A COMPARATIVE STUDY OF POROUS SUPPORT FROM SAYONG AND KANKARA CLAY

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A porous supports were fabricated from Sayong ball clay and Kankara clay for wastewater treatment application using simple compaction method. The influence of sintering temperature (900-1200 °C) and starch addition (5-30 wt%) on the physical properties and flexural strength of the porous support were studied. Thermo-gravimetric analysis, particle size distribution, microstructure, phase, porosimetry analysis and strength analysis were studied to characterize the porous supports. The apparent porosity and pore diameter of Kankara porous support (48-55%; 6.62nm) was found to be higher than that of Sayong porous support (0.07-40%; 5.11nm). In contrast, the bulk density of Sayong porous support (1.15-1.93g/cm^3) was higher than that of Kankara porous support (1.08-1.25g/cm^3). However, the flexural strength of Kankara porous support (34-3MPa) shows sharp decrease compared with Sayong porous support (21-9MPa). This shows that Sayong porous support has better physical properties and flexural strength compared with Kankara porous support. Starch has been a good pore former in fabrication of the ceramic membrane. Sintering temperature and starch content have strong influence on the physical and flexural strength of the porous support. Therefore, the properties of the porous support can be varied by controlling the sintering temperature and starch content.

Keywords: *Porous support, compaction, sintering temperature*, *flexural strength.*

Introduction

Ceramic materials offer some excellent advantages such as high chemical and thermal stability, separation efficiency, and high-pressure resistance compared to the polymeric membrane counterparts in many industrials processes such as membrane for wastewater treatment (Sarkar et al., 2012). The properties of clay mineral as membrane material in terms of mechanical, chemical and thermal properties can be compared with those of engineering ceramics and superior than polymer. These materials are cheap to process in terms of materials cost and sintering temperature. Due to the high cost of engineering ceramics, clay minerals have been used to produce porous materials in novel areas such as membrane, gas filters, molten metal filters and gas sensors. Clay minerals can be a source of ceramic materials such as mullite, cristobalite and nephiline syenite ceramics (Castelein et al., 2001; Jana et al., 2010). Clays are normally used to refractories and to increase the refractoriness of ceramic bodies.

These natural deposits can be used directly without any upgrade in the quality. Clay-based porous support is still under the development stage. Clay-based ceramic membranes from Morocco and Tunisia were reported for the treatment of solution containing dyes, salts , tannery, textile, electronic cuttlefish effluents from industries (Saffaj et al., 2006; Khemakhem et al., 2009; Majouli et al., 2011). In addition, the potential use of these membranes for microfiltration and ultrafiltration applications in the chemistry, food, and biotechnology industry have been reported (Jana et al., 2010; Emani et al.,2013a; Emani et al., 2013b).

Characterization in terms of thermal and physical properties of membranes depicts the suitability of particular membrane for a specific application. For optimum

separation, thermal, chemical and physical characteristics play vital role in the formulation of a porous support for specific application. The objective of this research is to characterize Sayong ball clay and Kankara clay for porous support fabrication in wastewater treatment. In addition, physical parameters (such as density and porosity), microstructure and flexural strength were investigated.

Experimental

The raw materials used in this work are Sayong ball clay from Perak, Malaysia and Kankara clay from local miners in Katsina state, Nigeria. Table 1 shows the material composition for both types of clay characterized by XRF (Philip PW2400). The SiO_2 content for both clay are almost similar. However, Kankara have high Al_2O_3 content than Sayong ball clay. Starch (Glow-San Sdn. Bhd.) has been added as a pore former. Experiments were done using the as-received starch, without any subsequent processing. The average particle size of clay used in this work is in a range of 50 -75 μm (the particle size distribution the raw materials was carried out by particle sizing machine Mastersizer 2000, Malvern Instruments). Thermo gravimetric (TGA) and differential thermal (DTA) analysis of raw powders were performed using a Diamond TG.DTA under nitrogen gas atmosphere at heating rate of 10 °C/min from 50-1000 ◦C.

Clay and 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 circular disk shaped green body having 30 mm diameter and 2.5 mm thickness. Then, the green bodies were sintered at the desired temperature for 2 hours with a heating and cooling rate of 10 °C/ min.

