Development of mixed matrix membrane comprising titanium (IV) oxide dispersed with octaisobutyl polyhedral oligomeric silsesquioxane

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Abstract. In designing mixed matrix membranes (MMMs) to improve gas separation performance, inorganic fillers such as titanium (IV) oxide (TiO₂) nanoparticles are commonly added due to their excellent intrinsic properties and high affinity towards CO₂. However, the addition of TiO₂ nanoparticles causes the formation of agglomerates which deteriorate the gas separation properties of the membrane due to their high surface energy and Van der Waals forces. In this study, MMMs comprising octaisobutyl polyhedral oligomeric silsesquioxane (OPOSS) incorporated with TiO₂ nanoparticles were successfully developed using phase inversion technique. MMMs were synthesized at different loadings of TiO₂ and OPOSS. The effectiveness of OPOSS as a dispersant was determined by using SEM, EDS and single gas permeation analysis. The optimum amount of TiO₂-OPOSS in the THF/DMAc casting solution was at 4wt% TiO₂ and 2wt% of OPOSS, as the agglomeration of nanoparticles did not occur based on the morphology and gas separation performance. The membrane with the highest performance was achieved by 4/2-T/OPOSS, which is at 1.8 of CO₂/CH₄ gas selectivity. Based on the findings, it can be concluded that the OPOSS did play an important role in enhancing the dispersion of TiO₂ nanoparticles in the polymer matrix as the TiO₂ agglomerates were not seen upon addition of OPOSS.

1. Introduction

One of the major advancements in membrane technology is the addition of inorganic materials in polymer matrix to form MMMs. This can improve the permeability of carbon dioxide whilst simultaneously maintain a high selectivity towards CO₂ gas. The working principle of MMMs is to incorporate an evenly distributed filler phase on a continuous polymer phase. The filler and polymer combined together should have distinctive features in terms of selectivity, permeability and chemical properties [1].

The addition of inorganic fillers into polymer matrix has a significant effect on the MMM’s gas separation performance as it is able to modify the gas transport properties through the membrane [2]. For the conventional fillers like zeolite, carbon molecular sieve and silica, they have been commonly added into the polymer matrix due to their excellent intrinsic properties. They are easily adaptable to the polymer matrix, especially for CMS and zeolite that have a defined pore structure which enhanced
gas selectivity [2]. These fillers also enhanced the gas separation efficiency of MMMs without raising the cost and energy consumption in the membrane preparation process. Furthermore, metal oxides such as MgO and TiO$_2$ have also receive some attention due to their nano-scale size that can achieve a higher interfacial area with the polymer matrix per unit volume. These metal oxides have a high specific area to enhance particle distribution in the polymer matrix and to prevent the formation of non-selective voids at the polymer and filler interface. As compared to nano-scale silica, metal oxides have the potential to be dispersed homogeneously in the polymer matrix. Metal oxides behave as inorganic fillers to enhance gas separation performance by interrupting the chain packing of polymer or by forming nanoscale agglomerates which change the gas molecules transport through membrane [2].

In a study conducted by Moradihamedani et al., TiO$_2$ nanoparticles were added into polysulfone (PSf) polymer matrix as an inorganic filler to form mixed matrix membrane. The nanoparticles distribution and agglomeration of TiO$_2$ nanoparticles were investigated from 0wt% to 7wt% of TiO$_2$. Based on the findings, homogeneous nanoparticles distribution were achieved at a lower loading of TiO$_2$ (≤3wt%) but agglomeration of TiO$_2$ which resulted in micro-voids formation was observed beyond 5wt% TiO$_2$ loading [3]. In addition, at higher TiO$_2$ loading, mixed matrix membrane produced has higher thermal stability. For the gas separation performance, for both CO$_2$ and CH$_4$ gases, permeances decreased with the use of lower TiO$_2$ contents (≤3wt%), while increased at higher TiO$_2$ loadings (5wt%). However, the selectivity of CO$_2$/CH$_4$ increased at lower TiO$_2$ loading and reduced upon higher TiO$_2$ content. This showed that incorporation of metal oxides nanoparticles at an optimum level is important to improve MMMs gas permeability while retaining its selectivity.

