Characterization of Polyethersulfone/Cloisite 15A Mixed Matrix Membrane for CO₂/CH₄ Separation

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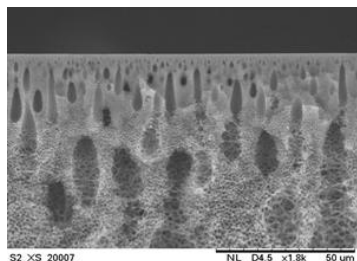
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Graphical abstract

Abstract

Asymmetric hybrid organic-inorganic clay mineral polyethersulfone (PES) flat sheet membranes were prepared from solution containing Cloisite15A® (C15A) in the mixture of solvent and polymer. Neat PES and MMM were prepared through dry/wet phase inversion method. The newly developed membranes were characterized by means of SEM. The effect of filler addition, evaporation time and coating protocol towards the performance of the membrane was investigated. The measurement was carried out at room temperature and the upstream pressure was 3 bar while the downstream pressure was atmospheric. Experimental results showed that selectivity for MMM fabricated with 0.25 wt% clay loading at evaporation time of 40 s is lower compared to those prepared at higher evaporation time. After coating with silicone rubber solution and heat treated, the resultant membranes exhibited selectivity enhancement of CO_2/CH_4 from 7.9 to 28.4 for pristine PES, while PES/C15A1 and PES/C15A2 showed a selectivity improvement of 2.29 to 18.72 and 10.24 to 33.49 each. Optimum evaporation time and appropriate coating and heat treatment have significant contribution in developing high performance MMM for gas CO_2/CH_4 separation.

Keywords: Mixed matrix membrane; polyethersulfone; nanoclay; gas permeation

■1.0 INTRODUCTION

Today, membrane technology for gas separation has evolved from the traditional polymeric membrane to a more sophisticated structure known as mixed matrix membrane with the degree of complexity varies with different filler types. Although promising improvement in terms of permeability and selectivity has been experienced in MMM compared to the polymeric membrane, issues on the the interfacial defects and expectation on the performance surpassing the upperbound limits are still unsolved. Zeolites, among others are the pioneered materials embedded in the continuous phase for gas separation and despite the continuous effort by researchers, only a limited number of types of zeolites were a successful organic-inorganic hybrid material [1, 2]. Attempts to fabricate a defect-free membrane with zeolite are further complicated by the inorganic surface chemistry of zeolites. Following this, the attention has been diverted to other superfine particles, namely metal organic framework (MOF) and carbon nanotubes (CNTs). MOF exists as combination of an inorganic cluster and an organic bridge with high surface area, sorption capacities, selective affinity for certain gases, and flexibility in chemical composition [3, 4] and is a promising materials for MMM. Carbon nanotubes on the other hand, have been applied as the

inorganics fillers in mixed matrix membrane for their superior improvement in the gas permeability [5]. However, MOF and CNTs are quite expensive to be used in the fabrication of MMM and despite the credible performance, synthesizing the nanofillers as an attempt to reduce the cost provides another challenge. Hence, an alternate filler that has the ability for enhancement of permeability and separation factor is needed to overcome the issues confronted by previous inorganic fillers. In view of this problem, clay minerals are said to be the new potential nanofillers due to their abundance resources, cheaper costs, and high aspect ratio and have been successfully incorporated into polymer/silicate layers (PLS) nanocomposites for various application.

Over the last decades, PLS nanocomposites have gained significant interest because of the improvement in the mechanical, thermal and other properties compared to conventional polymers [6]. Montmorillonite (MMT) was the commonly used layered silicates (LS) due to their high chemical and mechanical resistance and a cheaper alternate to other fillers, and interestingly only a small amount of this material was needed in the fabrication of nanocomposites [7]. The ability for this silicate layers to form intercalated or exfoliated structure in the resultant nanocomposite is another advantage that signifies the use of nanoclay minerals in polymer composite

nanotechnology. Although layered silicates have been use as fillers for nanocomposites for various application such as food packaging, ultrafiltration, pervaporation, and in fuel cell [8–10] only few works have reported the potential in gas separation. Incorporation of nanoclays in the hybrid membrane provides a new approach in the development of a mixed matrix membrane for gas separation. The present study, therefore, focuses on preparing the membranes from hybrid materials made of polyethersulfone and Cloisite15A®. The effect of the presence of nanoclay in PES membrane towards the morphological properties as well as the permeability of pure CH_4 and CO_2 gases, and their selectivity were investigated.

