

## Effect of Starch Addition on Microstructure and Strength of Ball Clay Membrane

Maisarah Mohamed Bazin<sup>a</sup>, Muhd Amirudin Ahmat<sup>a</sup>, Nurhanna Zaidan<sup>a</sup>, Ahmad Fauzi Ismail<sup>b</sup>, Norhayati Ahmad<sup>a\*</sup>

<sup>a</sup>Department of Materials, Manufacturing and Industrial Engineering, Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81300 UTM Johor Bahru, Johor, Malaysia

<sup>b</sup>Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

\*Corresponding author: nhayati@fkm.utm.my

### Article history

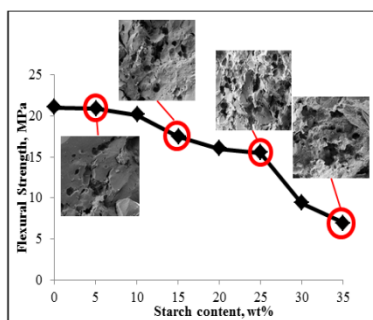
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### Graphical abstract



### Abstract

The use of starch as pore-forming agent is one of the frequently used methods to produce porous ceramics membrane with controlled microstructure (porosity and pore size) because corn starch are cheap, non-toxic and environmental friendly. A membrane with the mixture 0–35 wt% of corn starch and ball clay were prepared by compaction process and sintered at 1200°C. Thermal analysis has been done to identify the minimum sintering temperature for ball clay. The sintered membranes show the range value of shrinkage is 4.5–22.76 % and apparent porosity of 9.14–31.83 % depending on the starch content. The pore structures were analyzed by FESEM. The strength of sintered samples was tested by 3-point bending test. The flexural strength reduced from 21–7 MPa. These clay membrane are promising porous ceramic structure for water filtration applications due to their excellent combination physical and mechanical properties.

**Keywords:** Ball clay; ceramic membranes; corn starch; apparent porosity; flexural strength

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### 1.0 INTRODUCTION

Ceramic membranes have become great interest in several industrial processes such as filtration, separation, and catalytic reaction due to their high thermal and mechanical stability, long life and good chemical stability [1-3]. Most of ceramic membranes available in market are made based on alumina. However, alumina is well known as an expensive material and utilizes high sintering temperature. Therefore, the production cost for alumina membrane is high. Another ceramic material should be put into consideration as a replacement to alumina to produce more low cost membranes with good physical and mechanical properties. Some researchers have used kaolin [4-6], clay [7-12] and fly ash [13] in fabrication of ceramic membranes. Previous work was done on ball clay by gel-casting [14] and shirasu balloon by spark plasma sintering [15].

The permeability efficiency of inorganic membranes depends on the microstructural features of the membrane which include pore size, pore size distribution, pore shape, porosity and tortuosity (interconnectivity) [16]. To increase the permeability of the membrane, a pore former such as calcium carbonate (CaCO<sub>3</sub>) [6, 12, 18-19] and starch [20-24] was added.

According to Nandi *et al.*<sup>17</sup> the calcium carbonate will dissociate into CaO during sintering process and release CO<sub>2</sub> gas [17]. The porous texture form from the path taken by the released CO<sub>2</sub> gas and therefore contributed to the membrane porosity. In contrary, the porous structure form by starch is occur when the starch is burn out during the sintering process and leave a pore in the membrane body. Starch are more preferable than calcium carbonate because starch are cheap, easy processing, commercial availability and the complete burn out of starch without ash residues [25].

Several types of starch has been used as a pore former such as corn starch [20-24], wheat starch [26] and cassava starch [27]. Starch is a natural biopolymer that consist of carbon, hydrogen and oxygen (C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>) [28-29]. Starches usually used as a components or processing aids in the manufacture of adhesives, textiles, paper, food, pharmaceuticals and building materials. Starches are widely use in various applications due to their thickening, gelling, adhesive and film-forming abilities [30].

In this work, corn starch has been used as a pore former in preparation of ball clay membrane using compaction method. The purpose of this study is to determine the effect of starch

addition at different weight percentage on the porosity and mechanical properties of the ceramic membrane.

## 2.0 EXPERIMENTAL

### 2.1 Materials

The material used in this work is Sayong ball clay from Perak, Malaysia. Table 1 shows the material composition of the ball clay characterized by XRF (Philip PW2400). The main components of ball clay are  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ .

**Table 1** Chemical composition of Sayong ball clay

Component	Wt%
$\text{SiO}_2$	60.7
$\text{Al}_2\text{O}_3$	32.2
$\text{K}_2\text{O}$	3.09
$\text{Fe}_2\text{O}_3$	2.9
$\text{TiO}_2$	0.424
$\text{MgO}$	0.216
$\text{CaO}$	0.211
$\text{Na}_2\text{O}$	0.181
$\text{Ce}_2\text{O}_3$	0.0449

### 2.2 Sample Preparation

The ball clay powder was sieved in a 150  $\mu\text{m}$  mesh standard screen to get uniform particle size. Corn starch (Glow-San Sdn. Bhd.) has been added to clay as a pore former. Ball clay and corn starch were mixed at different weight percentage as shown in Table 2. The mixture was milled using stirrer machine (IKA RW 20) with an addition of ethanol as a medium for 1 hour at 1300 rpm. The slurry was then dried in an oven for 24 hours. Dry powder was sieve again to get homogeneous powder particles. An essential of mixture powder with addition of glycerol which act as a binder was pressed with stainless steel mold under pressure of 60 MPa with holding time 10 minutes using universal testing machine (Instron 600 DX) to form a 80 mm x 30 mm x 6.5 mm (length x width x height) rectangular bar. Then, the green bodies were sintered at 1200°C for 2 hours with a heating and cooling rate of 10°C/min.

**Table 2** Weight percentage of corn starch and ball clay content in fabrication of membrane

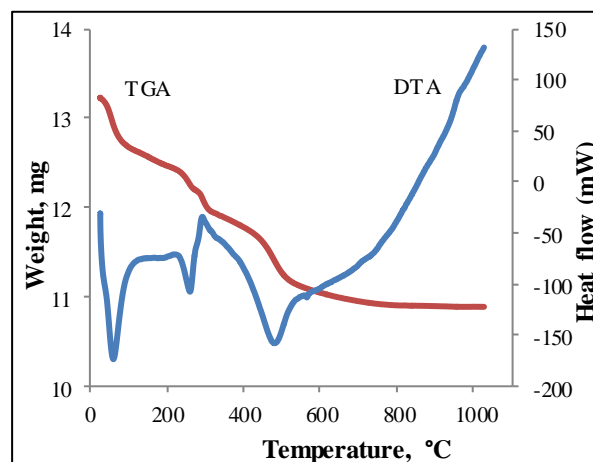
Sample	Corn starch content (wt%)	Ball clay content (wt%)
S1	0	100
S2	5	95
S3	10	90
S4	15	85
S5	20	80
S6	25	75
S7	30	70
S8	35	65

### 2.3 Characterizations

Thermogravimetric (TGA) and differential thermal (DTA) analyses of raw powders were performed using a Diamond TG.DTA under nitrogen gas atmosphere at heating rate of 10°C/min from 50 to 1000°C. Bulk density and apparent porosity of membrane were measured according to Archimedes' principle with an immersion medium of distilled water, following the ASTM C373-88 standard. Shrinkage of the membrane was calculated by the thickness measurements before and after the sintering process. The surface morphology of the sintered clay membrane at different corn starch weight percentage was analyzed using Field Emission Scanning Electron Microscopy (FESEM: Zeiss Supra 35VP). Three-point bending strength measurement were done on the rectangular bars (80 mm x 30 mm x 6.5 mm) using Universal testing machine (Instron 5982) according to ASTM C-1161-02c. A span of 40 mm and crosshead speed of 0.5 mm/min were used. Five specimens were used to obtain average values.

### 3.0 RESULTS AND DISCUSSION

Figure 1 shows the thermal analysis of raw ball clay mixed with corn starch and glycerol. Thermal analysis of ball clay was carried out to identify the minimum sintering temperature to obtain a stable sintered body. The weight reduction occurs at two stages. The first one begins at around 155°C and finishes at 290°C. The chemical combination water of clay is removed and the complete breakdown of corn starch occurs at this stage [28]. Second stage occurs around 370°C to 530°C. At this stage, the dehydroxylation of ball clay and removal of remain corn starch occur. The corn starch was completely degraded at temperature < 700°C. Based on this result, a sintering profile of the ball clay membrane has been determined as Figure 2. Green samples were heated to 200°C and held for 10 minutes to remove the water and glycerol. Then, the temperature rose up to 500°C and maintained for 30 minutes to remove the corn starch completely. Thereafter, the samples were sintered at 1200°C for 120 minutes and followed by furnace cooling.



