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INVESTIGATION ON THE EFFECT OF SINTERING TEMPERATURE ON KAOLIN HOLLOW FIBRE MEMBRANE FOR WATER APPLICATION

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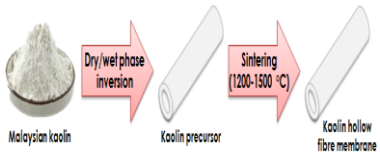
Graphical abstract



Abstract

Ceramic membrane has the ability to surpass the utilisation of polymeric membrane in the application that requiring high temperature and pressure condition, as well as harsh chemical environment. Due to the high cost of ceramic membrane, various attempts have been made to use low cost ceramic materials as alternatives to well-known expensive metal oxides. In this work, local Malaysian kaolin has been chosen as ceramic material since it is inexpensive and easily available in Malaysia for the preparation of low cost hollow fibre ceramic membrane. The aim of this work is to study the effect of sintering temperature on the morphology, properties, and performance of kaolin hollow fibre membrane by sintering the prepared precursor at different target temperatures ranging from 1300°C to 1500 °C. The experimental results demonstrated that the kaolin membrane sintered at 1400 °C has influenced the formation of sufficient dense sponge-like structure of skin layer, resulting in good water flux of 74 L/h.m^2.

Keywords: Malaysian kaolin; hollow fibre membrane; sintering temperature; sponge-like structure; precursor

1.0 INTRODUCTION

Ceramic membrane has the ability to surpass the utilisation of polymeric membrane in various application that requiring high temperature and pressure. However, the application of ceramic membrane is well-known as less economical in comparison with polymeric membrane due to the relatively elevated cost. The commercialised ceramic membranes found in the market are majorly manufactured from expensive metal oxides such as alumina, which hindering the wide application of ceramic membrane in various applications. The advancement in research at the later stage has been introduced the application of various inorganic materials in membrane preparation, for instances titania, silica, and zirconia as the alternative materials to alumina [1, 2, 3], unfortunately these ceramic membranes remains to be significantly high cost since there are quoted to be at least 10 times expensive than the polymer membranes [4].

Further research in the fabrication of ceramic membrane has favoured towards the application of cheaper raw materials such as fly ash [5] and natural raw clay [6]. From the previous works that have been successfully conducted to utilise cheaper raw materials, it was found that kaolin has become one of the important raw materials for the preparation of inexpensive ceramic membranes. For example, Bouzerara *et al*. [7] reported their works on the application of local Algerian kaolin and dolomite as inexpensive raw materials for the fabrication of porous ceramic membranes from kaolin and kaolin-doloma mixtures. In addition, porous ceramic tubular membrane also has been successfully prepared using local Tamazert kaolin in the study conducted by Bouzerara *et al*. [8]. Thus, local Malaysian kaolin has been selected as the sole ceramic material to be used in this study for the preparation of kaolin hollow fibre membrane.

According to Liu and Li [9], sintering temperature influences greatly on the membrane properties, thus they stipulated that the sintering temperature should be chosen at around three-fourth of the material's melting point. Previous work by Sarbatly [10] on the fabrication of kaolin flat sheet membrane, he suggested that the kaolin membrane that sintered at ≥1300 °C possessed sufficient membrane properties compared to the membrane that sintered at <1300 °C. This finding provided the preliminary data in the selection of suitable range of target temperature to be applied during the sintering process. So, the effect of applied sintering temperature at 1300-1500 °C on the membrane morphology, properties, and performance has become the aim of this study.

2.0 METHODOLOGY

2.1 Materials

In this study, kaolin powder (Kaolin (Malaysia) Sdn. Bhd.) with average particle size of 2-4 μm was consumed as the low cost ceramic material. In addition, polyethersulfone (PES) (Solvay Advanced Polymers), polyethylene glycol 30-dipolyhydroxystrearate (Arlacel P135) (Uniqema), and *N*-methyl-2-pyrrolidone (NMP) (Merck) were also used as the polymer binder, dispersant, and solvent, respectively for the preparation of ceramic suspension. On the other hand, tap water was used as the internal and external coagulant during the spinning process.

2.2 Membrane Preparation

The first step in the membrane preparation was the preparation of ceramic suspension solution. The suspension solution consisting of kaolin powder (40 wt%), PES (5 wt%), NMP (54 wt%) and Arlacel P135 (1 wt%) was prepared by dissolving Arlacel P135 first in NMP, followed by the addition of kaolin powder. The suspension solution was milled for 48 h in planetary ball mill to ensure the well mixing of kaolin powder, solvent, and additive, and milled continuously for another 48 h right after the addition of PES. The suspension solution was then degassed under vacuum until no air bubbles were seen on the surface of suspension before being transferred into a stainless steel container prior to spinning process.