■2.0 EXPERIMENTAL

2.1 Materials

Commercial polyethersulfone (PES, RADEL A-300A) from Solvay Advanced Polymers (Alpharetta, GA, USA) was chosen for the polymer phase. N-methyl-2-pyrrolidone (NMP) and ethanol, both supplied by Merck were used as the solvent and non-solvent. Cloisite15A® was supplied by Southern Clay Products, Inc., USA and was surfactant modified with dimethyl, dehydrogenated tallow, quaternary ammonium. PES and Cloisite15A® were preconditioned in the oven at 60∘C overnight to remove the moisture while other chemicals were used as received.

2.2 Membrane Fabrication

Flat sheet asymmetric membrane was fabricated by dry-wet phase inversion technique. The mixture component between polymer, solvent and non-solvent was prepared by dispersing a desired amount of Cloisite15A® in the solvent followed by the addition of polymer. A small amount of dope was poured onto a clear and flat glass plate and casted before being immersed in a coagulation bath. The resulted flat sheet was transferred in a second water bath (25∘C) for overnight and was further submerged in another tank filled with methanol for 1 hour the next day. Subsequently, the membranes are left to dry at room temperature for 3 days.

2.3 Membrane Coating

Dried membranes were cut into a circular disc 13.5 cm^2 in area and immersed in a coating solution containing 3 wt% polydimethylsiloxane (Dow CorningSylgard 184) in n-hexane for 10 minutes and dried in the oven at 60∘C overnight. After the drying process, the membranes are ready for the gas permeation test.

2.4 Characterizations

The surface and cross section of the membrane was examined by SEM-EDX scanning electron microscope (Zeiss DSM 960) with potentials of 20 kV under magnifications ranging from 600× to 10,000×. Membrane was cut into smaller pieces, immersed in liquid nitrogen and fractured. The samples were then mounted on sample stubs and coated in a sputter-coater with gold. SEM provides graphical representation of the morphological properties of the membrane and distribution of the nanoparticles in the polymer matrix.

2.4 Gas Permeation Testing

Pure-gas permeation properties for CO_2 and CH_4 for PES/Cloisite15A® MMMs were measured by using variable-pressure constant-volume method with a bubble soap flow meter. The test was conducted at room temperature at different downstream pressure of 3 bar. A circular membrane with 13.5 cm^2 effective area was placed on a sintered metal plate and pressurized at the feed side and each sample was measured for three times. The permeances of the gases were calculated by the following equation:

$$\frac{P_i}{l} = \frac{1}{A \Delta p} \frac{dV_i}{dt}$$

Where P/l is the gas permeance of a membrane in GPU, i represents the gas penetrant i, V is the volume of gas permeated through the membrane (cm^3, STP), A the effective membrane area (cm^2), t the permeation time (s) and Δp is the transmembrane pressure drop (cmHg). The selectivities reported for each membrane were obtained by the following relationship:

$$\alpha_{i/j} = \frac{(P_i/l)}{(P_j/l)}$$

where i/j is the selectivity of gas penetrant i to gas penetrant j, P_i/l and P_j/l are the permeance of gas penetrant i and j, respectively.