The XRD analysis of the powder and sintered samples was performed with Bruker D8 Advance machine. The microstructures were observed using Field Emission Scanning Electron Microscopy (FESEM: Zeiss Supra 35VP). Average pore size and pore size distribution (PSD) were analyzed by nitrogen absorption, Micromeritics ASAP 2020. The density and porosity of the sintered samples were measured according to Archimedes' principle using distilled water, following the ASTM C37-88 standard. The flexural strength of the sintered samples were tested with a three-point bending method on 80 mm x 30 mm x 2.5 mm rectangular bars using universal testing machine (Instron 5982). A span of 40 mm and crosshead speed of 0.5 mm/min was used, following the ASTM C-1161-02c standard. Five specimens were used to obtain average values.

Result and Discussion

Table 1 shows the chemical composition for both clays from XRF analysis. Sayong ball clay and Kankara clay consist mainly of SiO_2 and Al_2O_3. The SiO_2 content for both clays are almost similar. However, Kankara clay has higher Al_2O_3 content (42.9%) than Sayong ball clay (23.78%). On the other hand, Sayong ball clay has large amount of alkaline oxides (K_2O and Na_2O), which corresponds to about 3.41% and Kankara clay only have 0.3 % of K_2O. The presence of earth-alkaline elements (MgO and CaO) indicates that both clays are rich in carbonates (Baccour et al., 2009).

Table 3.1: Chemical composition of Sayong and Kankara clay

Component	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	Na_2O	CaO	TiO_2	Others
Sayong clay (wt %)	51.28	23.78	0.46	1.34	1.48	2.07	0.81	0.36	18.42
Kankara clay (wt %)	55.4	42.9	0.3	0.3	0.04	-	0.06	0.05	0.02

The thermo-gravimetric analysis was carried out to identify the minimum sintering temperature to obtain a stable sintered body and to establish a heating schedule. Fig. 1(a) shows the thermal analysis of raw Sayong ball clay mixed with corn starch and glycerol. 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 (Alves et al., 1998). Second stage occurs around 370 °C to 530 °C. At this stage, the dehydroxylation of Sayong ball clay and removal of remain corn starch occur. The corn starch was completely degraded at temperature < 700 °C.

On the other hand, Kankara clay has various endothermic and exothermic peaks during heating to 1200 °C, as shown in Fig. 1(b). The first endothermic peak occurs at a temperature within 70-100 °C; this peak is due to the removal of hygroscopic water present in the clay. The exothermic peak at 480-500 °C is due to the dehydroxylation of kaolin and conversion of kaolin to metakaolin. The exothermic peaks at 980-1000 °C are due to conversions of metakaolin to spinel and amorphous silica, while at 1100 °C, spinel and amorphous silica converted to mullite; the crystallization, densification and growth of mullite from spinel and amorphous silica proceed at higher temperature (above 1100 °C) through viscous flow sintering. The TGA analysis shows a various decreases in mass due to the glycerol burn out, transformation of kaolin to metakaolin, spinel formation and finally mullite.

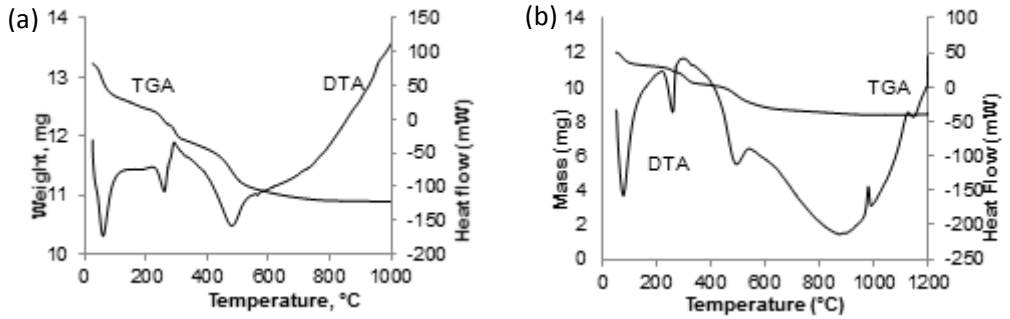

Figure 1: Thermo-gravimetric analysis of (a) Sayong ball clay and (b) Kankara clay.

