

Preparation and Characterization of Mixed Matrix Membrane based on Polysulfone (PSF) and Lanthanum Orthoferrite (LaFeO₃) for Gas Separation

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ABSTRACT

The aim of this study is to investigate the effects of polysulfone (PSF) and lanthanum orthoferrite (LaFeO₃) incorporated mixed matrix membrane (MMM) on gas permeation and selectivity properties. PSF/LaFeO₃ MMMs were prepared with various weights loading of LaFeO₃. The membranes obtained were characterized using scanning electron microscope (SEM), thermal gravimetric analysis (TGA) and Fourier-transform infra-red (FT-IR). The gas transport properties of MMM were measured using single gas permeation set up (CO₂, CH₄, O₂ and N₂) at ambient temperature, and feed pressure of 2, 4 and 6 bar. The permeation test showed that the mixed matrix membrane exhibited high permeability. With increasing LaFeO₃ weight loading to 1.0%, the highest permeability values were 47.74 GPU for CO₂, 29.85 GPU for CH₄, 57.56 GPU for O₂, and 40.66 GPU for N₂. The results also showed that by incorporating 1.0wt% of LaFeO₃ into PSF matrix, the highest CO₂/CH₄ and O₂/N₂ selectivity of 1.60 and 1.42 respectively were obtained. Overall, all the resultants MMM showed higher permeability and selectivity compared to pure PSF membrane.

Keywords: Polysulfone, lanthanum orthoferrite, mixed matrix membrane, permeability, selectivity, gas separation

1.0 INTRODUCTION

Membrane technology is a promising alternative to the conventional absorption column in the field of gas separation as the absorption based technology suffers from huge energy consumption and large amine solution flow rate, which result in significant increases in the electricity cost [1]. Meanwhile, membrane-based gas separation offers energy efficiency with low capital investment, simplicity and ease of installation, low operation and maintenance cost, low weight and space requirement with high process

flexibility [2].

One of the criteria in selecting membrane for a particular application is membrane material. Generally, there are three types of membrane materials; polymer, inorganic and mixed matrix membrane. Polymers are the most commonly used membrane materials as they are relatively cheaper for large scale industrial application [3]. They are also favorable due to the ease of processing and high packing density [4]. Even though polymer membranes are more favored in industrial gas separation, inorganic membranes are becoming an interest among

researchers due to their ability to operate at harsh conditions, and be highly selective and permeable for specific molecules [5].

The combination of polymer and inorganic membranes, which is called mixed matrix membranes (MMMs), had been explored to beat the trade-off limit. Studies showed excellent potential of MMMs in gas separation field, but deciding the best ratio of polymer and inorganic is a hassle due to the concern of compatibility between the two materials during formation of MMM. Unfortunately, fabricating a defect-free MMM for gas separation application is still a challenge. The difficulties in fabricating MMMs are relating to the interface adhesion between polymer and inorganic filler that may cause voids formation in the resultant MMM. These voids are unhealthy to the gas permeation performance because they create addition pathways for the gas molecules to go through instead of going through the inorganic fillers. This situation will result in higher permeability, thus corrupting the gas separation performance.

There are many attempts made to surpass these problems, including the use of compatibilizer such as 2,4,6-triaminopyrimidine (TAP). A study by Yong *et al.* [7] showed a successful fabricated interfacial void-free MMMs consisting of polyimide (PI) and zeolite 13X by introducing 2,4,6-triaminopyrimidine (TAP). The membranes showed the higher gas permeability for He, N₂, O₂, CO₂, and CH₄ with little expense of selectivity compared to the PI/TAP membrane. Besides that, coating the membrane with polydimethylsiloxane (PDMS) is also an alternative to fixed bad gas separation performance. Chong *et al.* [8] coated PSF membranes with a layer of PDMS to evaluate their performance in gas separation for oxygen

enrichment. Results from the gas permeation study revealed that the PSF membrane coated with PDMS offered higher permeance and selectivity compared pristine PSF membrane with O₂ and N₂ permeability of 18.31 and 4.01 GPU, respectively an O₂/N₂ selectivity of 4.56.