**Figure 1** Thermal analysis curves of raw ball clay powder and corn starch mixture

Effect of percentage of corn starch content on shrinkage and density of ceramic membrane was shown in Figure 3. The shrinkage value increased from 4.5% to 22.76% for corn starch

content of 0 wt% to 35 wt%. The shrinkage might be occurred due to the losses of moisture and burn out of the corn starch during sintering process. For 0 wt% corn starch content, the shrinkage occurs mainly due the losses of moisture. However, the density of the membrane is decreased as the corn starch content is increase. The density value is in the range of 2.21 g/cm<sup>3</sup> to 1.71 g/cm<sup>3</sup>. The decrease in density value is caused by the formation of pore by corn starch removing. A similar finding was also obtained by other authors using different starch content by various preparation process of porous structure [26-28, 31].

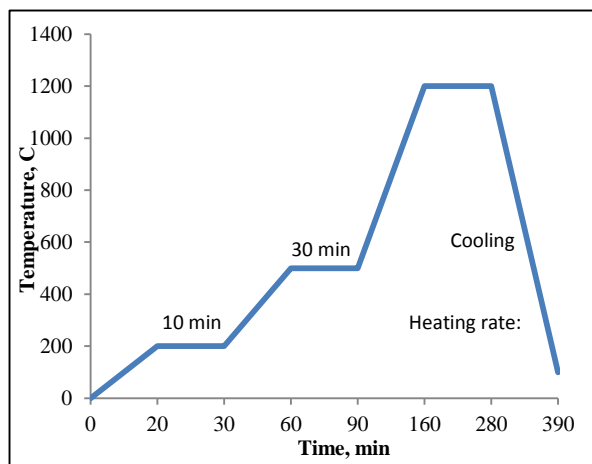


Figure 2 Sintering profile for ball clay membrane

From the changes of apparent porosity as a function of corn starch content in Figure 4, it can be seen that the apparent porosity increased from 9.14% to 31.83% as the added amount of corn starch increased from 0 wt% to 35 wt%. This result is in good agreement with Li *et al.* [26] and Yang *et al.* [31]. The optimum apparent porosity can be observed at 20 wt% of corn starch, which is about 25% porosity. As the corn starch burn out during sintering process, it will leave a pore in the sintered body which contributed to apparent porosity. At 0 wt% corn starch content, the pore may form from the contact between powder particles during sintering.

Figure 5 shows surface morphology of the sintered ceramic membrane for 5 wt%, 15 wt%, 25 wt% and 35 wt% of corn starch. More pores can be observed at higher corn starch content, which leads to more porous structure. The connectivity between pores higher with increasing corn starch content, as can be seen in Figure 5(d) (35 wt% corn starch content). The formation of the pores may be the reason for lower density of ball clay membrane at higher corn starch content. Overall, the pore size increased as the corn starch content is increased. An average of pore size measured from the FESEM microstructure are 5.08  $\mu\text{m}$ , 6.97  $\mu\text{m}$ , 7.34  $\mu\text{m}$  and 8.31  $\mu\text{m}$  for 5 wt%, 15 wt%, 25 wt% and 35 wt% of corn starch respectively.

Flexural strength of ball clay membrane is given in Figure 6. The greatest flexural strength was found to be associated with the ball clay membrane without corn starch addition, which is about 21 MPa. The study conducted by Lee *et al.* [32] shows that the flexural strength of the fired clay ceramics at 1200°C is 27 MPa, which is similar with strength of sintered ball clay. Nevertheless, the flexural strength of the ball clay membrane reduced when the corn starch content is higher. Chandradass *et al.* [33] has also reported the similar trends of flexural strength during prepare an alumina ceramic using starch consolidation

method. Strength of the ceramic membrane depends on the presence of the defects, such as pores, which act as stress concentration [33]. The presence of open and closed pores as shown in Figure 5 may reduce the flexural strength of the membrane. The flexural strength is proportional with the apparent porosity of the ceramic membrane.