By using the dry/wet phase inversion technique [11, 12, 13], the suspension solution was extruded (flow rate of 9 mL/min) with the internal coagulant (flow rate of 10 mL/min) through a spinneret into an external coagulation bath with air gap of 5 cm. The hollow fibre precursors formed were immersed in the external coagulation bath for 24 h to accomplish the completion of phase inversion process. The precursors were then dried at room temperature overnight before being sintered.

By using different target temperatures (1300 °C, 1400 °C and 1500 °C), the sintering process was carried out in tubular furnace by increasing the temperature from room temperature to 600 °C at the rate of 2 °C/min and being held for 2 h, followed by increasing of temperature from 600 °C to target temperature at the rate of 5 °C/min and being held for 5 h. Lastly, by reducing the temperature from target temperature to room temperature at the rate of 5 °C/min, the sintering process was ended. The overall steps involved in the preparation of kaolin hollow fibre membrane could be summarised in Figure 1 below.

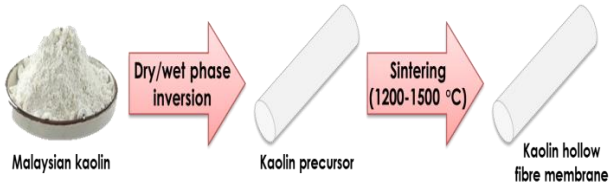


Figure 1 Step-by-step of overall process

2.3 Membrane Characterisation

The morphology of kaolin hollow fibre membrane was examined by using scanning electron microscopy (SEM) (TM 3000, Hitachi) for obtaining the micrographs of the cross-section and outer surface of membrane. For sample preparation, the membrane was fractured to obtain the neat cut of its cross section and placed on metal holder before being sputter-coated with gold under vacuum for 3 min.

The porosity of kaolin hollow fibre membrane was measured by following Archimedes method using Mettler Toledo (ASTM C373). The porosity was calculated using following equations

$$V_p = (W_{sat} - W_{dry}) / \rho_{fluid} \quad (1)$$

$$V_b = (W_{sat} - W_{sub}) / \rho_{fluid} \quad (2)$$

$$\Phi = (V_p / V_b) \times 100 \quad (3)$$

where V_p and V_b are pore volume and bulk volume (cm^3), respectively. W_{sat}, W_{dry} and W_{sub} are weight of saturated, dry and submerged of samples (g), respectively. ρ_{fluid} is density of fluid used (in this study, water was used (1.000 g/cm^3)) while Φ is porosity of kaolin hollow fibre membrane (%).

2.4 Membrane Performance

The water flux and bovine serum albumin (BSA) rejection tests were carried out using the ultrafiltration system in cross-flow filtration mode. The water flux was measured under steady state condition and calculated by using [14]

$$F = V / (A \times t) \quad (4)$$

where F is water flux ($L/h.m^2$), V is volume of water permeated through membrane (L), A is membrane surface area (m^2) and t is the sampling time (h).

By using BSA as feed with concentration of 500 ppm, BSA rejection was tested and calculated according to [15]

$$R = (1 - C_p / C_f) \times 100 \quad (5)$$

where R is BSA rejection (%), C_p is concentration of BSA in permeate (mg/L), and C_f is concentration of BSA in feed (mg/L).

3.0 RESULTS AND DISCUSSION

3.1 Morphology of Membrane

In this study, the effect of sintering temperature on the morphology of kaolin hollow fibre membrane was examined by SEM as shown in the Figure 2 and 3. Since kaolin precursor did not undergo sintering process yet, the presence of polymer binder and dispersant could be clearly seen in Figure 2 (a), 3 (a1), and 3 (a2). When the kaolin precursor was sintered at certain target temperature, the formation of grain growth would take place. During the grain growth process, both the grains and pores were increased in size but decreased in number. As a result, the higher sintering temperature would induce the membrane densification and shrinkage further which was obviously observed from Figure 2 (b), (c), and (d). The membrane densification and shrinkage would later lead to the decrease of membrane thickness, as indicated in Figure 2 (b), (c), and (d) for 0.56 mm, 0.50 mm, and 0.44 mm wall thickness of membrane that sintered at 1300, 1400, and 1500 °C, respectively.

