Morphological Investigation of Alumina Asymmetric Membrane by Manipulating the Sintering Temperature Profile

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Abstract. Ceramic materials have been widely utilized due to its attractive properties including high resistance to extremely harsh environments; chemical and heat, and its durability to the remarkable mechanical strength. Inorganic flat sheet films in this study were prepared by dry-wet phase inversion process followed by sintering method, which expected to produce very unique micro-structures leading to improvement in performance for various applications including catalytic reactions and filtration processes. Aluminium oxide was chosen as the main material due its known capability in filtration processes, membrane reactors and membrane catalysis applications. Polyethersulfone (PES) was used as an organic binder in the membrane dope formulation. Besides alumina and PES, the dope solution was consisted of N-methyl-2-pyrrolidone (NMP) and arlacel as solvent and additive, respectively. The main aim of this study is to investigate the effect of sintering temperature on the morphology and structure of the prepared membranes. Scanning electron microscope (SEM) was used to examine the membrane structure. Since the morphology of a membrane highly influences its mechanical properties, the membrane strength was measured using tensile test. From the SEM, preliminary cast membrane structure displayed a long finger-like near the outer and inner walls sandwiched a sponge-like structure that provided the membrane strength.

Introduction

Gas purification involves the removal of vapor-phase impurities from gas stream. One of the gas purification processes is membrane permeation. Over the last three decades, membrane technology has brought in a lot of attention and turn into most popular unit operation for a several of important application based on gas separation [1,2].

In late 1970s to 1980s, membrane gas separation systems were started to be applied commercially [3]. The applications at the timewere quite limited, mainly for the separation of hydrogen from petroleum refineries and the H\(_2\)/CO ratio adjustment for the production of synthesis gas. Since then, the membrane-based gas separation is accepted in many applications [3].

Membrane technology gained wider acceptance because it offers substantial economic, environmental and safety benefits [4]. Chemical stability of membrane is the most crucial factor in membrane fabrication. Membrane material is vulnerable to chemical attack when liquid absorbent with high load of carbon dioxide (CO\(_2\)) that is corrosive in nature. Thus, it will be a problem to the membrane system. Thermal stability of a membrane is also important to ensure the efficiency of a purification system [11]. At high temperature, membrane material may undergo degradation or decomposition. Therefore, the selection of material for membrane is very crucial.
One of the methods in overcoming this problem is using high thermal and mechanical strength ceramic material such as alumina. Ke *et al.* mentioned that most industries have particular interest in ceramic separation membrane rather than polymeric membrane because ceramic has excellent durability under extreme condition and chemical and thermal stability; they also function efficiently within organic and biological systems, and at high temperatures; and they can be cleaned readily by steam-treatment, while maintaining a long operational life [4].

Aluminium oxide (Al$_2$O$_3$) or alumina is the most widely used oxide ceramic material more often than any other advanced ceramic material [9]. Major applications of alumina are used as a catalyst support for variety of reaction, favoured filler for plastics, widely used as an abrasive because of its hardness and strength, used to remove water from gas streams, used in paints for reflective decorative effect, and used as a few experimental and commercial fiber materials for high performance application. One of the recent research is the usage of alumina as a support in the development of catalytic membrane reactors that done by García-García *et al.* Other recent research is the use of alumina directly in gas separation while serving as the membrane porous support for the dense membrane formation [9]. The preparation of a ceramic membrane depends on the several preparation conditions such as particle size, size distribution, alumina content in the suspension and sintering environment by affecting the size and distribution of porous formation and the dense layer formation on the outer surface of the membrane [7].

The main aim of this study is to investigate the effect of sintering temperature on the morphology and structure of the prepared membranes.