■3.0 RESULTS AND DISCUSSION

3.1 Characterization of Mixed Matrix Membrane

The morphological structure of the cross section of the membrane and the distribution of the nanoparticles were examined by scanning electron microscope (SEM). Figure 1 shows the crosssectional membrane morphology of the pristine membrane and MMM at different evaporation time. In Figure 1a, morphological characteristics of the crosssectional images of PES showed the typical long fingerlike (macrovoids) structure with the thickness of the membrane in the range of 185 μm. On the other hand, MMM (Figure 1b and 1c) showed a spongelike structure for the MMM with a denser porous substructure for a lower evaporation time. No evidence of agglomeration or interface void can be found in Figure 1b, suggesting that the nanoclay particles were well dispersed throughout the membrane. In a recent work by Liang *et al.* [11] they have found that the use of higher loadings of MMT can lead to severe agglomeration causing pinholes or other defects to the membrane. Only small agglomeration of MMT was reported in the polymer matrix for the nanoclay loading of 2 wt% which is relatively higher in comparison to the loading used in this work (0.25 wt%). Hence, agglomeration of nanoclay particles is our work is less expected. However, due to the lower content of filler, it is worth noting that detecting the particles in the membrane can be challenging. Previous works have also reported that the use of lower loading contributes to good dispersion of the fillers hence improvement in the selectivity [12,13]. Interestingly, Figure 1c showed the existence of the nanoparticles in the polymer matrix concentrated near the dense skin layer of the MMM. Although having the fillers to be aligned closer to the skin layer has been emphasized for significant effect on separation, the reason behind this phenomena occurring in our work is still unclear. In addition to

this, because of the lower nanoclay content, possibility for agglomeration is minimal since the tendency for the particles to be in contact with each other is reduced hence hindering aggregation of nanoclay particles. Generally, gas separation is governed by the thin skin exists on the top layer of the membrane generated during the phase inversion process. Referring to Yamasaki *et al.* [14], formation of the skin layer is largely influenced by the evaporation time, such that a thinner skin layer is likely to be created with the reduction of evaporation time. In this work, SEM images showed that a thinner skin layer was evident in the MMM (Figure 1b) while a thicker skin layer was observed for the MMM fabricated with a higher evaporation time (Figure 1c).
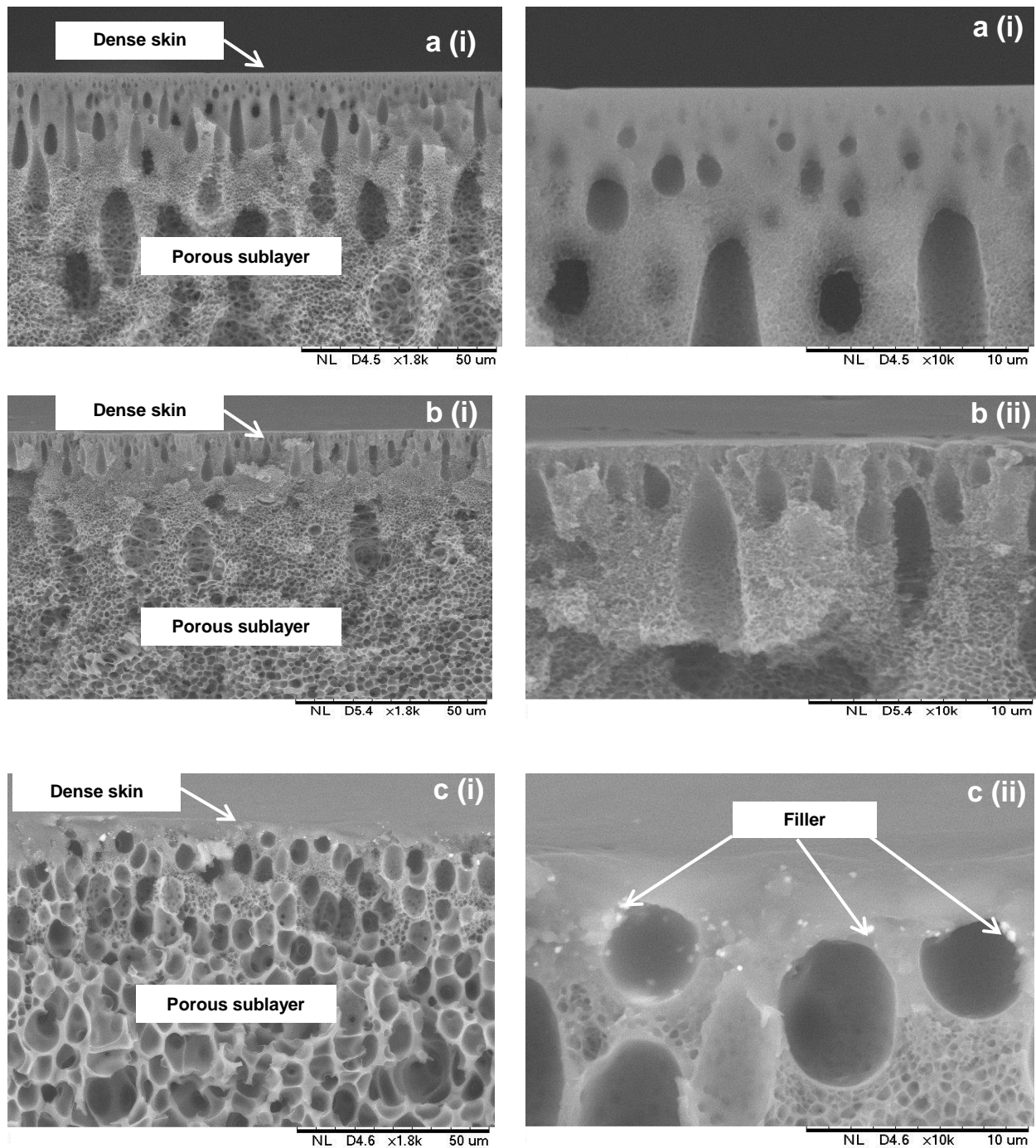
Figure 1 SEM crosssection images for pristine PES and MMM: (a) PES, (b) PES/C15A (evaporation time:40s) and (c) PES/C15A2 (evaporation time:600s) at (i) lower magnification and (ii) higher magnification

