

ENHANCED BIOGAS (CO₂/CH₄) SEPARATION PERFORMANCE OF HYBRID MIXED MATRIX MEMBRANE BY INCORPORATING NANOSILICA PARTICLES INTO POLYETHERSULFONE

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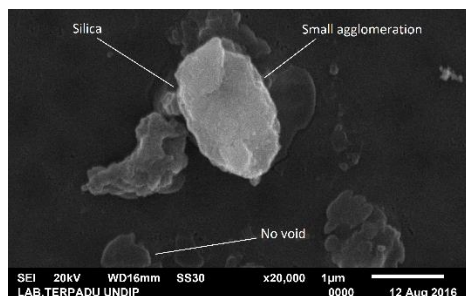
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Graphical abstract



Abstract

This paper studies the gas transport properties of PES-nanosilica hybrid mixed matrix membrane for biogas purification. Problem statement: The hybrid mixed matrix membrane was produced to improve the membrane separation performance for biogas purification. The membrane was produced via dry-wet phase inversion method, in which the nanosilica was incorporated into polyethersulfone membranes and the prepared membrane was performed on biogas separation experimental test. Quantitative result: The SEM images analysis confirmed that nanosilica surface had taken important role in gas transport properties. Moreover, the nano-gaps (voids) between polymer and nanosilica particles were disappeared in the polyethersulfone hybrid mixed matrix membrane. The results revealed that the good nano-silica dispersion leads to enhance the properties of gas permeation up to 200% and slightly increased the selectivity about 0.9% of the nanosilica concentration 8 wt-%. Conclusion: It can be concluded that incorporation of nanosilicas particles into the matrix of polyethersulfone polymer significantly enhanced the membrane structure and separation properties.

Keywords: Hybrid mixed matrix membrane, nano-silica, biogas separation, polyethersulfone membrane, composite membrane

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1.0 INTRODUCTION

The increasing energy needs of citizen is one of the most important issue that will be faced in the recent years. An environmental friendly energy source needs to be found along with the effort to find a long term renewable energy sources. Biogas is a renewable energy source that has a great opportunity to take advantage of certain categories of biomass to meet most of the world's energy needs. Anaerobic digestion is a natural process utilizing methanogenic microorganism in oxygen-limited

environments to convert organic substance into methane gas [1]. However, due to the low quality of biogas it caused the use of biogas is limited, this low quality is because biogas contains CO₂ (20-45 vol%) and H₂S (0-1 vol%) as the impurities of main component CH₄ (55-80 vol%). Hence, the purified biogas with high methane content can be utilized for household fuels application, vehicle machines fuel or electricity generation. It is very necessary to make biogas is easy to be transported. This could be performed by compressing thi biogas in a vessel after removing CO₂, H₂S and water vapor. To increase the

caloric value of biogas can be achieved by the enrichment of methane in biogas with removing the content of carbon dioxide (CO₂). The removal of CO₂ from the biogas beside can enhanced the caloric value of biogas combustion, it can also lowering the green house effects. The recent technologies to remove acid gas (CO₂ and H₂S) and caloric value enhancement limited on physical and chemical methods such as amine based separation, cryogenic separation, and membrane based separation [2, 3]. Membrane based separation of gases propose benefits over the conventional separation technologies such as distillation, absorption, amine treatment, and scrubbing [4, 5]. Gas separation using membrane technology offers many significant advantages such as compact and modular design so it easily to be scaled-up or scaled-down, membrane based technology can by operated in mild condition (ambient temperature) and membrane technology is low energy consumption so it greatly reduces the electricity and fuel consumption. The incorporation of inorganic material in membrane matrix has attracted attention in recent membrane studies [6-7].