Polysulfone (PSF) is a thermoplastic polymer with great thermal stability, permeability and also resistance to chemicals. Dehghani Kiadehi *et al.* [9] fabricated carbon nanofibers (CNFs)/PSF MMMs that exhibited increment in permeability and selectivity with increasing CNF concentration. The permeability of CNFs/PSF membrane rise from 2.134 to 12.03 Barrer for CO₂ gas. Lek & Abd Rahman [10] prepared PSF mixed matrix membrane filled with zeolite 4A particles and obtained high permeability of CO₂ and selectivity of CO₂/N₂ of the membrane at 11.641 GPU and 1.397 respectively. Waheed *et al.* [11] fabricated MMMs with the combination of PSF and 4-aminophenazone (4-AMP) functionalized mesoporous silica extracted from rice husk ash, and the results revealed that the membranes showed high permeabilities, and significant higher CO₂/CH₄ and CO₂/N₂ selectivities, 32.79 and 33.31 respectively. Ahn *et al.* [12] prepared MMMs from polysulfone (PSF) containing embedded nonporous fumed silica nanoparticles and investigated the effect of silica nanoparticles in PSF membranes on gas permeability. The study showed that O₂ permeability is approximately four times higher and CH₄ permeability is over five times greater than in a pure PSF membrane. Kubica *et al.* [13] fabricated PSF and copper terephthalate (CuTPA) MMMs. The study found that membranes containing highly porous CuTPA were annealed at two different temperatures

and it was found that higher temperature results in higher both membrane permeability and selectivity.

Perovskite-type compounds have also been applied as nanofillers in MMMs for gas separation. Roh *et al.* [15] prepared MMMs with poly(vinyl chloride)-g-poly(oxyethylene methacrylate) (PVC-g-POEM) and mesoporous MgTiO₃ perovskite. The study showed that the MMM with MgTiO₃ exhibited a CO₂ permeability improvement of 140% up to 138.7 Barrer without a large loss of CO₂/N₂ selectivity. Park *et al.* [16] developed MMMs with comb polymer (CP) composed of poly(ethylene glycol) behenyl ether methacrylate (PEGBEM) and poly(oxyethylene methacrylate) (POEM) (PEGBEM-POEM), and MgCO₃ as filler. The study achieved excellent CO₂/N₂ selectivity of 93.8 and CO₂ permeance of 30.9 GPU that surpasses other MgCO₃ MMMs prepared using commercially available polymers such as PEBAX (a polyether block amide) and poly(ethylene oxide) (PEO).

In this work, PSF and lanthanum orthoferrite (LaFeO₃) were fabricated into MMMs to study the effects of PSF and LaFeO₃ ratio on gas permeation properties and selectivity. LaFeO₃ is a perovskite-type compounds that have ABO₃ structure with various properties such as they can be insulators, dielectrics, magnetic materials, ionic conductors, electronic conductors, mixed conductors, or superconductors [14]. Studies proved that this type of material can also be incorporated into MMMs with suitable polymers and exhibits good permeability and selectivity results particularly for CO₂ and N₂ gas separation. Characterization on the structure and morphology of the fabricated membranes were investigated using scanning electron microscopy (SEM), thermal

gravimetric analysis (TGA) and Fourier-transform infra-red (FT-IR). The pure gas permeation properties of CO₂, CH₄, O₂ and N₂ at 25°C, and pressure of 2, 4 and 6 bar are also reported.

2.0 CERIA-CARBONATE MEMBRANE PREPARATION

2.1 Preparation of LaFeO₃

Preparation of LaFeO₃ was conducted by using the method proposed by Qi *et al.* [17]. Lanthanum (III) nitrate hexahydrate, La(NO₃)₃·6H₂O, iron (III) nitrate nonahydrate, Fe(NO₃)₃·9H₂O and citric acid monohydrate (C₆H₈O₇·H₂O) were purchased from Sigma-Aldrich Ltd. and are analytical grade. According to stoichiometric preparation of lanthanum orthoferrite (LaFeO₃) the calculated amount of La(NO₃)₃·6H₂O and Fe(NO₃)₃·9H₂O were dissolved in citric acid solution at 60°C of constant stirring. The amount of citric acid needed was equal to the molar amount of metal nitrates in the solution. As both metal nitrates visually dissolved, 25% ammonia solution was added dropwise to adjust the pH to 7 and subsequently stabilize the sol. The nitrate-citrate sol was then poured into ceramic crucible and heated slowly to 120°C. The changes in viscosity and color of the sol to brown confirmed the formation of dry gel. The dry gel was later subjected to react at 200°C for 24 hours. This activation process transformed the dry gel into loose powder. The obtained as-synthesis powder was the LaFeO₃ nanocrystalline with fine crystal powder and no further calcination at high temperature needed.

