESULTS AND DISCUSSION

Morphology of Asymmetric PI-Zeolite Mixed Matrix Membranes

An understanding of how preparation conditions lead to different morphologies is vital for generating mixed matrix membranes with desirable transport properties. The FESEM analysis was performed in order to investigate the effect of preparation process such as the effect of medium polymer concentration on the morphology of mixed matrix membranes and the relation with the separation performance of these membranes. As suggested by previous studies (Vu *et al.*, 2003; Jiang *et al.*, 2005) that the main problems faced during fabrication of mixed matrix membrane were surface effects, aggregation and poor polymer-sieve contact. Koros and co-workers Vu *et al.* (2003) observed that mixed matrix membrane with zeolite and glassy polymer possessed poor polymer-sieve contact. It was found that the mixed matrix membrane contained the unselective voids of about 0.1-0.2 μm around the sieves. Moreover, the interface between a polymer matrix and inorganic filler plays an important role to determine the performance of fabricated mixed matrix membranes. Therefore, in this study, the feasibility of fabrication mixed matrix membrane at medium polymer concentration was investigated. Hence, the characterization and comparison of polyimide-zeolite for uncoated and coated would be further discussed.

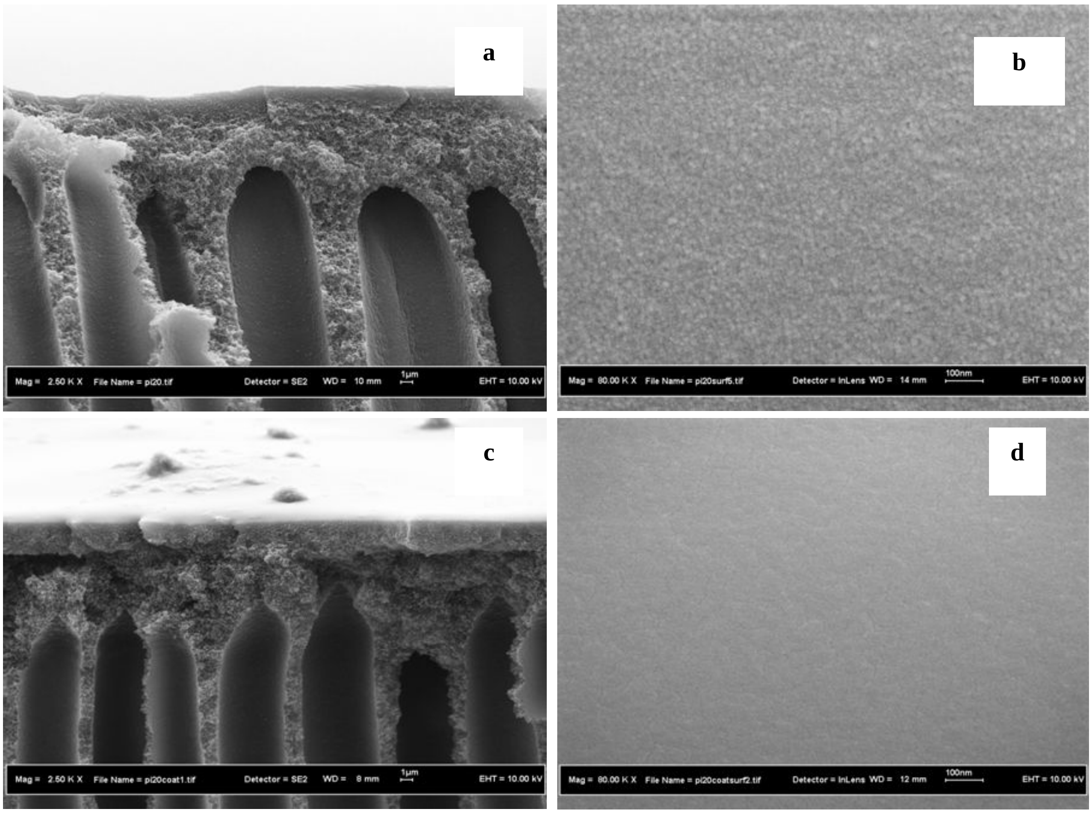

Figure 3. SEM picture of asymmetric uncoated neat polyimide membrane at the: (a) uncoated membrane cross section and (b) outer surface image layer (c) coated membrane at cross section and (d) at outer surface image layer

FESEM characterization was carried out on the fabricated membrane in order to determine the qualitative analysis of polyimide-zeolite mixed matrix membrane. The FESEM micrographs of the polyethersulfone –zeolite mixed matrix hollow fiber membrane are shown in Figures 3-5. Figures 3a-d illustrates the partial cross-sectional area of representative neat polyimide membrane with uncoated and coated. As can be seen from the SEM micrographs, of all membranes exhibited the porous structure. The skin layer of neat PI membrane became increasingly denser when membrane was subjected silicone coating as shown in Figures 3c-d. Figure 3 also suggests that the neat PI membrane clearly reveals the presence of some macrovoids under the skin layer. Moreover, both neat membranes coated and uncoated have substructure relatively thick and have pore sizes suitable for Knudsen diffusion, the determining step of the overall selectivity is the Knudsen diffusion occurred in the substructure. Additional silicone coating only seals defects of the outermost skin, thus the overall fiber selectivity is not improved.