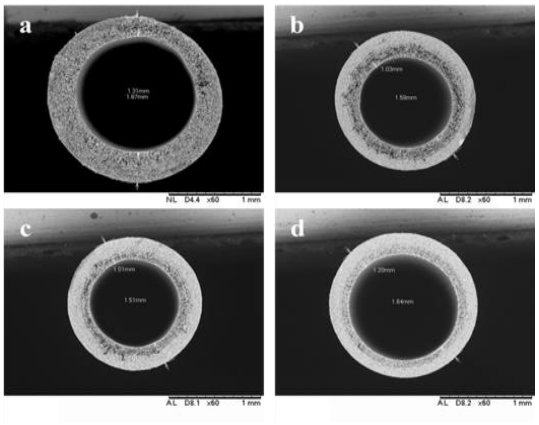


Figure 2 SEM images of overall morphology of (a) kaolin hollow fibre precursor and kaolin hollow fibre membrane sintered at (b) 1300 °C, (c) 1400 °C, and (d) 1500 °C

Besides that, the membrane structure was comprised by the dense sponge-like structure at the outer region and the porous sponge-like structure at the inner region of membrane, as shown in Figure 3 (b1), (c1), and (d1). The porous sponge-like structure of inner region was reduced as higher sintering temperature was applied due to the densification of membrane. The nearly similar observation was also found by Zhang *et al.* [16] for cordierite hollow fibre membrane with the outer thin sponge-like structure and the inner macro-void structure, that prepared by the same spinning technique and sintering process at target temperature of 1300-1400 °C. As for the surface structure of membrane, higher sintering temperature was also attributed to the shrinkage and reduction of pores on the outer membrane surface as observed in Figure 3 (b2), (c2), and (d2).

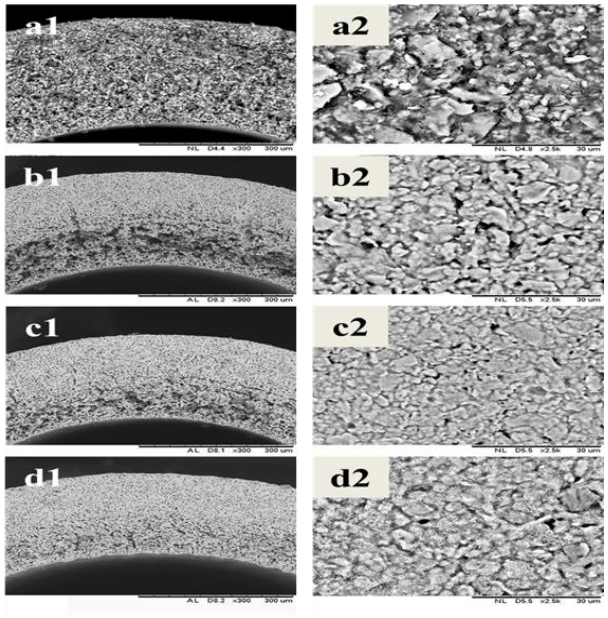


Figure 3 SEM images of (1) cross-sectional and (2) surface structure of (a) kaolin hollow fibre precursor and kaolin hollow fibre membrane sintered at (b) 1300 °C, (c) 1400 °C, and (d) 1500 °C

3.2 Porosity of Membrane

Figure 4 shows the porosity of kaolin hollow fibre membrane that sintered at different sintering temperatures. From the results obtained, there was a trend of decrease in porosity with the increase of sintering temperature applied. This trend could be resulted by the growth of necks between the ceramic particles that was occurred at high sintering temperature, contributing to closely-packed arrangement between the ceramic particles, thus resulting in the reduction of membrane porosity. The obtained result was in correlation to the densification of porous sponge-like structure of membrane as shown in Figure 3. In addition, the similar trend in decreasing membrane porosity was also observed in the study by Paiman *et al.* [14] for yttria-stabilized zirconia hollow fibre membranes that sintered at sintering temperature ranging from 1250 °C to 1400 °C.