2.2 Preparation of PSF Membrane

For the purpose of comparison with various weight loadings of LaFeO₃, polymeric membranes of PSF were prepared first. 20wt% of dried PSF polymer was dissolved in n-methyl-2-pyrrolidone (NMP) solvent, stirred for 24 hours and poured onto a clear, flat glass plate. Stainless steel casting knife (wet-casting thickness of 220 μm) was used to spread the solution to a uniform thickness. The glass plate with the membrane was then immersed immediately into water bath. The prepared membranes were immersed in water bath for 24 hours followed by air-drying for 24 hours at room temperature.

2.3 Preparation of PSF/LaFeO₃ Mixed Matrix Membranes

The synthesis procedure for MMMs was similar as described above for neat polymer membrane with an additional step of dissolving LaFeO₃ with the weight loadings of 0.5wt%, 1.0wt% and 1.5wt% into NMP on magnetic plate separately for 4 hours. Then, the solutions were mixed with the prepared PSF solutions separately for another 12 hours. The membranes were casted by using the same procedure as described above.

Casted membrane was further modified by coating the membrane with Sylgard 184 (polydimethylsiloxane, PDMS) using the method proposed by Madaeni *et al.* [18]. First, the coating solution was prepared by mixing the precursors Sylgard 184A/184B at a ratio of 10:1 by volume PDMS base and hardener with the weight ratio of 10 to 1. The mixture was added to n-hexane to obtain a homogeneous solution of 3wt%. The previously casted PSF/0.5 membrane was fixed on a plate glass using tape to prevent the movement

and penetration of coating solution under support. Then, it was immersed in coating solution of PDMS for 3 min. The membrane was withdrawn and additional solution was removed. The prepared composite membrane was dried at room temperature for 5 days.

2.4 Characterization

Brunauer–Emmett–Teller (BET) surface area analysis was carried out on LaFeO₃ powder using BELSORP-max Ver 1.3.0 instrument by mean of N₂ adsorption at -196.15°C.

Scanning electron microscope (SEM, Hitachi TM3000) was used to study the surface and cross-section morphology of the membranes. Thermal degradation was conducted by thermal gravimetric analysis (TGA). Fourier transform infrared (FTIR) spectrums were evaluated in the frequency range of 400 – 4000 cm⁻¹.

2.5 Gas Permeation

The permeation performances of membranes were evaluated with fixed temperature at room temperature and variable feed pressures of 2, 4 and 6 bar. The pure gases used in the tests were methane (CH₄), carbon dioxide (CO₂), oxygen (O₂) and nitrogen (N₂). The tests were carried out at least 3 times to get the average value. The gas permeability rate for gas *i*, P_i , was determined [19] by using Equation (1):

$$P_i = \frac{Q_i l}{A(p_1 - p_2)} \quad (1)$$

where P_i is the membrane permeability (GPU), Q_i indicates the permeate flow rate (cm³(STP)/s), l is the thickness of membrane (cm), A is the membrane area (cm²), p_1 and p_2 are the pressure in feed side and permeate side, respectively (cmHg), subscript *i* is defined as CH₄, CO₂, O₂ or N₂. The

permeability coefficient is expressed in the unit of GPU (1 GPU = 1×10^{-6} cm³ (STP) cm/cm² s cmHg).

Besides that, the selectivity of the two gas components was also calculated. Selectivity is the ratio of the permeability of the individual gases. It was calculated using the ratio of permeabilities for pair of gases of CO₂/CH₄ and O₂/N₂, as follows:

$$S_{CO_2/CH_4} = \frac{P_{CO_2}}{P_{CH_4}} \quad (2)$$

$$S_{O_2/N_2} = \frac{P_{O_2}}{P_{N_2}} \quad (3)$$

where S refers to the selectivity of CO₂/CH₄ and P is the permeability (GPU).