Based on the XRD result (Fig. 2), the main phase present in raw Sayong ball clay are quartz, kaolinite and muscovite. After sintering, the phases remained in the support sintered at 900 °C and 1000 °C (Fig. 3(a)). At 1100 °C, the kaolinite starts to

disappeared. Finally, only quartz remained at 1200 °C sintered samples. The peaks correspond to the quartz are not changed in the entire XRD pattern. It indicates that the quartz does not affected by the sintering temperature. Therefore, it could be pointed out that there is no significant weight loss for quartz as depicted by the TGA curve (Fig. 1(a)). In contrast, Kankara clay contains kaolinite as the major constituent phase, with some trace of illite and quartz (Fig. 2). The relative low intensity peak of the quartz peak in the kaolinitic clay indicates insignificance presence of free silica; free silica in kaolinitic clays promote the formation of cristobalite after sintering at temperature above 1100 °C. Clays with low free silica promotes the formation of mullite ceramic after sintering above 1100 °C. After sintering at 900 °C, muscovite phase was detected (Fig. 3(b)). At 1000 °C and 1100 °C, the intensity of muscovite peak diminished. Further increased the sintering temperature to 1200 °C shows a formation of mullite phase. At lower sintering temperature (900-1100 °C), the formation of muscovite may occur due to the relative high K_2O content. The kaolinite phase disappeared due to the conversion of kaolinite to metakaolinite.

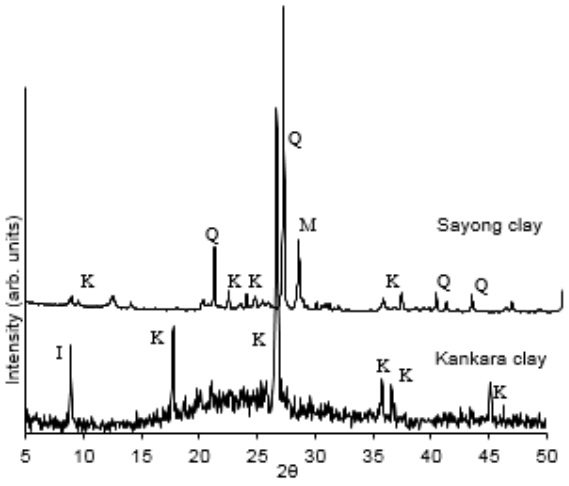

Figure 2: XRD of raw Sayong ball clay and Kankara clay powders

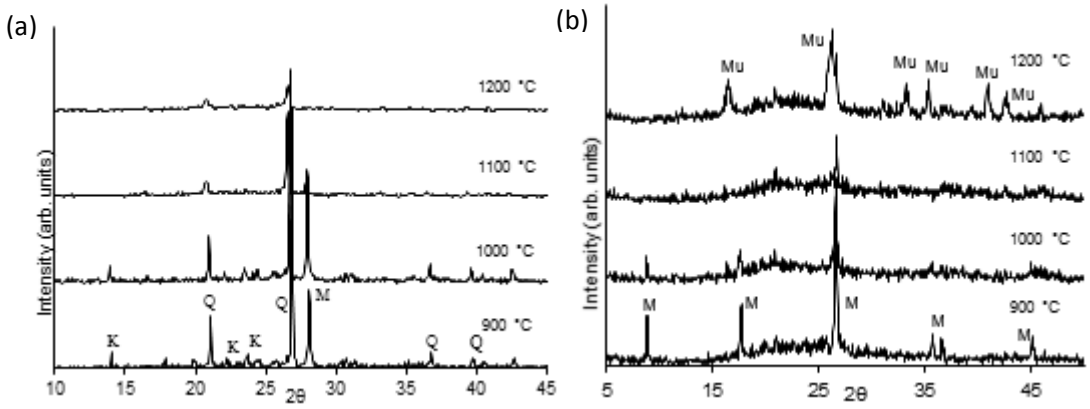

Figure 3: XRD pattern of the sintered samples at different temperatures. (a) Sayong clay; (b) Kankara clay. ((K) Kaolinite, (Q) Quartz, (M) Muscovite, (Mu) Mullite).

The raw materials were characterized for particle size distribution to get an idea of the particle size and the uniformity of the particles. The porosity and pore size

depends on the particle size of the raw materials. Fig. 4 shows the particle size distribution for Sayong ball clay and Kankara clay. Majority of the particles are distribute in the ranges between 8 and 15 μm. 90% of the particles having a diameter below 20 μm. The average particle size of the Sayong ball clay and Kankara clay powder are found to be 14.54 μm and 12.8 μm, respectively.