Emerging inorganic fillers such as graphene and polyhedral oligomeric silsesquioxane (POSS) have been extensively studied in many fields of science and engineering. Recent advances demonstrated their potential to enhance the gas transport properties of MMMs. For fabrication of nanocomposites, graphene which is a new category of carbon nanomaterials can be used as a substitute to CNTs due to its outstanding electrical, thermal, structural and mechanical properties. On the other hand, POSS which possesses unique cage structure and nano-scale diameter has also received interests among researchers. POSS is a hybrid of inorganic and organic composition, $R_n(SiO_{1.5})_n$ where the $R$ group can be from a wide range of the organofunctional group. It has a size of 1-3nm which is the smallest possible silica particles [4]. Due to the organic group attached to the POSS cage, it can be easily incorporated into a polymer matrix. The organic group provides resin compatibility whereas the various functionalities on POSS can be used to bind on various fillers to form nanomaterials.

Although mixed matrix membranes were produced and extensively researched for CO$_2$/CH$_4$ separation, MMMs still possess some limitations. The agglomeration of nanofillers in the polymer matrix appears to be an important challenge faced in the fabrication of MMMs. The issue arises when inorganic materials, especially for inorganic nanoparticles are embedded into a polymeric membrane. Due to the small size of nanoparticles, they often have very high surface activity. As a result, the particles tend to gather and form aggregates to create aggregates of micron size. This lowers their surface energy so that their stability in the polymer matrix can be increased [5, 6]. Titanium (IV) oxide, TiO$_2$ is one of the nanoparticles that was widely used in the manufacture of nanocomposite membranes. Hence, TiO$_2$ precipitation often occurs at higher loading when preparing MMMs, leading to the formation of non-homogeneous TiO$_2$ in MMM [7]. Due to the agglomeration of fillers, non-selective defects are produced in the mixed matrix membrane such as large pinholes and macro-voids which cannot be reached by polymer segments. These defects in the polymer matrix would deteriorate the gas separation performance as permeability of the membrane increases drastically with no selectivity. In addition, the compatibility between polysulfone polymeric membrane, TiO$_2$ nanoparticles and POSS inorganic fillers remains a major issue in the fabrication of MMMs. The interface compatibility between the polymer and inorganic filler determine the success of MMMs fabrication. The adhesion problem at the polymer/filler interface results in voids formation which deteriorate the performance of gas separation as gas molecules could pass through the voids, making MMMs less selective [8].
In this study, octaisobutyl POSS is expected to act as both inorganic filler and dispersant for TiO$_2$ nanoparticles which improved the dispersion and distribution of particle fillers in the polymer matrix. The objective of this study is to overcome TiO$_2$ agglomeration by using octaisobutyl POSS. The MMMs were synthesized via dry-wet phase inversion process. The cross-section morphologies and distribution of titanium elements, as well as the separation performance for CO$_2$ and CH$_4$ gases were tested for the MMMs.

2. Materials and methods

2.1. Preparation of TiO$_2$-OPOSS/PSf MMM

Asymmetric MMMs were prepared from dope solutions containing octaisobutyl polyhedral oligomeric silsesquioxane (OPOSS, Hybrid Plastics) with a purity ≥ 99.9%, titanium(IV) oxide (TiO$_2$, Sigma-Aldrich) with a purity ≥ 99.5% and polysulfone (PSf, Sigma-Aldrich) with a molecular weight of ~35000. The binary solvent used consists of tetrahydrofuran (THF, Merck) and dimethylacetamide (DMAc, Merck). The chemical structure of octaisobutyl POSS is depicted in figure 1. Prior to the experiments, different total inorganic fillers loading was tested for both TiO$_2$ and OPOSS which included 6wt% (3wt% of OPOSS and 3wt% of TiO$_2$), 8wt% (4wt% of OPOSS and 4wt% of TiO$_2$), 10wt% (5wt% of OPOSS and 5wt% of TiO$_2$), 12wt% (6wt% of OPOSS and 6wt% of TiO$_2$) and 14wt% (7wt% of OPOSS and 7wt% of TiO$_2$). The optimum total filler loading was found to be 6wt% (3wt% of OPOSS and 3wt% of TiO$_2$) as it has the highest gas separation performance among all. Hence, the total inorganic fillers content was maintained constant at 6wt%. The ratio of OPOSS and TiO$_2$ was varied from 0 to 6 wt%, as shown in table 1.