3.0 RESULTS AND DISCUSSION

3.1 LaFeO₃ Characterization

The BET surface analysis carried out confirms that the synthesized LaFeO₃ nanoparticles showed the inverted correlation between the mean particle size and specific surface area (SSA). The synthesized LaFeO₃ has specific surface area (SSA) of 28.037 m²g⁻¹ and total pore volume of 0.251 cm³g⁻¹. The SSA value for the synthesized LaFeO₃ is in the moderate range. It is known that high surface area leads to agglomeration of nanofiller in polymer matrix and it is not favorable to produce high performance MMMs.

3.2 Membrane Characterization

3.2.1 Morphology of PSF/LaFeO₃ Mixed Matrix Membranes

Figure 1 shows the surface morphologies of the MMMs with various LaFeO₃ contents. In Figure 1(a), the neat PSF membrane exhibited

clean surface appearance with no LaFeO₃ particles on the surface, which is typical for smooth polymer membranes. When LaFeO₃ particles were added, white patchy surface morphologies were obtained. With the increase in LaFeO₃ contents, the particles formed large aggregates that occupied the polymer matrix as shown in Figure 1 (c) and (d). The SEM cross sectional images of the membranes as shown in Figure 2 further proved that LaFeO₃ particles formed larger aggregates as the weight loading increases.

Figure 2 shows SEM images of a cross sectional morphologies of a pure PSF membrane and LaFeO₃ incorporated MMMs prepared with different weight loading LaFeO₃. As shown in the Figure 2 (a), neat PSF membrane shows a typical porous cross sectional structure of a PSF membrane as demonstrated by Mohamad *et al.* [20]. However, small white LaFeO₃ particles are visible from the cross sectional view of PSF/0.5, PSF/1.0 and PSF/1.5 in Figure 2 (b), (c) and (d). The MMM containing 0.5wt% LaFeO₃ shows a few LaFeO₃ particles distributed throughout the PSF matrix. With the LaFeO₃ concentration increased, it is apparent that the LaFeO₃ particles started to agglomerate and formed larger white particle as shown in Figure 2 (c) and (d). This condition agrees with the statement that the tendency to agglomerate in MMMs structure increases at higher filler contents, and this can distort the MMMs performance via formation of non-selective voids [9]. This problem is due to the partial incompatibility of filler-polymer interface and could cause large voids formation in the PSF matrix, which induced reduction of permeability as well as gas selectivity.

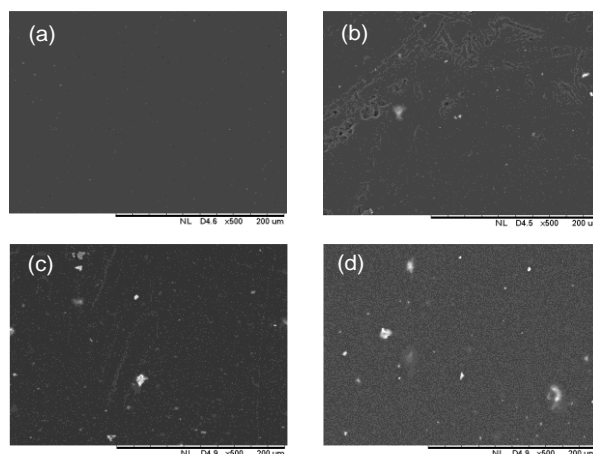


Figure 1 SEM images of membrane surfaces with LaFeO₃ contents (a) 0%, (b) 0.5%, (c) 1.0% and (d) 1.5%