Mixed matrix membrane concept integrates the synergistic of effective separation properties of the molecular sieves and simple processing and favorable mechanical properties of polymers. The many previous studies stated that the improvement of mixed matrix membrane separation performance can be performed by incorporating nonporous or porous inorganic filler such as silica, alumina, zeolite, carbon nano tubes, activated carbon, and carbon nano tubes. Currently, the incorporation of nanosilica and carbon nano tubes in the fabrication of mixed matrix membrane have been devoted as potential nano filler [8-10]. Nanocomposite membrane normally used nanosized particle as inorganic filler such as nanosilica, clay, carbon nano tubes (CNTs) and activated carbon to improve the mechanical, thermal, and electrical properties of polymers. The nanocomposite polymers properties of nanosilica containing matrix depends on some factors in addition to the polymer: the concentration of nanosilica loaded, interaction of filler surface and polymer matrix and post-treatment of hybrid membrane [11].

Hybrid membrane consisting of polysulfone of polyimide as polymer material and mesoporous silica spheres as inorganic filler increased the permselectivity with the increasing of inorganic filler concentration [12]. It was reported that this behavior is due to (a) filler has a higher permeability compared with polymer and (b) the filler addition induced the changes of polymer structure. The cellulose acetate-silica nanocomposite membranes was fabricated to study the separation properties of paraffin's and olefin's such as ethane/ethylene and propane/propylene [13]. They stated that the permeability enhanced with increasing of silica concentration in membrane matrix and the permeability of olefins is greater than paraffins.

As mentioned, nanosilica incorporation in membrane fabrication have been proposed as great potential material for a various kind of application such as polymer reinforcement. Nevertheless, the utilization of nanosilica as reinforcement material in polymer has been a challenge because of the difficulties to achieve good dispersion and interfacial adhesion of nanosilica and polymer matrix to avoid the formation of nanogaps between nanosilica and polymer which leads on lowering the selectivity performance of membrane. Therefore, this research is focused on fabrication of hybrid mixed matrix membrane with nanosilica as inorganic filler for bio gas separation.

2.0 METHODOLOGY

2.1 Materials

Polyethersulfone (PES) as polymer was purchased from Solvay Advanced Material (USA). PES polymer was dried at 120°C for 12 h before being used. N-methyl pyrrolidone (NMP) was supplied from merck as polymer solvent. Nanosilica as inorganic nano particle filler was purchased from Nano Center Indonesia with particle size 50 nm.

2.2 Fabrication of PES-nanosilica Hybrid Mixed Matrix Membrane

Hybrid mixed matrix membrane was fabricated by preparing the dope solution comprising of 22 wt-% of Polyethersulfone (PES) polymer, 78% N-methyl pyrrolidone as solvent, and nanosilica with various concentration of 1.5 and 8 wt-% in total solid. The stable and stable dope solution was prepared by the following procedures. An appropriate amount of nanosilica was added into the NMP solvent and constantly mixed for 24 h to avoid particle aggregation. Subsequently an appropriate amount of PES was added to the mixture. The dope solution was mixed for 24 to obtain stable and homogeneous dope solution. The homogeneous dope solution was placed under vacuum condition for 3 hours to eliminate air bubbles. The polymeric dope solution was casted into flat sheet membrane via dry-wet phase inversion method. The solution was casted on the clean flat glass plate and the solution was flattened using casting knife with membrane thickness 150 µm.

2.3 Post Treatment (Silicone Rubber Coating) Procedure

To overcome the generation of voids in the membrane due to the formation of nanogaps, an assembled of nanosilica hybrid mixed matrix membranes were immersed in a coating solution comprising of polydimethylsiloxane 3% in n-hexane solvent for 24 h. The coated membrane then was thermal cured in oven at 120°C for 72 hours to cure

the silicone rubber coating. Afterwards, the separation performance of prepared membranes were investigated by using pure methane gas and carbon dioxide gas permeation test as samples of biogas.

2.4 Morphological Characterization of Mixed Matrix Membrane

The analyzing of membrane structure was performed using Scanning Electron Microscopy (SEM) to investigate the presence of nanogaps between nanoparticles and polymer matrix. The analysis was performed by fracturing the membrane in LN₂. The prepared membrane was assembled on a double surface tape aluminium disk and then the sample holder was placed and evacuated in a sputter coater with gold. The magnified image of membrane was displayed on the monitor.