The MMMs were prepared by using the dry-wet phase inversion method. Firstly, TiO$_2$ and OPOSS were added into 7.5 mL of THF and 2.5 mL of DMAc solvent (73 wt%) at room temperature. To ensure homogeneous dispersion of fillers in the binary solvent, the mixture was stirred and sonicated for 30 minutes. Subsequently, 3.3325 g (27 wt%) of PSf pellets were added batch-wise to improve the interfacial interaction of inorganic fillers within the polymer matrix with continuous stirring at 200 rpm and 50°C [9]. The solution was continuously stirred to remove trapped micro-bubbles for 24 hours followed by sonication for 4 hours. Next, a casting knife with a gap setting of 200 μm was used to cast the resulting dope solution on a levelled glass plate. The membrane was left under convective evaporation for 10 seconds and immersed in distilled water for 24 hours. The membrane instantaneously peeled off from the glass plate and was removed from the water bath after 1 day. The synthesized membrane was dried for 48 hours at room temperature prior to characterization.

![Figure 1. Molecular structures of octaisobutyl POSS [10].](image-url)
Table 1. The composition of TiO$_2$-OPOSS/PSf MMMs.

| Sample      | TiO$_2$ Content (wt%) | POSS Content (wt%) |
|-------------|-----------------------|--------------------|
| 0/6-T/OPOSS | 0                     | 6                  |
| 1/5-T/OPOSS | 1                     | 5                  |
| 2/4-T/OPOSS | 2                     | 4                  |
| 3/3-T/OPOSS | 3                     | 3                  |
| 4/2-T/OPOSS | 4                     | 2                  |
| 5/1-T/OPOSS | 5                     | 1                  |
| 6/0-T/OPOSS | 6                     | 0                  |

2.2. Characterization

The fabricated membranes were characterized with scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS) and single gas permeation test. The micro-scale images of TiO$_2$-OPOSS/PSf MMMs were analyzed with SEM (Hitachi TM 3030 Tabletop Microscope) to evaluate the membrane morphology. After cracking the membranes cryogenically in liquid nitrogen, the samples are sputter coated with platinum or gold at a voltage of 15kV. The surface and cross sections of MMMs were analyzed to demonstrate the membrane morphology and structure and to detect the existence of TiO$_2$ when fillers were added. EDS (Bruker Quantax 70) was used to examine the elements present in the MMMs with magnification between 1000X and 3000X at an operating acceleration voltage of 5.00kV. The dispersion of TiO$_2$ nanoparticles in the membrane matrix was also examined. After the sample was positioned on a sample holder, a focused beam of electrons is bombarded on it. The information on the elemental composition of samples were obtained through the x-ray spectrum emitted.

In terms of membrane separation performance, single gas permeation tests were carried out on CO$_2$ and CH$_4$ to measure permeance and ideal selectivity of the membrane. Pure CO$_2$ and CH$_4$ gases at a purity of 99.99% and a soap bubble flowmeter was used to calculate the flow rate of gas through the membrane. The gas permeation test was performed at 25°C and 5 bar. The gas flow rate was calculated by using equation (1):

$$Q = \frac{V}{t}$$  \hspace{1cm} (1)

where $Q$ is the volumetric gas flowrate (cm$^3$/s), $t$ is the time required (s) for gas bubbles to travel the specified volume and $V$ is the volume (mL) [9]. The membrane permeance was calculated using equation (2):

$$\frac{P}{l} = \frac{Q \times 273.15}{\Delta p \times T \times A}$$  \hspace{1cm} (2)

where $P/l$ is the gas permeance across the membrane in cm$^3$ (STP) / cm$^2$.s.cmHg, $Q$ is the volumetric gas flowrate (cm$^3$/s), $A$ is the effective membrane area in the permeation cell (cm$^2$), $T$ is the absolute temperature (K) and $\Delta p$ is the pressure drop across the membrane (cmHg). Gas permeance is recorded in the unit of GPU. Equation (3) measured the ideal selectivity for CO$_2$ and CH$_4$ gas of membranes [11]:

$$\alpha_{CO_2/CH_4} = \frac{(P/l)_{CO_2}}{(P/l)_{CH_4}}$$  \hspace{1cm} (3)

where $\alpha_{CO_2/CH_4}$ is the ideal selectivity of CO$_2$ to CH$_4$, $(P/l)_{CO_2}$ represents permeance of CO$_2$ and $(P/l)_{CH_4}$ is the permeance of CH$_4$. 