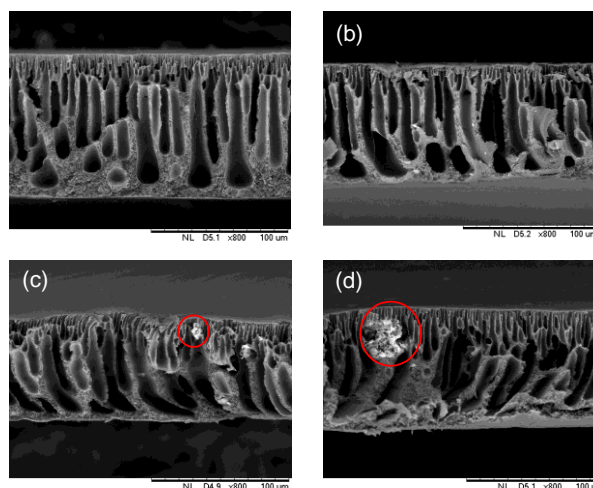


Figure 2 SEM images of membrane cross sections with LaFeO₃ contents (a) 0%, (b) 0.5%, (c) 1.0% and (d) 1.5%

3.2.2 Thermal Analysis of PSF/LaFeO₃ Mixed Matrix Membrane

The thermal properties of unfilled PSF and LaFeO₃-filled PSF MMMs were characterized by TGA analysis (see Figure 3). Neat PSF membrane experienced weight loss below 460°C that can be connected with evaporation of NMP solvent and moisture from the membrane. Meanwhile, MMMs with LaFeO₃ content show no mass loss until 460°C. This indicates complete removal of NMP solvent from the developed membranes. From the

figure, the degradation temperature of neat PSF membrane is around 500°C, which agrees with a work reported by Rafiq *et al.* [21]. Generally, adding LaFeO₃ nanoparticles in PSF polymer matrix lead to slight improvement of the thermal stability of membranes. The weight residue of pure PSF membrane was about 18.2% which was significantly smaller than PSF/LaFeO₃ MMMs. PSF/1.0 MMMs shows the highest weight residue followed by PSF/0.5 and PSF/1.5 MMMs. This was attributed to the observed uniform dispersion of LaFeO₃ nanoparticles within the PSF

matrix and so their stronger interaction with this polymer, resulting in

formation of superior chemical network structure in MMMs.

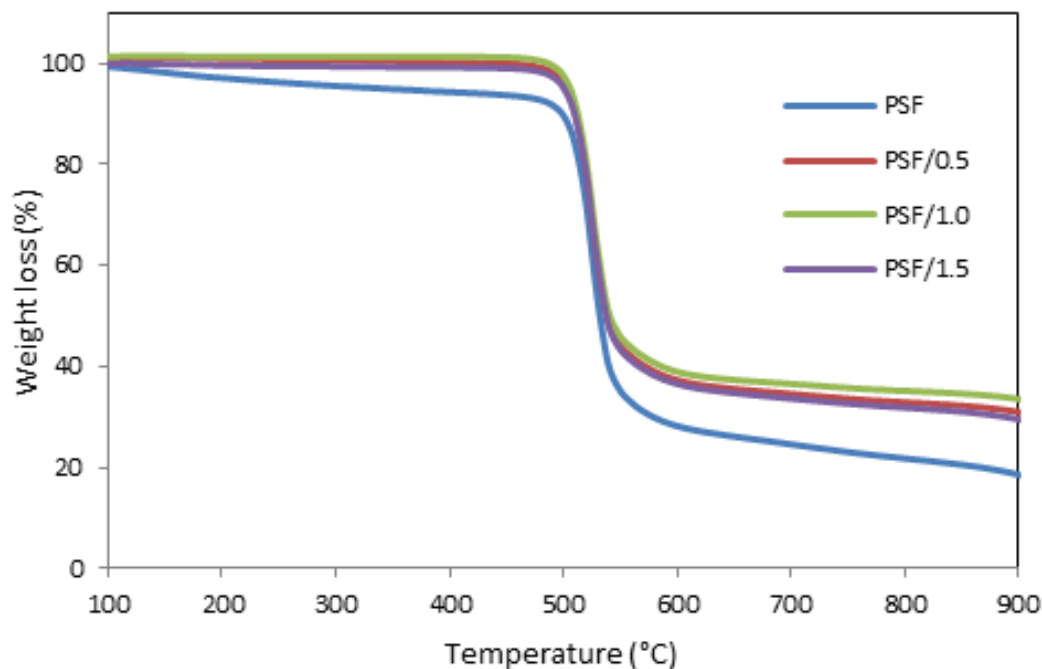


Figure 3 TGA analysis of the PSF/LaFeO₃ membrane

3.2.3 FTIR Spectroscopy of PSF/LaFeO₃ Membranes

Figure 4 presents FTIR spectra of the PSF/LaFeO₃ mixed matrix membranes and pure PSF membrane. The FTIR spectrum of pure PSF membrane