The FESEM micrographs of the polyimide–zeolite mixed matrix membrane at medium polymer concentration are shown in Figures 4-5. Figures 4-5 presents the partial cross-sectional area of representative PI-zeolite mixed matrix membrane with and without silicone coating. Figures 4a-c clearly reveals the presence of some agglomeration of zeolite and voids in the interface of zeolite and polymer matrix. As suggested by previous study that during fabrication of polyimide-zeolite membrane, one factor plays a great importance is particle agglomeration due to sedimentation or migration to the surface (Vu *et al.*, 2003; Jiang *et al.*, 2005; Li, 2006). Due to the totally different physical properties and difference in density between zeolite and polymers, precipitation of zeolite may occur during the MMM preparation, resulting in formation of inhomogeneous zeolite and polymer phases in the filled membrane. The agglomeration of zeolite will cause the pinholes that cannot be reached by polymer segments, forming as non-selective defects in the MMM. On the medium concentration of polymer was generally the zeolite particle do not have enough time to precipitate; while the solvent was rapidly evaporated to form membrane. Moreover, the zeolite particle will tend to form agglomeration.

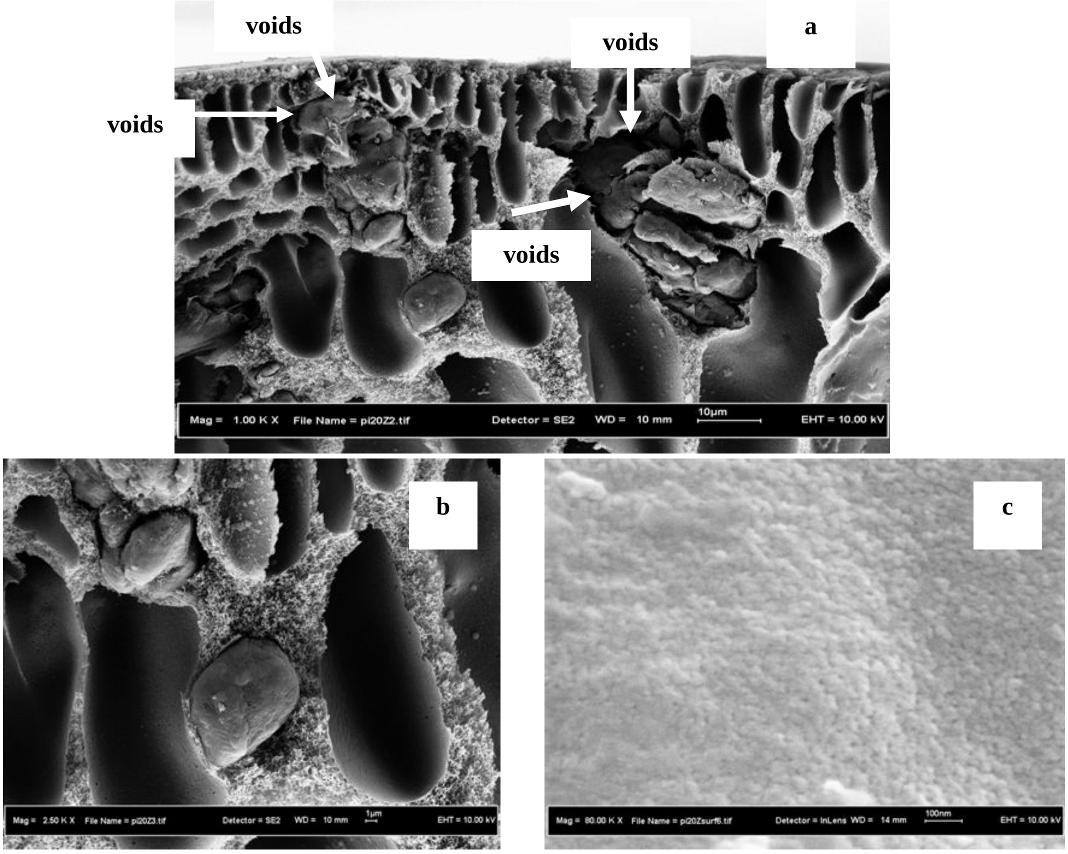

Figure 4. SEM picture of asymmetric uncoated polyimide-zeolite mixed matrix membrane at the: (a, b) cross section and (c) outer surface image layer

