POLYIMIDE-ZEOLITE MIXED MATRIX MEMBRANE (MMM) FOR BIOGAS PURIFICATION

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Abstract

Biogas has being become significant potential as an 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 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.

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

Introduction

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%). 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]. The H_2S content poses serious problems of odor, toxicity for human and animal health, and corrosion [2]. If biogas is cleaned up sufficiently, biogas has the same characteristics as natural gas (NG) [3]. 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 also represent potentially 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 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].

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 [6]. 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 [7]. 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 [8-9]. Among oh these polymers, aromatic polyimide were well known has the excellent properties, e.g. high thermal stability, chemical resistance, mechanical strength, and low dielectric constant [4]. However, due to the general limitations in polymeric membrane performance such as low permeability [10] many research efforts have been focused on developing membranes with selective inorganic fillers. One such system is a hybrid membrane. 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. The intent of this type of membrane is to take advantage of the low cost and good processability of polymers with the excellent separation performance of zeolites.

An effort to decrease polymer cost of polyimide and increase processability, Kusworo et al. [11] has mixed PI and polyether sulphone (PES) with ratio 20:80 by 25 wt% of total polymer in N-Methyl-2-pyrrolidone (NMP). These membrane composites offer relatively low cost of polymer besides easy to cast the polymer solution so it will reduce the mixing power. Therefore, the objective of the present study is to synthesize and characterize the high selectivity of CO_2/CH_4 of polyimide-zeolite mixed matrix membrane at medium polymer concentration for biogas purification. In the present study was also examined the effect of coated and uncoated mixed matrix membrane on the separation performance of fabricated membrane.

Experimental
Material selection
The selection consideration of polymers and fillers in this research is to obtain the MMM formed have high permeability and selectivity of CO_2/CH_4. The polyimide polymer is selected due to it's characteristics that polyimide polymer formed by 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. [12], 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 dope preparation. *N*-methyl-pyrrolidinone (NMP) from Merck was selected as the solvent due to its low toxicity. The chemical structure of the polyimide is shown in Fig. 1.
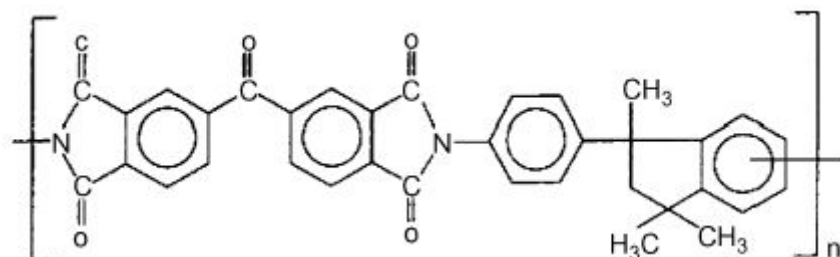
Figure 1: Chemical structure of polyimide

Zeolite molecular sieve was selected due to their high selectivity and compatibility towards polar compounds, such as H_2S [12]. Therefore, the inorganic filler molecular sieve involved was zeolite 4A purchased from Aldrich and the particle size was 2 μm. In order to remove the adsorbed water vapour or other organic vapors, all zeolite particles were dehydrated at 300 ^{o}C for 3 h before use.

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 ensure the asymmetric 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.

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), can be calculated as follows:

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

where Q_i is the volumetric flow rate of gas i, Δp is pressure difference across membrane (cmHg), A is membrane affective surface area (cm^2) and l is membrane skin thickness (cm). The ideal separation factor $\alpha_{i/j}$ can be calculated by using equation below:
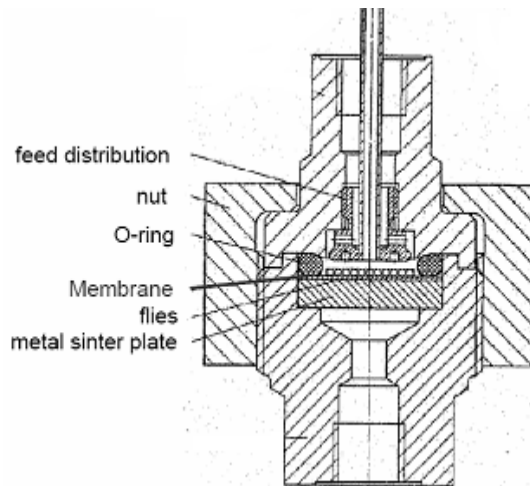
$$\alpha_{i/j} = \frac{(P/l)_i}{(P/l)_j} \tag{2}$$

Figure 2: Gas permeation test cell

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 study [13-14] that the main problems faced during fabrication of mixed matrix membrane were surface effects, aggregation and poor polymer-sieve contact. Koros and co-workers [13] 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.