shows characteristic infrared bands at around 1151 and 1168 cm⁻¹ (SO₂ symmetric stretch), 1242 cm⁻¹ (Aryl-O-aryl C–O stretch), 1323 cm⁻¹ (SO₂ asymmetric stretch), 1386 cm⁻¹ (asymmetric –CH₃), and 1585 cm⁻¹ (C=C) [9].

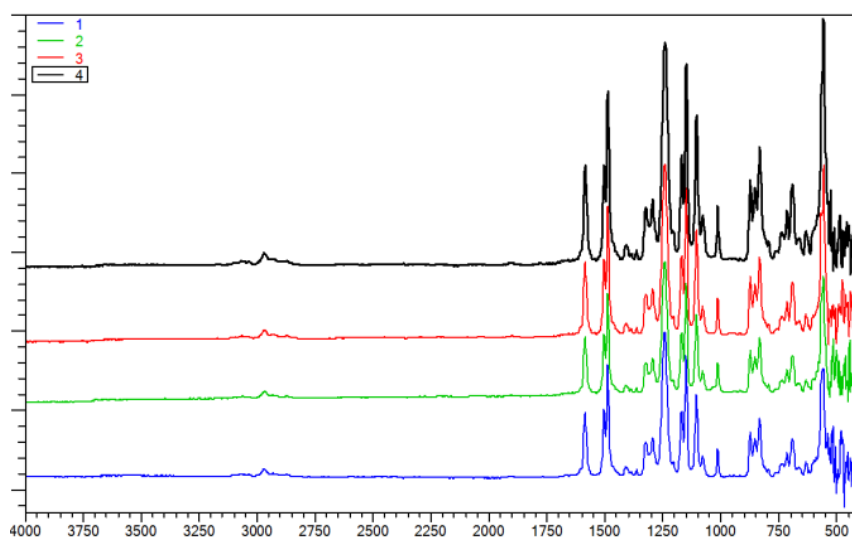


Figure 4 FTIR spectra of PSF/LaFeO₃ membrane: (a) 0wt%, (b) 0.5wt%, (c) 1.0wt% (d) 1.5%.

The FTIR spectra of PSF/LaFeO₃ are similar to those of neat PSF membrane, with the only difference around infrared bands of 400-570 cm⁻¹ occurred in the MMMs, which is attributed to LaFeO₃ addition in the membranes. This result indicates the presence of LaFeO₃ particles in the membranes, which corresponds with a study by Hosseini *et al.* [22] that exhibited bending vibration of O-Fe-O and the stretching vibration of Fe-O at around 400-560 cm⁻¹. Besides, a study by Qi *et al.* [17] also showed strong absorptive band at around 555cm⁻¹ which corresponds to Fe-O stretching vibration.

3.3 Gas Separation Performance

3.3.1 Effect of LaFeO₃ Loadings

In order to investigate the effect of LaFeO₃ loading on the MMM gas separation performance, PSF/LaFeO₃ MMM with different LaFeO₃ loadings were fabricated. For comparison, neat PSF membranes were also prepared with the same procedure. Table 1 shows the CH₄, CO₂, N₂, and O₂ single gases permeability and selectivity of the fabricated membranes. The CO₂ permeability of the PSF/LaFeO₃ mixed matrix membranes initially increased with increasing LaFeO₃ concentrations. The CO₂ permeability of the PSF/LaFeO₃ membrane reached 47.74 GPU at a LaFeO₃ loading of 1.0wt%. When the LaFeO₃ concentration was increased to 1.5wt%, the CO₂ permeability decreased to 37.52 GPU. This trend can also be observed for CH₄, O₂ and N₂ gas. Beside, gases selectivity for the MMMs are also higher than those without LaFeO₃ loading and increases with increasing LaFeO₃ loading until 1.0 wt% at fixed pressure, as indicated in Table 1. The selectivity reduces when the content of LaFeO₃ reaches

1.5wt%. This behavior (<1.0wt%) results from an increase in fractional free volume (FFV) due to the inefficient chain packing, as well as the presence of extra void volume at the interface between polymer and LaFeO₃ nanoparticles. Somehow, excessive loading of LaFeO₃ (1.5wt%) produced large agglomeration which consequently blockage the passage of gas transports thus reduced its permeability and selectivity.