The effect of silicone coating on the morphology of PI-zeolite mixed matrix membrane was depicted in the Figure 5. The FESEM micrographs reveal that the mixed matrix membrane with silicone coating has denser on the outer skin layer compared to uncoated membrane. Furthermore because of the silicone coating effect the packed chains in the polymer matrix denser and the packed structure in the outer skin layer provide a high degree of size and shape discrimination between the gas molecules. Figure 5a-b depict that the interfacial gaps between polymer host and zeolite can be reduced by post treatment membrane with silicone rubber coating. Moreover, the smooth surface of PI-zeolite membrane in the Figure 5b indicates that the zeolite particle adheres well to the polymer matrix. Foremost, by referring to Figures 4-5, the differences in adhesion between PI-zeolite with post treatment using silicone rubber coating can be successfully distinguished. The post treatment using silicone rubber can seal the voids between zeolite and polymer host.

Thermal Gravity Analysis

Thermal stability is one of the most important properties of polymer nanocomposites membrane. Decomposition temperature, vary differently depending on the interaction of polymer matrix and inorganic filler. This characterization is conducted to study the relationship between the thermal decomposition temperatures with the weight loss of the composition. From the TGA curve, although the onset thermal decomposing temperature is the same but the weight losses of the composition are differing according to its content. The weight loss of the composition is shown in Table 1. The same thermal decomposing temperature is used to identify the rate of each composition to diffuse as already shown in Table 1.

Table 1. Effect of silicone rubber on the thermal stability of PI-zeolite mixed matrix membrane

Onset Thermal Decomposing Temperature at 550°C			
Composition	Weight before Decomposing, mg	Weight loss, mg	% weight loss
Neat PI	6.4500	3.657	56.7
Uncoated PI-zeolite	6.0600	3.399	56.1
Coated PI-zeolite	5.8400	3.159	54.1

The silicone rubber coating has a great effect on the onset decomposing temperature. Introducing silicone coating to the 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 silicone coating subjected to PI-zeolite mixed matrix membrane 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 zeolite, so the diffusion of small molecules was retarded although under the high temperature.

The influence of silicone rubber on the glass transition temperature of PI-zeolite mixed matrix membranes are tabulated in Table 2. The T_g of the mixed matrix membranes increased about 0.9-1.5°C with the addition silicone rubber on the mixed matrix membrane as depicted in Table 2. This phenomenon indicates that the surface modification of mixed matrix membrane using silicone rubber coating affects the mechanical properties.

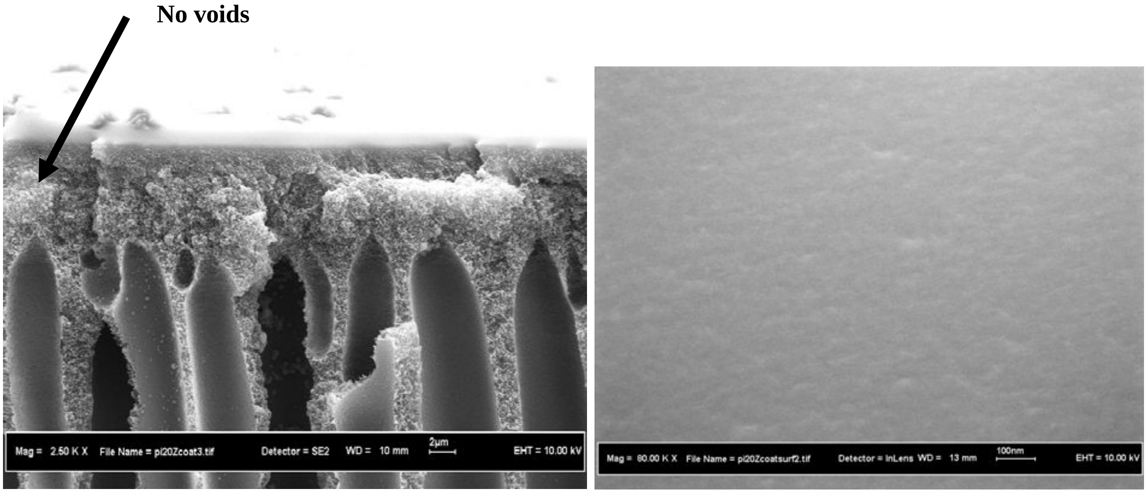

Figure 5. SEM picture of asymmetric coated polyimide-zeolite mixed matrix membrane at the: (a) cross section and (b) outer surface image layer

However, Li *et al.* (2006) observed that the main factors causing the increase of T_g with an increase of zeolite loading is due to a fair interfacial interaction between polymer and zeolite. As presented in Table 2, it can be concluded that the silicone rubber coating could induce the adherence between polymer matrix and zeolite particles.