According to Ismail *et al.* [15], the thickness of the skin layer is dependent on the increase of the amount of the nonsolvent additive loss as the evaporation time increases as a denser and thicker skin layer is formed when the composition of the outermost region was moved to miscible region from the initial phase boundary line. In other words, the increased loss of solvents causes a more concentrated nascent at the surface and upon phase inversion, the structure freezed hence resulted a thicker skin layer. From the SEM images, the size of the microvoids present in the substructure increased with the increase of evaporation time and similar observation was reported by Ismail *et al.* [15]. Figure 1a-c also illustrates the changes in the morphologies from long fingerlike macrovoids to a more denser substructure (microvoids) upon the addition of nanoclay particles while an increased in evaporation time showed a bigger circular microvoids.

3.2 Effect of Cloisite15A® on MMM Gas Separation

In order to investigate the effect of nanoclay addition on the gas separation properties, MMM with 0.25 wt% Cloisite15A® loading (hereafter referred as PES/C15A1) was fabricated and compared with neat PES membrane. Another MMM with similar loading was fabricated to study the effect of the evaporation time towards the performance of the membrane (PES/C15A2). The CO_2(2.70 GPU) and CH_4(0.095 GPU) permeance and CO_2/CH_4 (28.38) selectivity shown in Table 1 for the pristine PES membrane are in good agreement with those reported in literature [11][16][17]. With the addition of nanoclay particles in MMM, the permeance for both CO_2 and CH_4 increased from 2.70 to 3.01 and 0.095 to 0.161 GPU, respectively. Subsequently, the CO_2/CH_4 selectivity decreased to 18.72 for PES/C15A1. In this study, the use of surfactant modified nanoclay enhances the polymer-filler compatibility and addition of the nanoparticles at a lower loading reduces the possibilities of void morphology of the MMM as supported by the SEM images (Figure 1a-c). According to Hashemifard *et al.* [18], an ideal morphology was obtained for PEI embedded with 0.5 wt% Cloisite15A® based on the FESEM crosssection images and performance of the MMM. Moreover, their work have also found that interfacial defects was caused by the incompatibility of the polymer matrix and surface of the filler for unmodified MMT. Hence, it is postulated that the increased in permeance and decreased in selectivity is probably due to the surface porosity or other defects of the MMM. It is observed that for a similar loading, MMM fabricated at a longer evaporation time exhibited a higher permeance for CO_2(9.77 GPU) and CH_4 (0.29 GPU) and increased in CO_2/CH_4 selectivity (33.49). Since the nanoclay particles are mostly located near the dense skin layer of the MMM for PES/C15A2, as previously discussed in SEM characterization, the tortuosity created by the high aspect ratio of nanoclay, barrier properties, and intercalated clay layers have contributed to high selectivity for PES/C15A2 [6,18]. The thickness of the membrane has also contributed to the increased in the selectivity given in Table 1, where PES/C15A2 has a selectivity of 33.49 compared to PES/C15A1 (18.72). Hence, the optimum evaporation time for MMM is in the range of 600s.