Table 1 Permeability and selectivity of PSF/LaFeO₃ MMMs at 2 bar

	Permeability (GPU)				Selectivity	
	CO ₂	CH ₄	O ₂	N ₂	CO ₂ /CH ₄	O ₂ /N ₂
PSF	19.84	16.68	19.13	16.09	1.19	1.19
PSF/0.5	40.50	29.03	49.38	35.47	1.40	1.39
PSF/1.0	47.74	29.85	57.56	40.66	1.60	1.42
PSF1.5	37.52	29.32	40.39	32.13	1.28	1.26

1 GPU = 10⁻⁶ cm³ (STP) cm / cm² s cmHg

3.3.2 Effect of PDMS Coating

Membrane with LaFeO₃ content of 1.0wt% was further modified to investigate the effects of PDMS coating on the gas separation performance. The modified membranes show reduction in permeability for all gases as shown in Table 2.

Table 2 Permeability and selectivity of modified PSF/1.0 membrane

	Permeability (GPU)				Selectivity	
	CO ₂	CH ₄	O ₂	N ₂	CO ₂ /CH ₄	O ₂ /N ₂
Uncoated	47.7	29.8	57.5	40.6	1.60	1.42
Coated	28.4	10.5	25.6	18.5	2.69	1.38

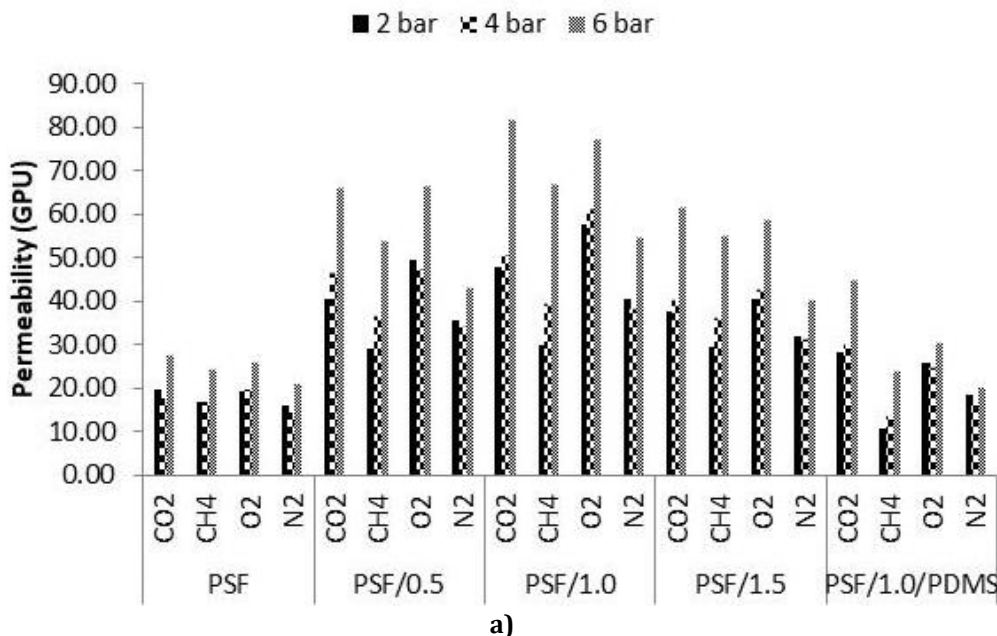
This is due to the ability of PDMS coating to minimize surface defects by forming a selective layer on the surface of the membrane and obstructed gases permeation that had caused the drop of