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.
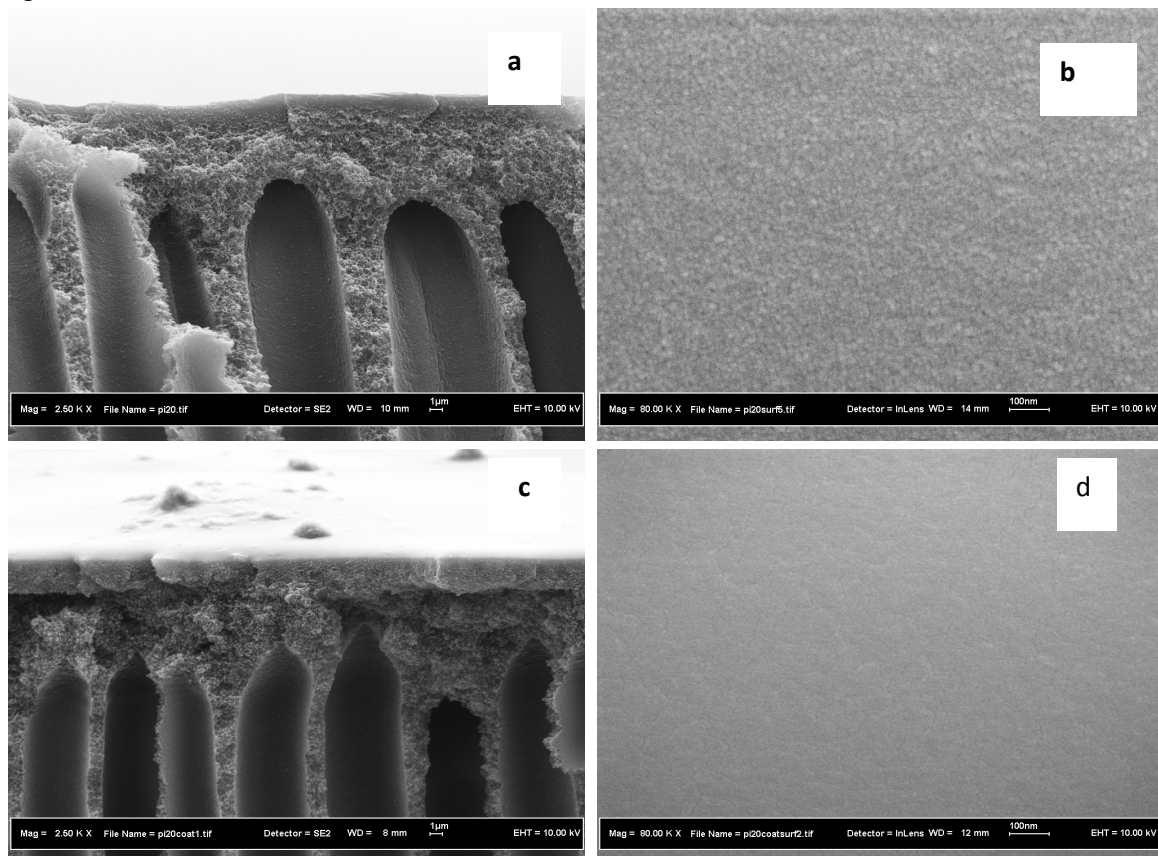

Figure 3: SEM picture of asymmetric uncoated neat polyimide membrane at the: (a) cross section and (b) outer surface image layer (c) coated membrane at cross section and (d) at outer surface image layer