Table 1 Effect of evaporation time and silicone rubber coating on pristine PES and PES/C15A1 and PES/C15A2 on CO_2 and CH_4 separation

Membrane	Nanoclay loading (wt%)	Evaporation time (s)	Uncoated membrane			Coated membrane		
			P_{CO_2} (GPU)	P_{CH4} (GPU)	$\alpha\ CO_2/CH_4$	P_{CO_2} (GPU)	P_{CH4} (GPU)	$\alpha\ CO_2/CH_4$
PES	0	40	12.38	1.57	7.89	2.70	0.095	28.38
PES/C15A1	0.25	40	7.84	3.415	2.29	3.01	0.161	18.72
PES/C15A2	0.25	600	17.98	1.76	10.24	9.77	0.29	33.49

3.3 Effect of Coating on Gas Separation Performance

As shown in Table 1, permeance for uncoated membrane is higher compared to coated membrane due to the contribution of the defects of the membrane hence affecting the selectivity. It is known that selectivity has a strong correlation between the pore size and surface porosity of the membrane and the enhancement of free volume in the skin[15] , therefore a standard coating procedure using silicone was carried out to improve the selectivity of the membrane. Generally all coated membranes showed higher selectivity and lower pressure normalized flux, or permeance for both CO_2 and CH_4. Uncoated PES showed an improvement in selectivity from 7.89 to 28.38, while selectivity for PES/C15A1 and PES/C15A2 increased from 2.29 to 18.72 and 9.77 to 33.49. Coating reduces the permeance of gas but impoves the selectivities by caulking the pinholes or defects on the membranes [17]. However, in some cases, the performance of the coated membranes can still be unsatisfactory due to several factors such as impropriate coating and curing protocol which means the defects of the membrane were not properly healed. We are aware that the complicated interaction between the polymer phase and the surface of the filler can also effect the results. However, since the nanoclay particles used in this work is surfactant modified, issues on interfacial defects seems to be least significant. Referring to Kusworo *et al.* [17], lower curing temperature requires a longer time for a proper drying process and the defects of the membrane will have a dominant effect on the gas separation if the coating was incomplete. A comparable result by using a higher curing temperature in his work showed an improved selectivity with curing temperature and time of 100°C and 3 days, respectively. Similarly, the low selectivity of PES/C15A1 in this work is probably due to the existence of pinholes or other surface defects because of the incomplete coating procedure with the use of lower curing temperature of 60°C and inconsistency in drying time.

■4.0 CONCLUSION

In this study, MMMs were successfully fabricated by combining polyethersulfone, RADEL A-300A and Cloisite15A® at a different evaporation time. The SEM images showed that the addition of nanoclay particles and different evaporation time changed the morphological structure of the membrane from long fingerlike to spongelike with smaller circular microvoids. Morphological structure of membrane fabricated at higher evaporation showed a thicker skinlayer and nanoclay particles were aligned near the skinlayer. A good distribution of the nanoclay particles with no evidence of severe agglomeration was also obtained. Experimental result also showed that coated

and heat treated membrane showed an improvement in the selectivity with a reduction in permeance. This study concluded that coated MMM (PES/C15A2) embedded with low loading nanoclay particles and fabricated with higher evaporation time gives a selectivity enhancement with respect to neat PES and PES/C15A1.

Acknowledgement

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