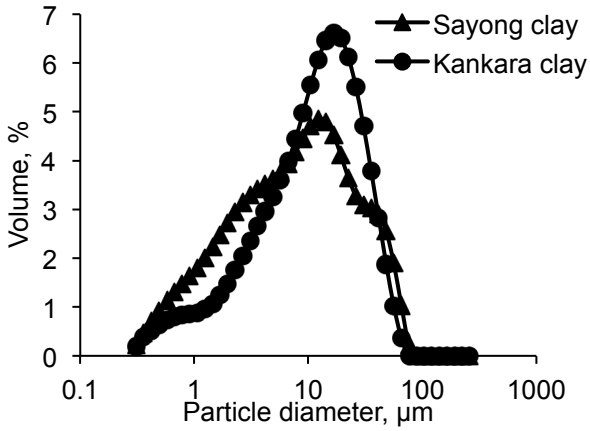

Figure 4: Particle size distribution of Sayong and Kankara clay.

Fig. 5 shows the SEM images of Sayong porous support and Kankara porous support at different sintering temperature. For Sayong porous support, at lower sintering temperature (900 °C) more rough surface and dot-like pores were observed (Fig. 5(a)). The porous support shows a highly porous structure and did not have full solid-state sintering process because there is still individual clay particles present (Johari et al., 2010). At higher sintering temperature (1200 °C), more consolidated structure was formed due to the densification of the porous support (Fig. 5 (b)). Furthermore, finer structure was detected, showing a well-bonded particles rather than detached particles. The neighboring pores join to forms larger pores (Nandi et al., 2008; Baccour et al., 2009). Kankara porous support shows a different behavior than Sayong porous support. At 900 °C, a consolidated structure was detected, with large pores as shown in Fig. 5 (c). When the sintering temperature increased to 1200 °C, more rough surface were shown and very fine pores was found. According to Bharma et al. (2014), the decreased in pore sizes with increasing sintering temperature might be due to the rearrangement of small and regular primary particles.

The effect of starch content on the microstructure of Sayong porous support and Kankara porous support were shown in Fig. 6. For Sayong porous support, finer pores can be observed at 5% starch, but the numbers of pores is small. When 30% of starch was added, the pores became larger and more pores were detected, which leads to more porous structure. Despite the slight larger pores after adding starch, the porosity is expected to increase with adding starch. However, Kankara porous support shows interconnection of pores at higher starch content (Fig. 6(d)). The increase in starch content makes single pores to coalesce and connect to one another after sintering.