### Table 1. Dope composition

<table>
<thead>
<tr>
<th>Al$_2$O$_3$/PES ratio</th>
<th>Ratio of Al$_2$O$_3$ (0.05-1 µm)</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1:20</td>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>54.00</td>
</tr>
</tbody>
</table>

**Experimental**

**Material.** Commercially available Al$_2$O$_3$ powders with two different particle diameters were used as the membrane materials [5,6,7]. In this experiment, 1µm and 0.05µm Al$_2$O$_3$ diameter were used. Polyethersulfone (PES) and N-methyl-2-pyrrolidone (NMP) were used to prepare the polymer solution. Arlacel was used as a dispersant. Tap water was used as the non-solvent coagulation bath.

**Preparation of Dope.** The required quantity of NMP was taken in one-liter wide-neck reaction flask and PES was slowly added over a period of 30 minute to form the polymer solution [5,6]. After the polymer solution was formed, Al$_2$O$_3$ (0.05 and 1 µm or a mixture of them) was then added into a polymer solution slowly. The ratio between Al$_2$O$_3$ and PES was 10, to ensure the prepared membrane had different pore sizes and porosities. The ratios between these particle sizes were kept constant in order to produce membranes with smooth surfaces and asymmetric structures [7]. The mixture was then stirred for 36 hours by a ball mill. Arlacel was also introduced into the solution to modulate its viscosity. After that, the dope solution was transferred to a stock bottle and was degassed using vacuum pump for approximately 30 min to remove air bubbles. The solution was cast onto a glass plate and left for evaporation process to occur for 30 seconds prior to solvent exchange in the coagulation bath. The flat sheet was left in the water bath for 24 h to complete the phase inversion before being sintered. Before sintering process, the membrane was cut in a square form. The membrane was then suspended in the furnace and fired in a controlled manner using a sintering profile as shown in Fig. 1. The sintered membranes were then taken out and ready for characterization.
**Scanning electron microscope (SEM).** The morphology and structure of prepared membranes were observed using a scanning electron microscope. These samples were positioned on a metal holder and gold coated using sputter-coating operated under vacuum. The SEM micrographs of both surface and cross-section of the membranes were taken.

**Tensile test.** The mechanical strength of the inorganic flat sheet membranes was characterized using the tensile test. The mechanical properties of the membranes were measured using a load cell of 2.5 kN and 1 mm/min speed. Sample was cut into 25 x 13.4 x 0.464 mm and then fixed on a holder. The strength was calculated from the following equation:

\[
\text{Strength (MPa)} = \frac{(\text{Load (N)})}{(\text{Area (mm)})}
\]  

(1)

**Results and discussion**

**Morphology Study of Al₂O₃ Flat Sheet Membrane.** SEM micrographs of the Al₂O₃ flat sheet and their sintered membranes are shown in Fig. 2 and Fig. 3. It can be seen from Fig. 2 that near the outer and inner walls of the membrane, long finger-like structures and that at the center of the flat sheet, sponge-like structure can be seen. The appearance of the flat sheet membrane structures shown in the figure could be attributed to the rapid precipitation of the polymer occurred at both the inner and outer flat sheet membrane walls resulting in long fingers. Consequently, the precipitated polymer hindered the rate of solvent and non-solvent exchange resulted in slow precipitation of the polymer in the middle of the wall giving the sponge-like structure at the center of the flat sheet [7].

![Fig. 2. SEM image of cross section of the flat sheet ceramic membrane. (a) sintered at 1250°C, (b) sintered at 1350°C, and, (c) sintered at 1450°C.](image)

Fig. 2 shows the flat sheet morphology resulting from sintering at 1250°C. The finger-like voids extends from the inner surface across approximately 50% of the flat sheet cross-section but void length at the outer surface was slightly less. A sponge-like region occupying approximately 35% of the flat sheet cross-section is present between the inner and outer finger-like voids. Such a structure was formed due to the several factors such as viscous fingering phenomenon and movement of particles. In this study, during the casting of the flat sheet ceramic membrane, pure water was used as the non-solvent and was immediately in contact with the high viscous of dope solution. Therefore, the hydrodynamically unstable viscous fingering takes place, resulting in finger-like
structures in the inner surface as long as the rate of viscous fingering is greater than that of phase inversion. As the sintering temperature increased, the finger-like structures of the membranes becoming more compact and shorter due to heating and ceramic particles rearrangement.