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 was also presented 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.
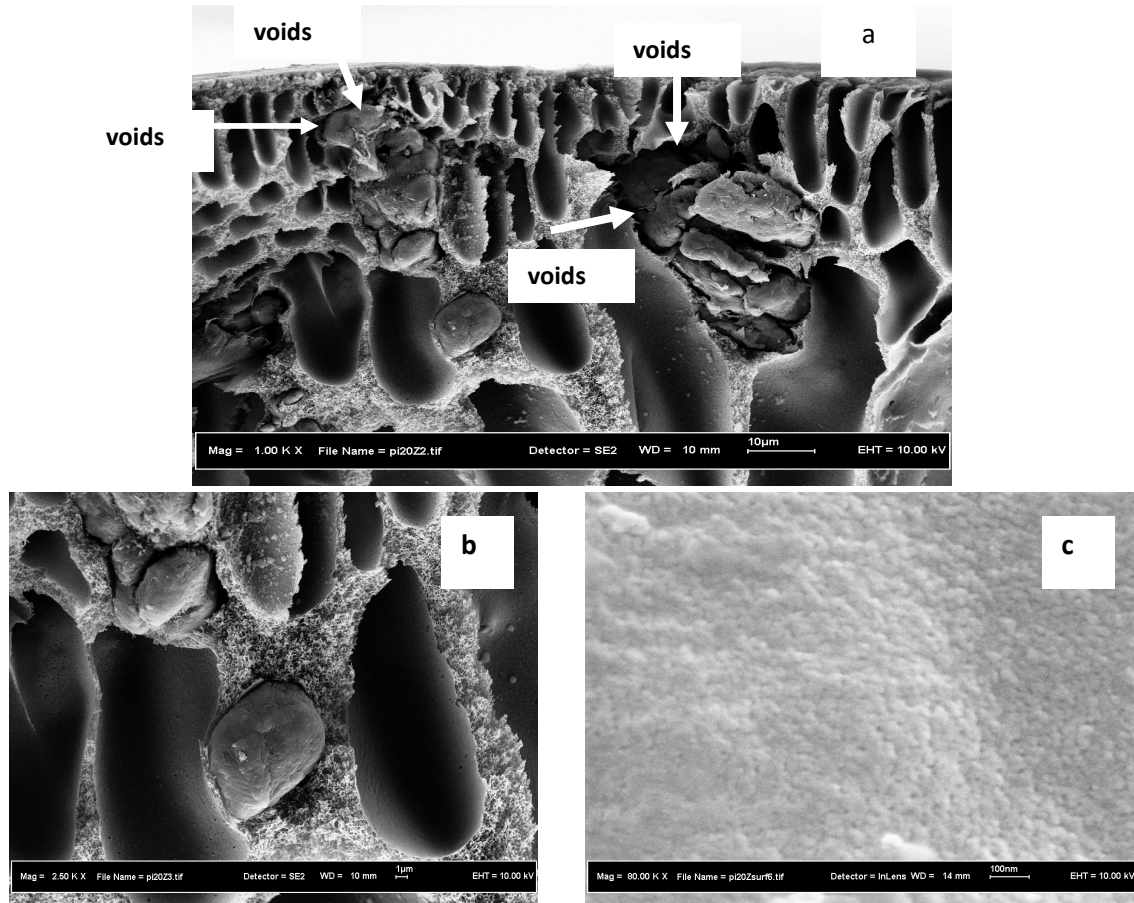

Figure 4: SEM picture of asymmetric uncoated polyimide-zeolite mixed matrix membrane at the: (a) cross section and (b) outer surface image layer

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 [13-15]. 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 zeolites 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.

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 uncoating 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 depicted that the interfacial gaps between polymer host and zeolite can reduce with 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.
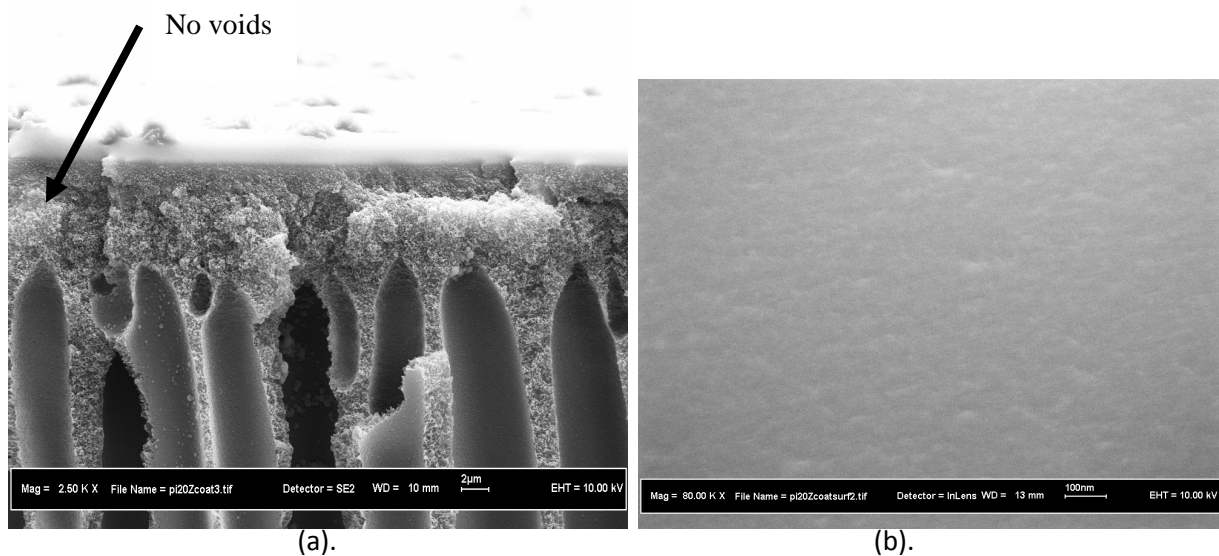
No voids

(a).   (b).

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

Gas separation performance of PI-zeolite mixed matrix membrane

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 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 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 1. The Table 1 summarizes the permeability and selectivity data of uncoated PI, coated PI, uncoated PI-zeolite and coated PI-zeolite. 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 [16]. 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.

Table 1: 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

As shown in Table 1, 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 behaviour 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

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

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.* [13] suggested that sedimentation 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 behaviour, 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 resulted 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. Table 1 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 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 unfavourable interaction between polymer and zeolite can be reduced using silicone rubber coating.

Conclusion

In this study, the polyimide-zeolite was fabricated for mixed matrix membrane 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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