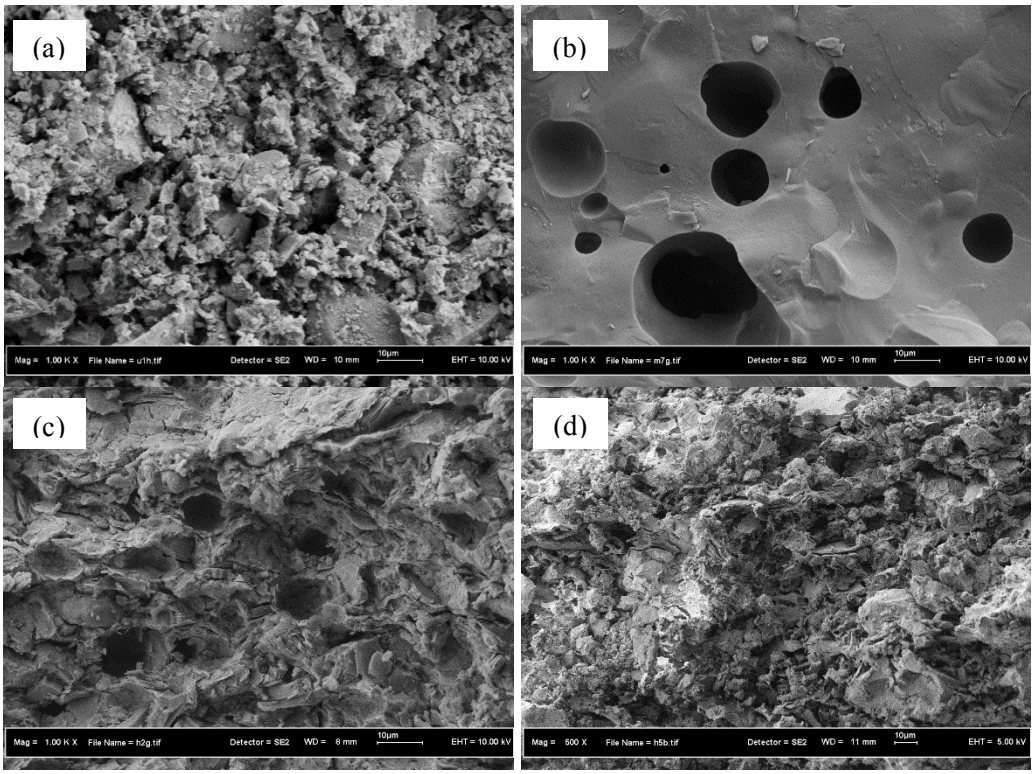

Figure 5: Effect of sintering temperature on the microstructure of Sayong porous support ((a) 900 °C; (b) 1200 °C) and Kankara porous support ((c) 900 °C; (d) 1200 °C for 30% starch

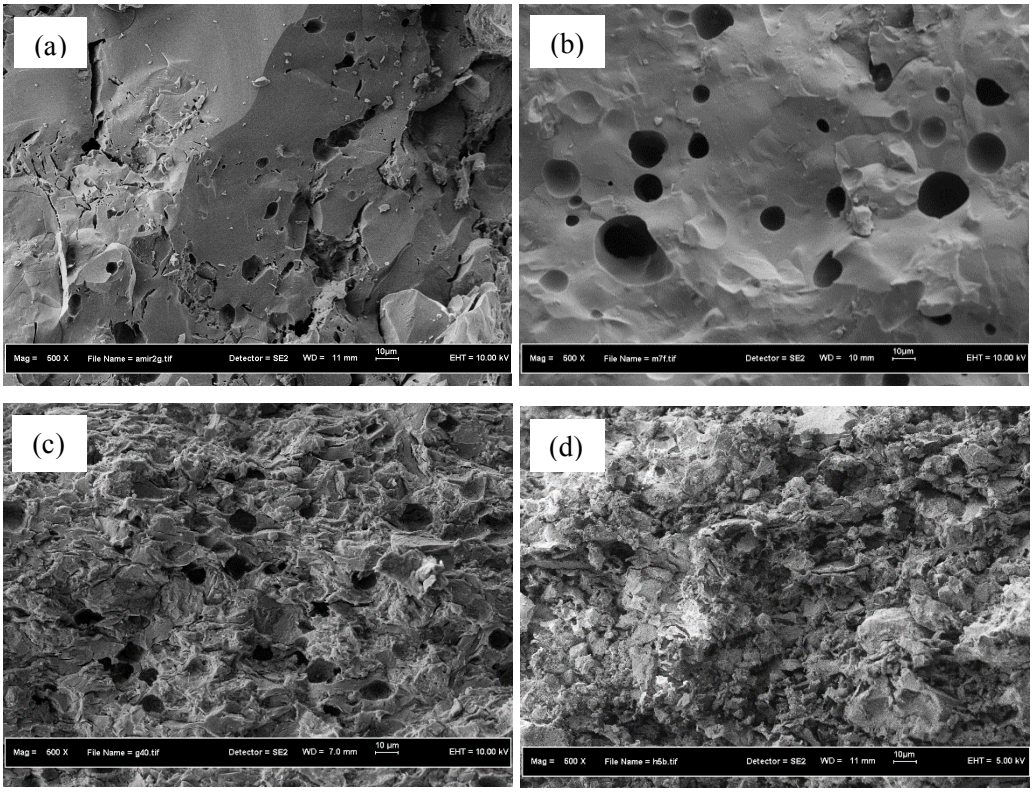

Figure 6: Effect of starch content on the microstructure of Sayong porous support ((a) 5%; (b) 30%) and Kankara porous support ((c) 5%; (d) 30%). Sintered at 1200 °C.

The density and porosity of the porous supports are strongly affected by the sintering temperature. The variation of density and porosity with sintering temperature are shown in Fig. 7(a) and 7(b), respectively. When the temperature increased, the density is increased and the porosity is decreased. The glassy viscous phase form during the sintering penetrates into the pores, closing them and isolating the neighboring pores, causing a densification process, which lead to low porosity. This result is in line with previous observations in the literature by Ngun et al. (2011). Kankara porous support have lower density and higher porosity than Sayong porous support. In addition, the range of the density increased and porosity reduced is small, which are from 1.08 to 1.25 g/cm^3 and 55 to 48 %, respectively. In contrast, the density and porosity of Sayong porous support increased and decreased in a large range, from 1.51 to 1.93 g/cm^3 and 40 to 0.07 %, respectively. The densification of clay especially kaolin began at a temperature of 1150 °C. High kaolin content in Kankara clay may retard the densification process at temperature low than 1150 °C.