Fig. 3. SEM micrographs of surface of the flat sheet ceramic membrane. (a) sintered at 1250°C, (b) sintered at 1350°C, and, (c) sintered at 1450°C.

Fig. 3 shows that the surface of the ceramic flat sheet membrane is similar to the polymeric membranes prepared via the phase-inversion technique. Further comparing the SEM photos, reveals that the pore quantity and pore size on the membrane surface may have changed after the sintering process, although the general structure is maintained. Such structure changed due to the chosen ceramic particle sizes, composition of the dope solution and the sintering temperature. Fig. 3 illustrates the evolution of the surface morphologies at different sintering temperatures between 1250°C and 1450°C with the sintering times of 4 hour. It can be seen that the porosities of the membrane surface are reduced greatly when the sintering temperature is increased. At the sintering temperature of 1250°C, there is an obvious change in the surface morphology and the interconnected pores are observed from the membrane surface as shown in Fig. 3a. At sintering temperature of 1350°C, the interconnected pores are still observed from the membrane surface as shown in Fig. 3b, although their porosities are much reduced compared to those sintered at 1250°C. When the sintering temperature is increased to 1450°C, the membrane surface becomes almost fully dense as shown in Fig. 3c. The above observation indicated that sintering temperature play important roles in the controlling the ceramic membrane porosity and structure.

Strength of Al$_2$O$_3$ Flat Sheet Membrane

Table 2. Tensile test for cast membrane before and after sintering

<table>
<thead>
<tr>
<th>Type of Sample</th>
<th>Area (mm$^2$)</th>
<th>Maximum Load (N)</th>
<th>Strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before Sintering</td>
<td>6.2176</td>
<td>5.3315</td>
<td>0.8574</td>
</tr>
<tr>
<td>After Sintering</td>
<td>6.2176</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The membrane that formed through the phase-inversion technique contains the Al$_2$O$_3$ and the PES polymer. During the sintering process, the PES polymer is expected to be removed, thus, the remaining Al$_2$O$_3$ flat sheet is ultimately formed. Therefore, the Al$_2$O$_3$ content in the dope solution plays an important role in determining the flat sheet mechanical strength. An increase of sintering temperature would enhance the mechanical strength [6], where, at higher temperature, the ceramic particles fused and developed larger grains, which gave higher strength. The increase of the Al$_2$O$_3$ content in the dope would result in a much more obvious effect on the flat sheet mechanical strength compared to the sintering temperature. Therefore, in order to produce Al$_2$O$_3$ flat sheet membrane with higher mechanical strength, the higher Al$_2$O$_3$ content in the dope solution must be maintained. In this study, Al$_2$O$_3$ was cast into a flat sheet membrane that had never been reported before. The cast membrane becomes unexpectedly too brittle after sintering process and easily broken even when holding with hand. Therefore, the tensile test was failed on the sintered membrane. Table 2 shows the result based on 2 cast membrane before sintering with the strength of 0.8574 MPa while after sintering, the data could not be measured because the membrane was too brittle due to the burnt-off of polymer binder and the very thin structure of the membrane.
Conclusion

Ceramic flat sheet membrane has been prepared by casting a dope solution, which was then sintered at elevated temperatures. The prepared membranes have the asymmetric structure including the sponge like layer at center and long finger-like layer located at the outer and inner walls of the flat sheet membrane. The finger-like structure in flat sheet membrane result from hydrodynamically unstable viscous fingering occurring at the interface between the dope solution and non-solvent. The membrane mechanical strength was measured using the tensile test. From the test, the strength before sintering obtained was 0.8574 MPa while after sintering the result could not be obtained because once the sample was cut according to the sample specification, the sample was broken. Thus, a thin asymmetric flat sheet is not recommended as a module for ceramic membrane in future.

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