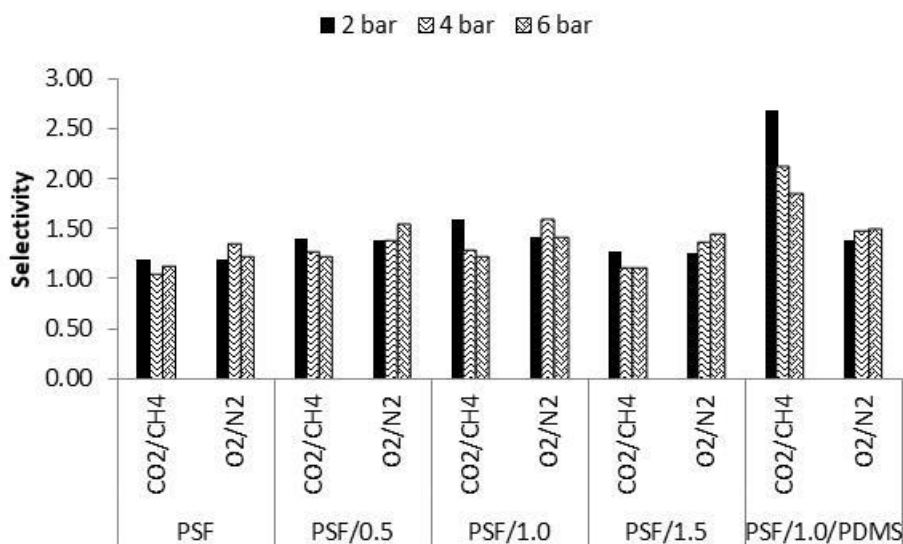
permeability. The order of permeability of the modified LaFeO₃-filled membrane for tested gases follows the sequence: CO₂ > O₂ > N₂ > CH₄. This demonstrates that the gas transport mechanism in this membrane can be defined by molecular sieving mechanism in which the molecules are separated by the size discrimination. According to this mechanism, the separation is caused by passage of smaller molecules of a gas mixture through the pores while the larger molecules are obstructed. Meanwhile, the CO₂/CH₄ selectivity of PDMS coated PSF/1.0 membrane shows a tremendous improvement from 1.60 to 2.69 compared to the uncoated PSF/1.0. High increment in CO₂/CH₄ selectivity could be related to the solubility of gases in PDMS. The ascending order of solubility of gases in PDMS is N₂ < CH₄ < O₂ < CO₂. However, no improvement is showed for the O₂/N₂ selectivity of the coated membrane. This reflects that the gas transport mechanism in this membrane

followed the molecular sieving and solution diffusion.

3.3.2 Effect of Feed Pressure

Pressure dependency of gas permeability is controlled by three main factors which are gas solubility, membrane compaction, and membrane plasticization by high penetrating gas like CO₂ and H₂S. Figure 5 shows the trend of fabricated MMMs for pressure of 2, 4 and 6 bar. As shown in the Figure 5a), gas permeability for all membranes increased with the increase in the operating pressure. On the other hand, the CO₂/CH₄ selectivity decreases when pressure increases (see Figure 5b). The O₂/N₂ selectivity for neat PSF and PSF/1.5 membrane increase slightly when the pressure reached 4 bar, but decrease at pressure of 6 bar. Meanwhile, the O₂/N₂ selectivity for PSF/0.5 and PSF/1.5 grow steadily when the pressure reached 6 bar.





b)
Figure 5 a) Gas permeability and b) selectivity of mixed matrix membranes as a function of feed pressure

4.0 CONCLUSION

In conclusion, MMMs containing PSF as polymer and LaFeO₃ as fillers were prepared with various concentration of LaFeO₃. The SEM images obtained for the cross-sectional area of the PSF/LaFeO₃ membranes indicated that LaFeO₃ particles were well dispersed in the PSF matrix at 0.5wt% LaFeO₃ loading. Further addition of LaFeO₃ weight loading up to 1.5wt% showed agglomeration of LaFeO₃ particles in the PSF matrix. Coating the membrane with PDMS enhanced the selectivity of CO₂/CH₄ but reduced the permeability of all tested gases compared to uncoated membrane. In addition, the increasing of the feed pressure resulted in the increase in gas permeability. Finally, the results revealed that these mixed matrix membranes are able to offer higher permeability and acceptable selectivity in comparison with the pure PSF membranes.

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