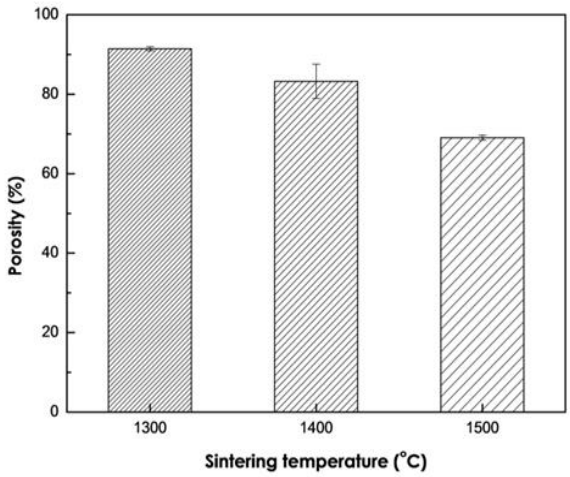


Figure 4 Porosity of kaolin hollow fibre membranes sintered at different sintering temperature

3.3 Performance of Membrane

The water flux of kaolin hollow fibre membrane that sintered at different sintering temperatures was presented in Figure 5. The results on water flux showed a decrease trend in an increase trend of sintering temperature. This finding was highly related to the pore size shrinkage and membrane densification that obviously occurred as higher sintering temperature was used. As the membrane became denser, the flow rate of water filtration became lesser. As a result, there was no water flux measured even at 5 bar of applied transmembrane pressure for kaolin hollow fibre membrane that sintered at 1500 °C since it has the densest membrane structure.

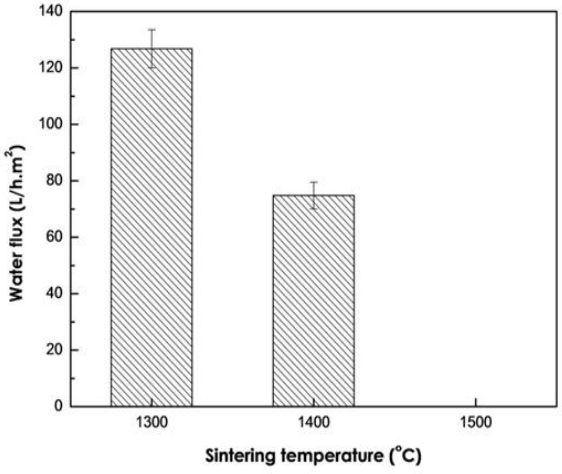


Figure 5 Water flux of kaolin hollow fibre membranes sintered at different sintering temperature

During the consolidation of precursor at high temperature, the densification of membrane were occurred, resulting in an increase trend in the protein rejection of membrane, as shown in Figure 6. This result was highly contributed by the denser structure and lesser porosity of membrane which reduced the amount of protein as feed solution to pass through the membrane, thus increased the membrane performance on protein rejection. However, there was no BSA rejection by kaolin hollow fibre membrane that sintered at 1500 °C, which was in contrast to the trend found in BSA rejection that affected by higher sintering temperature. This finding might be highly influenced by the elimination of channels and pores for permeate to pass through the membrane, as in good agreement with the result in water flux by kaolin hollow fibre membrane that sintered at 1500 °C shown in Figure 5.

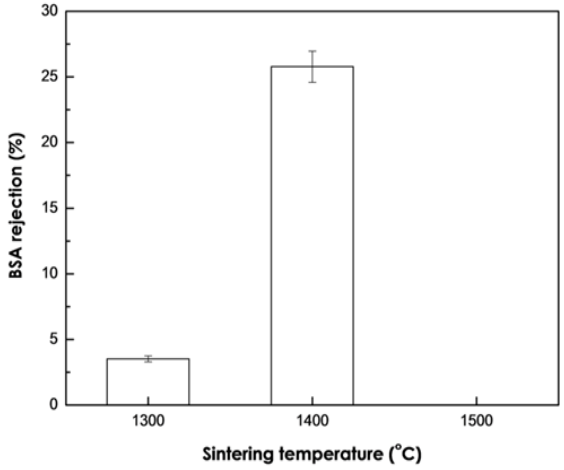


Figure 6 BSA rejection of kaolin hollow fibre membranes sintered at different sintering temperature

4.0 CONCLUSION

The low cost kaolin hollow fibre membrane was successfully prepared by using different target temperature during the sintering process. By increasing the sintering temperature, it was found that the membrane undergone densification and shrinkage, which later on affected the properties and performances of kaolin hollow fibre membrane. Based on the results obtained, it can be concluded that the sintering temperature of 1400 °C has influenced the formation of sufficient dense sponge-like structure of skin layer, resulting in a porous membrane structure with porosity of 83% and a good water flux of 74 L/h.m^2. This preliminary data could provide the new insight on the preparation of porous ceramic hollow fibre membrane using kaolin as the low cost ceramic material for the application in separation of oily wastewater.

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