3.0 RESULTS AND DISCUSSION

3.1 Fabrication and Characterization of PES-nanosilica Hybrid Mixed Matrix Membranes

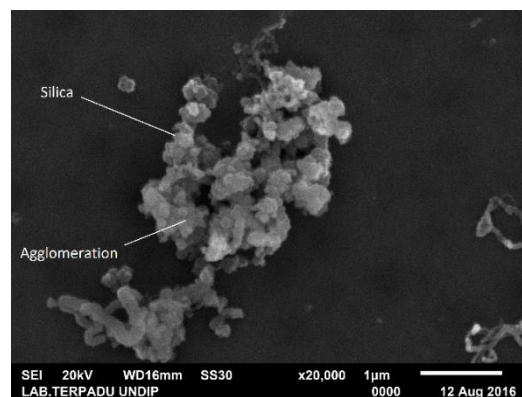
Figures 1(a)-(b) show the SEM image micrograph of the surface section of the PES-8 wt-% nanosilica hybrid mixed matrix membrane in different magnification. As shown in the Figure 1, the nanosilica particles were observed to be good surface coverage through out the PES membrane. Figure 1(b) showed that the polymer chain attached on the nanosilica surfaces and no unselective voids were observed, it indicates that nanosilica has better adhesion properties with PES polymer matrix. This could be explained from the nanosilica properties used in this research. The surface of the nanosilica has been treated with silane. Hence, the silica particles were covered with silanol group which has acidic properties. This silanol functional group could react with polymeric molecules induced to the generation of attachment layer between PES matrix and nanosilica inorganic filler. However, in the mixed matrix membrane with 8 wt-% nanosilica incorporation was observed an agglomeration of silica particles and formed a fine silica domain in PES matrix as depicted in Figure 1(a). Even though some silica particles formed an aggregation and nanosilica domains, at higher magnification of SEM image displayed in Figure 1(b) shows that the nanosilica particles are well attached within PES matrix.

The agglomeration of nanosilica particles probably caused by high concentration of silica particles in the mixed matrix membrane. For a more thorough investigation of the surface SEM image revealed that silica agglomeration/silica domain was observed obstructive on membrane surface as shown in Figure 1(b). The agglomeration of silica particles could defects the structure of skin layer delivering in high gas permeability and low separation factor (gas selectivity). The generation of silica aggregate could

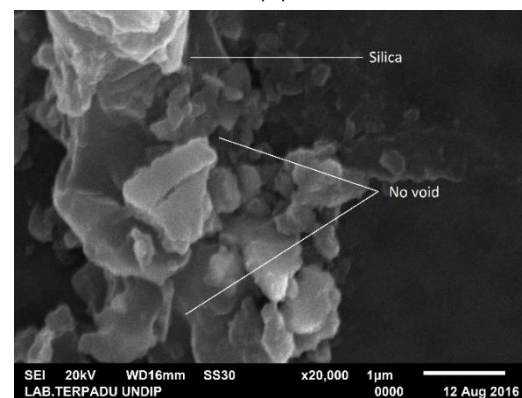
be due to the presence of high concentration of nano particles. To remove the agglomeration of nanosilica particles, the concentration of nanosilica loaded in PES polymer should be reduced, in other way the agitation in dope solution preparation should be prolonged.

The SEM surface section images of 1.5 wt% nanosilica-PES hybrid mixed matrix membranes are depicted in Figure 2, respectively. Figure 2 showed that PES-nanosilica hybrid mixed matrix membrane was successfully formed. It was found small aggregation of nanoparticles. It also observed that nanosilica particles are well dispersed in PES matrix. Figure 2 also shows that nanosilica particles are attached within the outermost layer structure. Therefore, the PES-nanosilica hybrid mixed matrix membrane with nanosilica incorporation displayed a good adhesion between nano filler and PES matrix and removes the nanogaps due to de-attachment of polymer in filler surface as depicted in Figure 2.