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3. Results and discussion

3.1. Membrane structure and morphology

Figure 2 shows the SEM micrographs of the asymmetric membranes prepared. It can be seen that the top layer of the MMMs has a thin dense layer which acts as the selective barrier [12]. Below the thin dense layer, long and finger-like pore structure extending towards the middle layer can be observed; while the sponge-like structure has present near the bottom layer of the MMMs. The finger-like structure and sponge-like structure act as the support layer to the dense selective layer. In this study, all the synthesized membranes prepared were observed to have the similar structures. The dense layer, finger-like layers and sponge-like structure observed were typical of flat sheet membrane structure prepared using the phase-inversion method [13, 14]. Firstly, the dense layer observed is due to the solidification of polymer dope solution after 10s of short convective evaporation [12]. The finger-like morphology obtained below the top layer of membrane shows that the THF/DMAc solvent and distilled water has a very high solvent exchange rate, which resulted in fast precipitation of the polymer. On the other hand, the sponge-like structure at the bottom layer was due to slow solvent and distilled water (non-solvent) exchange. This is because the precipitated polymer at the top layer obstructed the rate of solvent exchange. This delayed the polymer precipitation at the bottom layer and formed a sponge-like structure [14, 15]. Mohsenpour et al. also observed similar membrane morphologies when TiO$_2$ was added as additives to PVDF polymer [14]. As the content of TiO$_2$ increased from 1wt% to 6wt%, it was observed that the finger-like layer extended deeper towards the bottom layer of the membrane. It was hypothesized that due to the increase in the depth of finger-like structure, the porosity of membrane would increase from figure 2 (a) to (f). This hypothesis is to be further validated by using mercury porosimeter analyser. By increasing the amount of TiO$_2$ from 1wt% to 6wt%, the hydrophilicity of the polymer solution increased as well. This increased the solvent and non-solvent exchange rates, resulting in a faster phase inversion and ultimately leading to the development of longer interconnecting channels within the membrane matrix [16].

Based on figure 3, as the loading of TiO$_2$ increased from 1wt% to 6wt%, large TiO$_2$ precipitates can be seen more obviously in the cross-section of the membrane matrix. The presence of TiO$_2$ nanoparticles on the membrane was confirmed by EDS analysis in figure 3, as shown in the white boxed. The elemental weight percentage of Ti element increased as the TiO$_2$ loading increased from 1wt% to 6wt%. Figure 3 also shows the titanium element mapping on the cross-section of the membrane structure. Based on the images, the TiO$_2$ nanoparticles formed micro-sized agglomerates throughout the membrane matrix. This is due to the attractive Van der Waals forces of TiO$_2$ and high surface energy nanoparticles. The nanoparticles clumped together to reduce their surface energy and increase particle stability within the membrane matrix [17]. When TiO$_2$ loading increased, the whole system is now dominated by the attractive Van der Waals forces, which lead to an increase in TiO$_2$ collision frequency. Hence, the higher the TiO$_2$ loading, the higher the degree of attachment and agglomeration of TiO$_2$ nanoparticles. As the ratio of TiO$_2$ to OPOSS varied from 1wt% to 6wt% for TiO$_2$ and 5wt% to 0wt% for OPOSS, the agglomeration of TiO$_2$ nanoparticles was found to reduce with only a small amount of OPOSS as shown from figure 3 (a) to (f). OPOSS acts as a dispersant by forming a greater energy boundary on the surface of TiO$_2$ nanoparticles, causing them to repel one another and thus prevented agglomeration [18]. Upon addition of OPOSS into the system, it was observed that the TiO$_2$ agglomeration was not severe and the titanium elements were distributed evenly across the membrane matrix as in figure 3 (c) and (d). The high amount of OPOSS usage as in figure 3 (a) and (b) did not provide a good dispersion of TiO$_2$ nanoparticles as a large clump of titanium element can be seen clearly. From figure 3 (c) and (f), the dispersion and distribution of TiO$_2$ nanoparticles were not ideal as TiO$_2$ agglomerates can still be found. This was due to the small amount of OPOSS used which could not fully cover the surface of TiO$_2$. 

3.1.1. Membrane structure and morphology
Figure 2. Cross section morphology of (a) 1/5-T/OPOSS, (b) 2/4-T/OPOSS, (c) 3/3-T/OPOSS, (d) 4/2-T/OPOSS, (e) 5/1-T/OPOSS and (f) 6/0-T/OPOSS MMMs. The white boxes denote the formation of TiO$_2$ agglomerates.
Figure 3. Titanium elemental mapping of (a) 1/5-T/OPOSS, (b) 2/4-T/OPOSS, (c) 3/3-T/OPOSS, (d) 4/2-T/OPOSS, (e) 5/1-T/OPOSS and (f) 6/0-T/OPOSS MMMs. The white circles denote TiO$_2$ agglomerations. The white boxes denoted the elemental weight percentage of Ti element in the membrane matrix.