Fig. 8 (a) shows the relationship of the density of porous supports versus percentage of starch content. Both porous supports show a continuous density reduction as the starch content is increased. When more starch was added, the possibility for the pore to form is higher as a result of starch burn out during the sintering process. This will cause a higher porosity at high starch content (Fig. 8(b)). The connectivity between pores increased with the increasing of starch content. Thus, lower the density and increase the porosity (Li et. al., 2013). However, Kankara porous supports have lower density and higher porosity than Sayong porous support. From the microstructure analysis (Fig. 6), it shows that Kankara porous supports have more pores than Sayong porous supports, at both low and high starch content. In addition, the high content of flux materials (K_2O, Na_2O and Fe_2O_3) in Sayong clay (Table 1) lead to the formation of a glassy viscous phase and thus facilitates the densification process (Milheiro et al., 2005).

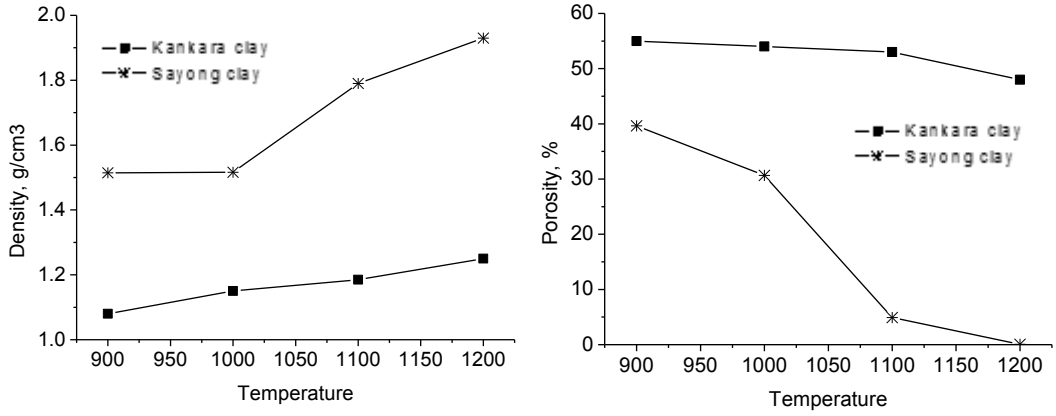

Figure 7: (a) Density and (b) porosity of the porous support at different sintering temperature.

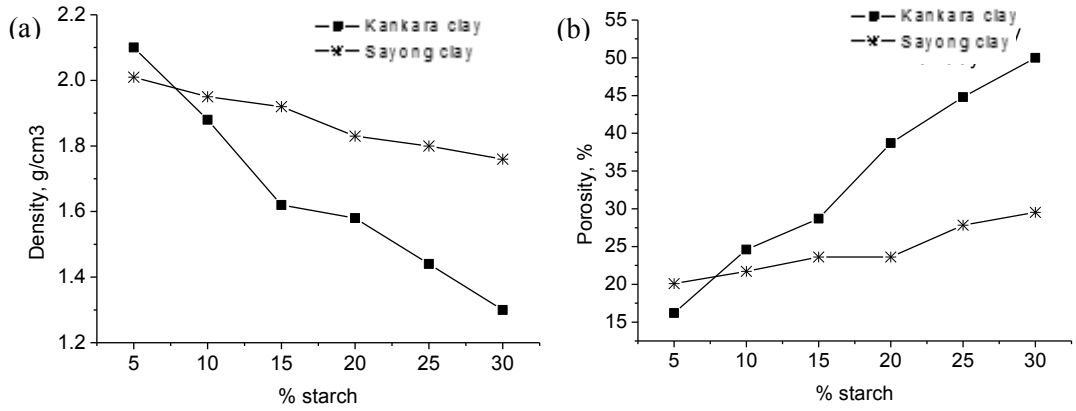

Figure 8: (a) Density and (b) porosity of the porous support at different starch content.