The gas separation performance test of PES-8 wt% nanosilica and PES-1.5 wt% nanosilica hybrid mixed matrix membranes were tested using a variation of pressure with a constant volume condition. The permeation of the pure gases (methane and carbon dioxide) through each prepared hybrid mixed matrix membrane was tested for 3 times runs. Table 1 shows the permeability of pure gases (CO₂ and CH₄) and the calculation result of ideal selectivity for CO₂/CH₄ gas pairs.



(a)



(b)

Figure 1 SEM images of PES- 8 wt % nano-silica hybrid MMMs at the (a) surface image layer (b) near active surface layer

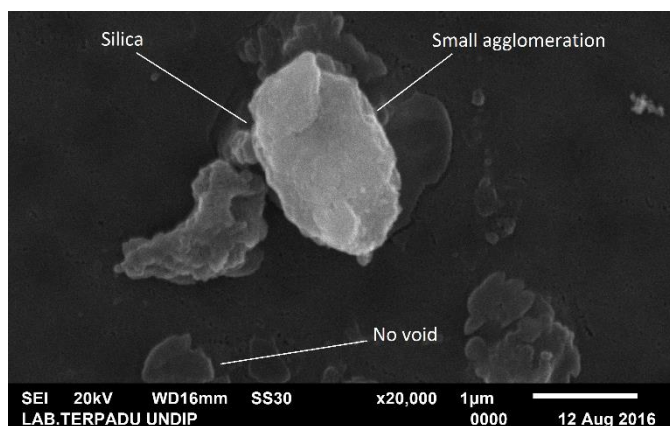


Figure 2 SEM images of PES- 1.5 wt % nanosilica hybrid MMMs at surface image layer

The permeability of all gasses increased as well as the increase of nanosilica concentration in the PES matrix. The concentration of 1.5 wt-% of nanosilica loading in PES polymer resulted up to 100% in the CO₂ permeability. Nonetheless, the selectivity increased up to 18% as displayed in Table 1. While at higher nanosilica loading (8 wt-%), the gas permeability increased drastically up to 200%. Although the permeability increased, the selectivity very slightly increased (0.9 %). Since the nanosilica particles were non-porous molecular sieve, this improvement of separation performance might be contributed by the nanosilica-gas interaction. The improvement in gas permeability could be influenced by the interference of polymer chain structure in the presence of nanosilica particles. This result confirmed the previous study by Moabdeb and Koros [14]. They stated that the enhancement in O₂/N₂ selectivity and Oxygen permeability through polymer/silica composite membrane compared with neat polymer membrane. The CO₂ permeability in the PES-nanosilica hybrid mixed matrix membrane in higher concentration of nanosilica (8 wt-%) is approximately 200% higher compared with neat PES membrane. The increase in permeability of higher concentration of nanosilica presence in PES matrix was expected that some gas passed the membrane through nanogaps in the interface of polymer and nanosilica. Incorporation of nanosilica with concentration of 8 wt-% shows small agglomeration in the membrane surface. It can be said that the higher concentration of 8 wt-% will form nanoparticles agglomeration. The consequences of the agglomeration is the the formation of nanogaps (voids) between nanoparticles and PES matrix and the membranes become less selective. The mechanism of gas transport which dirives is Knudsen diffusion rather than solution-diffusion. The selectivity of Knudsen diffusion mechanism depends on gas's molecular weight. The recommendation of nanosilica incorporation in PES membrane is not more than 8 wt-%.