3.2. Gas permeation properties

The gas transport properties of synthesized MMMs which includes permeance and ideal selectivity were obtained. As shown in figure 4, the permeance of CO$_2$ is in the range of 3.03 to 23.92 GPU, while the CH$_4$ permeance was in the range of 2.62 to 80.09 GPU. The selectivity of CO$_2$ to CH$_4$ for the synthesized MMMs was in the range of 0.3 to 1.8. For 1/5-T/OPOSS and 2/4-T/OPOSS MMMs, the membranes may possess severe defects (macro-voids or interfacial defects at the dense selective layer) as the permeance for CH$_4$ was faster than the permeance for CO$_2$ gas. This can be due to the agglomeration of TiO$_2$ as shown in figure 3 (a) and (b). The high amount of OPOSS (4 and 5 wt%) did not improve the dispersion of TiO$_2$ nanoparticles but created macropores and interfacial defects on the selective layer which allowed CO$_2$ and CH$_4$ to pass through. Hence, the ideal selectivity of CO$_2$ and CH$_4$ was very low. On the other hand, the gas permeance of the remaining MMMs showed increment.
in the CO\textsubscript{2} and CH\textsubscript{4} permeance. In addition, the ideal CO\textsubscript{2}/CH\textsubscript{4} selectivity of 3/3-T/OPOSS, 4/2-T/OPOSS, 5/1-T/OPOSS, and 6/0-T/OPOSS were 1.2, 1.8, 1.6 and 1.4 respectively. Based on the SEM images in figure 2, it was noticed that the depth of the finger-like structure increased with the increment in TiO\textsubscript{2} nanoparticles. This increases the porosity of the membrane due to the formation of larger finger-like cavity [16]. Hence, the gas permeance of CO\textsubscript{2} and CH\textsubscript{4} also increased due to the increment in the membrane porosity.

It was found that the optimum gas transport performance is at 4/2-T/OPOSS, where it has the highest ideal selectivity. At this ratio, the TiO\textsubscript{2} nanoparticles in the membrane matrix are fully covered with a layer of OPOSS. The isobutyl group of OPOSS on TiO\textsubscript{2} increased the nanoparticles overall diameter and reduced the surface energy of TiO\textsubscript{2} [9]. The OPOSS helped to improve dispersion of TiO\textsubscript{2} by stabilizing the surface energy of atoms [18]. Since OPOSS did not react with one another, it acted as a dispersant by replacing the strong contact adhesion force by a weaker non-covalent adhesion force, which caused the nanoparticles to disperse [19]. It was observed that 2 wt\% of OPOSS addition was adequate to disperse TiO\textsubscript{2} nanoparticles in the synthesized MMMs. However, it was noticed that the selectivity of synthesized MMMs was quite low. This might be due to the incompatibility between OPOSS and TiO\textsubscript{2} nanoparticles in PSf polymer matrix.

![Figure 4. Permeance and ideal selectivity of TiO\textsubscript{2}-OPOSS/PSf MMMs.](image)

4. Conclusion
Flat sheet TiO\textsubscript{2}-OPOSS/PSf mixed matrix membranes were fabricated using the dry-wet phase inversion technique. The loading of TiO\textsubscript{2} and OPOSS was found to have a small effect on the membrane morphologies and nanoparticles distribution. The SEM analysis revealed that TiO\textsubscript{2} nanoparticles agglomeration was found even at the lowest TiO\textsubscript{2} loading (1wt\%). However, with the use of an adequate amount of OPOSS, TiO\textsubscript{2} was found to distribute evenly in the polymer matrix as supported by EDS analysis. Based on the gas separation performance results, it was found that the highest permeance was achieved by the 1/5-T/OPOSS due to the formation of macro-voids and defects on the synthesized membrane. On the other hand, the highest CO\textsubscript{2}/CH\textsubscript{4} selectivity was achieved by 4/2-T/OPOSS. The dispersing ability of OPOSS was found to be useful to stabilize TiO\textsubscript{2} and potentially other nanoparticles such as magnesium oxide, MgO. Further experiments can be conducted...
by using different types of polyhedral oligomeric silsesquioxane to study its effect as a dispersant on TiO$_2$ nanoparticles. Moreover, quantification analysis should also be carried out to further validate the qualitative results from SEM and EDS images.

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