Fig. 9 shows the effect of starch content on the strength of Kankara and Sayong clay. The strength of Kankara and Sayong porous support decreased from 34 to 3 MPa and 21 to 9 MPa with increasing starch content from 5 to 30%, respectively. The strength of Kankara porous support reduced more steeply than Sayong porous support. Overall, Sayong porous support have higher strength than Kankara porous support, except at 5% starch addition. The reduction of strength closely related to the high porosity at high starch content. Pore act as the stress concentrator that reduce the strength of porous supports. Porosity have a deleterious influence on the strength since the pores present in the porous support body will reduce the cross-sectional area across which the load is applied (Callister, 1997). This result is in good agreement with the results report elsewhere (Li et al, 2013; Yang et al., 2008).

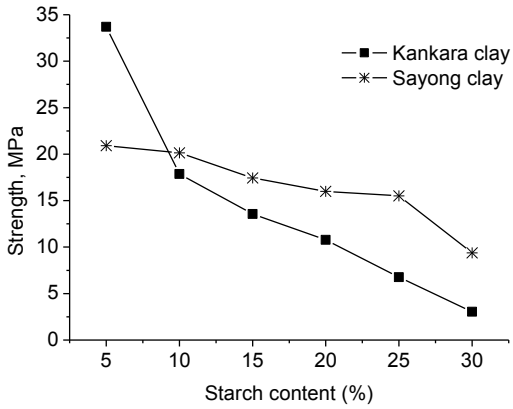

Figure 9: Effect of starch content on strength of the porous supports.

The pore size distribution measured from the nitrogen absorption is shown in Fig. 10. Both porous supports exhibit multimodal pore size distribution since it represent more than two distinct or overlapping peaks. The wide distribution of the pore size may result from non-uniform pore shape. The average pore diameter of Sayong porous support and Kankara porous support derived from BJH adsorption model are 5.11 nm and 6.62 nm, respectively. Kankara porous support has larger pore size than Sayong porous support. This may cause the higher porosity and lower strength of Kankara Porous support compared to Sayong porous support at 30% starch content.

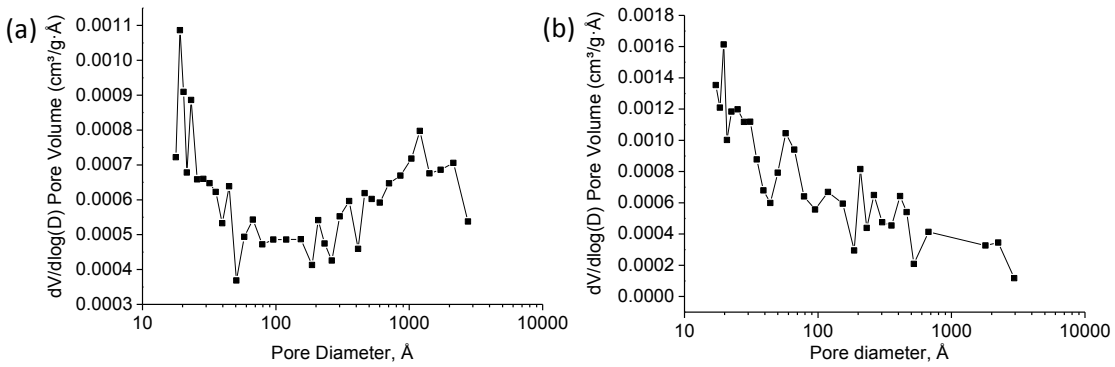

Figure 10: Pore size distribution of (a) Sayong porous support and (b) Kankara porous support with 30% starch content.

Conclusion

Sayong ball clay and Kankara clay are the valuable source of ceramic for the production of porous clay-based support. For both clays, the apparent porosity increased with increase in starch content, while the density is decreased. On the other hand, the porosity is decreased while density is increased with increasing sintering temperature for both type of porous supports. The apparent porosity and pore diameter of Kankara porous support (48-55 %; 6.62 nm) was found to be higher than that of Sayong porous support (0.07-40 %; 5.11 nm). In contrast, the bulk density of Sayong porous support (1.15-1.93 g/cm^3) was higher than that of Kankara porous support (1.08-1.25 g/cm^3). However, the flexural strength of Kankara porous support (34-3 MPa) shows sharp decreased compare to Sayong porous support (21-9 MPa).The morphology of the porous support shows the increased in porosity with increasing starch content. The BJH isotherm shows Kankara porous support has larger pore diameter compare to the Sayong porous support, due to the high apparent porosity of the Kankara porous support. Sintering temperature plays a vital role in determining the properties of porous supports from clay minerals.

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