Table 1 Gas permeability of pure gasses in the PES-nanosilica hybrid MMMs

Membrane	Pure gas permeability (GPU)*		Selectivity
	CO ₂	CH ₄	CO ₂ /C H ₄
PES without silica	25.42± 0.25	1.12± 0.02	22.69
PES-nano silica (1,5wt %)	56.75± 0.18	2.15± 0.13	26.40
PES-nano silica (8 wt %)	78.23± 0.01	3.43± 0.37	22.81

*GPU = 1 x 10⁻⁶ cm³ (STP)/cm² s cmHg

3.2 Effect of Silicon Coated membrane on Gas Transport Properties

In the PES-nanosilica hybrid mixed matrix membrane, the nanogaps (unselective voids) were not completely removed as discussed in Section 3.1. Hence, the contribution of membrane coating using silicone rubber on the gas transport performance of fabricated PES-1.5 wt% nanosilica hybrid mixed matrix membrane was investigated. Gas transport properties of coated membrane was also affected by thermal curing time. The curing time was performed by drying the coated membrane under vacuum oven at 120°C for 72 h [15]. The comparison of permselectivity for each pure gas between silicone rubber coated membrane and uncoated PES-nanosilica hybrid mixed matrix membrane. Based on the experimental result can be observed that the PES-1.5 wt-% nanosilica hybrid mixed matrix membrane with silicone rubber coating performed low gas permeability but high selectivity for separation properties of CO₂/CH₄ compared to the uncoated membrane.

Table 2 shows the highest membrane selectivity observed from PES-1.5 wt% nanosilica hybrid mixed matrix membrane was 39.13 for CO₂/CH₄ separation factor. From this phenomenon, it can be stated that coating using silicone rubber successfully push the Knudsen diffusion of gas transport mechanism. This is might be due to the repression of the void defects at the outermost active skin layer have been coated by silicone rubber. The membrane surface was modified by eliminating the voids on the membrane surface, therefore resulting in higher selectivity and lower permeability. Thus, the combination of molecular sieving and solution diffusion are dominating the gas transport mechanism in this coated membrane. It indicates that nanogaps (voids) formed by the low adhesion between nanosilica surface and PES polymer could be removed by combination of nanosizing of inorganic filler and silicone coating. Due to the well attachment with polymer and without unselective nanogaps (voids), the nanosilica particles would be more promising as nano-filler wich contributes in gas transport mechanism [16,17]. Hence, the permeability of CO₂ for coated PES-nanosilica hybrid mixed matrix membrane was about

79 % higher than the uncoated neat PES membrane. However, as shown in Table 2, the CH₄ permeability decreased for coated PES-nanosilica.

The silicone rubber coating remove the nanogaps between nanosilica and PES. The gas passes the membrane through solution-diffusion mechanism rather than Knudsen-diffusion mechanism. The permeability of CO₂ is higher than CH₄, it indicates that CO₂ has higher solubility in silicone rubber than CH₄. Based on this experimental result, the silicone rubber coating not only acts as the voids blocking agent but also plays an important role as the selective layer of the membrane.

Table 2 Gas permeabilities of CO₂ and CH₄ in the PES-nanosilica hybrid MMMs

PES-nanosilica	Pure gas permeability (GPU*)		Selectivity CO ₂ /CH ₄
	CO ₂	CH ₄	
uncoated	56.75±0.18	2.15±0.13	26.40
coated	65.35±1.08	1.67±0.14	39.13

*GPU = 1 x 10⁻⁶ cm³ (STP)/cm² s cmHg

4.0 CONCLUSION

In this study, Hybrid mixed matrix membrane of polyethersulfone (PES) with new inorganic filler such as nanosilica was successfully fabricated. An effort to enhance the gas separation properties of the membranes also has been performed by silicone rubber coating. Based on the experimental results and discussion, it can be concluded as follow.

- (i) Fabrication of well uniformly dispersed nanosilica in PES membranes were successfully performed. From the SEM images investigation, the defects of surface were not observed on the nanosilicas hybrid mixed matrix membrane. The fine non-porous surface of nanosilica could help the improvement of attachment between nanosilica particle and polymer matrix.
- (ii) The well coverage of nanosilica on the membrane surface provided a good influence to the PES polymer. The permeability of pure gas (CO₂ and CH₄) increased about 100% and slightly increase the selectivity about 18% as compared to neat PES membrane. It makes nanosilica as an favorable inorganic filler for hybrid mixed matrix membrane fabrication.

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