Table 2. Effect of silicone rubber on the glass transition temperature of PI-zeolite mixed matrix membrane

Membrane	T_g (^oC)
Neat PI	319.5
Uncoated PI-zeolite	320
coated PI-zeolite	321.7

Gas Separation Performance of PI-zeolite Mixed Matrix Membrane

The effect of modification on gas separation performance is important parameter in membrane modification for gas separation. Thus, this testing was carried out in order to study the membrane effectiveness due to the effect of coating on polyimide-zeolite 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 CO_2 and CH_4 to represent the biogas product. The gas permeation properties for each flat sheet polyimide-zeolite mixed matrix membrane were measured by using variable pressure constant volume method. The permeability and selectivity for tested gases CO_2/CH_4 obtained are presented in Table 3. Table 3 summarizes the permeability and selectivity data of uncoated PI, coated PI, uncoated PI-zeolite and coated PI-zeolite.

Table 3. Biogas purification performance of PI-Zeolite mixed matrix membrane

Membrane	Single gas permeance (GPU)		Selectivity
	CO_2	CH_4	CO_2/CH_4
Uncoated neat PI	25.23	31.37	0.80
Coated neat PI	10.51	0.58	18.2
Uncoated PI-zeolite	168.04	169.18	0.99
Coated PI-zeolite	110.5	13.9	7.9

Generally, the idea to put inorganic filler into organic polymer to enhance gas permeability of polymer nanocomposites membranes due to the disturbed polymer chain packing by the nanofillers (Ramanathan *et al.*, 2005). Therefore, the well dispersed and good adherence of polyimide-zeolite will be effectively increased the gas permeability due to more effectively insert between polymer chains of the matrix. As shown in Table 3, the permeability of uncoated PI and uncoated PI-zeolite membrane for all gases were very high. These results indicated that these membranes have a big porosity or many voids were formed on the uncoated PI-zeolite mixed matrix membrane as shown in the Figure 4. However, the selectivity values for uncoated neat PI and uncoated PI-zeolite at 20% wt polymer concentration for all gases were very low. These might be an indication of the Knudsen diffusion phenomena resulted in the membrane due to the presence of severe voids between zeolite particles and agglomeration as shown in Figure 3a-b and Figure 4. Generally, Knudsen-diffusion controls the permeation of gas through porous membrane and the selectivity for binary gas in Knudsen-diffusion is given by equation as follow

$$\alpha_o = \left[\frac{M_A}{M_B}\right]^{1/2} \tag{3}$$

where M_A and M_B are the molecular weights of component A and B, respectively. Equation 3 indicated that Knudsen-diffusion does not offer attractive separation factors, especially for gases of comparable molecular weight. The previous study of Vu *et al.* (2003) suggested that agglomeration of molecular sieve particles usually was caused by low viscosity of mixed matrix slurries. As supported by the FESEM in Figure 4, the gas transport could occur through the submicron gaps between the polymer matrix wall and the zeolite particles. As the gas transport through those unselective voids, it had been assumed to be the Knudsen diffusion behavior, the permeability of CH_4 and CO_2 became larger due to gas flowing through the interface between zeolite particles and polymer matrix. Moreover, 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. Hence, the selectivity of the resulting membrane was lower than that of the neat polymer.

In this study, we investigated the effect of simple post treatment to seal the unselective void on the PI-zeolite membrane using silicone rubber. Gas separation performance of coated membrane was also influenced by thermal curing time. In this study the coated membrane fibers was dried in a vacuum oven at temperature 120^0C for 72 hours. 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 PI-zeolite membrane.

From the tabulated data obtained, it can be observed that the PI-zeolite mixed matrix membrane fabricated with medium polymer concentration coated with silicon rubber yield low permeability and increase the selectivity in the separation of CO_2/CH_4 compared to the uncoated membranes. The increase of selectivity from 0.99 to 7.99 might be caused by suppression of Knudsen diffusion mechanism using the silicone rubber coating. 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 membrane surface, hence resulting in increase selectivity and low permeability. Therefore, the gas transport mechanism that dominated this coated membranes are a combination of molecular sieving and solution diffusion. This phenomenon indicated that the voids generated by the unfavorable interaction between polymer and zeolite can be reduced using silicone rubber coating.

CONCLUSION

In this study, mixed matrix membrane polyimide-zeolite was fabricated 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 simple post treatment such as silicone rubber coating can be used to reduce the interface voids between inorganic particles with polymer host in the fabrication of mixed matrix membrane. The coated PI-zeolite mixed matrix membranes had increased the CO_2/CH_4 selectivity and reduce permeability of methane gas. The PI-zeolite mixed matrix membranes have been potentially applied on the biogas purification

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