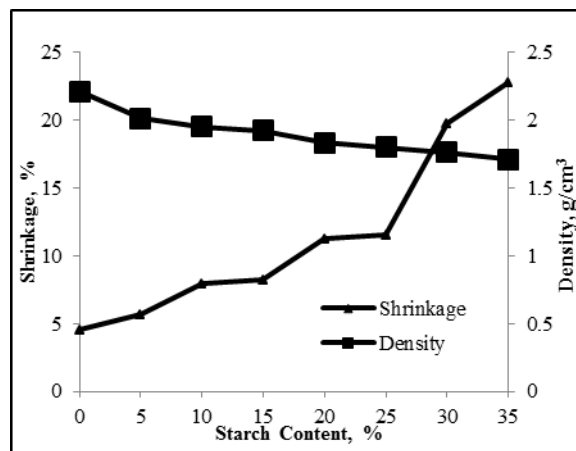


Figure 3 Effect of starch content on shrinkage and density of Sayong ball clay membrane

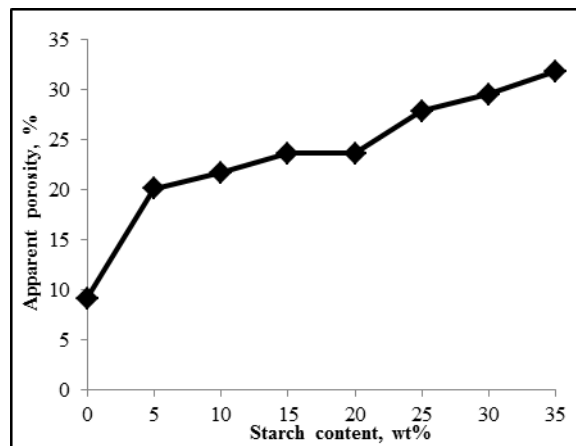


Figure 4 Apparent porosity of ball clay membrane at different corn starch content

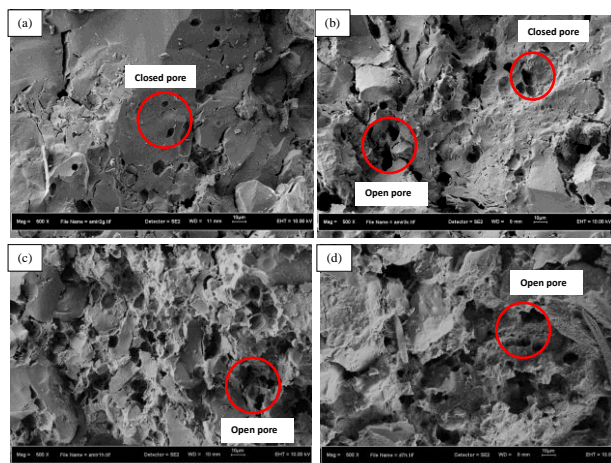
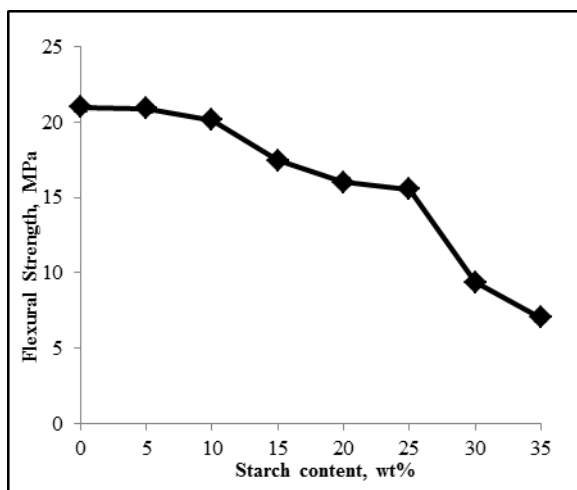


Figure 5 FESEM image of the cross section of ball clay membranes with (a) 5 wt%; (b) 15 wt%; (c) 25 wt%; (d) 35 wt% of corn starch content



**Figure 6** Influence of corn starch content on flexural strength of ceramic membrane

#### 4.0 CONCLUSION

A ball clay membrane has been prepared by simple compaction method with addition of corn starch as a pore former. The different weight percentage of corn starch did affect the shrinkage, apparent porosity and flexural strength of the membrane. The shrinkage increased up to 23% at 35 wt% corn starch while the apparent porosity increased to 32%. The apparent porosity achieved optimum value at 20 wt% corn starch. In contrary, the flexural strength of ball clay membrane reduced as the corn starch content increased. The optimum flexural strength is obtained at 25 wt% corn starch because above this value, there is a sudden change in the strength value. From the result found, the appropriate amount of corn starch content is 20-25 wt%. Excessive starch content would lead to the collapse of the porous structure.

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