

Flexural Strength and Crack Propagation of Porous Clay- Precipitated Calcium Carbonates

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Abstract

Porous clay-precipitated calcium carbonates were prepared via polymeric sponge replication method using precipitated calcium carbonates (PCC) and red clay as raw materials. Different compositions of precipitated calcium carbonates (PCC) which is 10 wt.% and 15 wt.% with 24 hours and 48 hours milling time were sintered at 1250°C for 2 hours respectively which influenced the flexural strength and morphology of the porous ceramic. The highest flexural strength (1.843 MPa) were obtained by 10 wt.% [CaCO₃]PCC milled at 24 hours related to the lowest percentage of porosity (81.00%). Mineralogical characterization of porous ceramic were determined via X-ray diffraction (XRD) shows the presence of crystalline phases such as anorthite (2CaAl₂Si₂O₈), gehlenite (Ca₂Al₂SiO₇) and esseneite (CaFeAlSiO₆) after sintering process. The morphological analysis via stereomicroscope shows that the porosity and struts were found due to presence of precipitated calcium carbonates that act as pore forming agent. The colour of porous ceramic between 10 wt.% [CaCO₃]PCC and 15 wt.% [CaCO₃]PCC shows significant difference due to iron oxide contained in the red clay which contributes to the colour of the samples. Crack propagates in the intergranular type of fracture mode due to resulted porous ceramic is a brittle material.

Keywords: Flexural strength; crack propagation; precipitated calcium carbonates; clay; porous ceramic

1. Introduction

Porous ceramic composites are widely used in various engineering application such as insulation for materials, heat exchangers, gas adsorbents, catalysts support and filtration. It were found out that in order to control the pores of porous ceramic composites were by the way they are formed and adjusting the particle size distribution of ceramic raw materials [1]. The various processing routes in order to produce porous ceramic composites includes replication method, sacrificial template, direct forming and casting method. Unique properties of porous ceramic such as porosity, density, strength, surface area and thermal shock resistance related to the nature and structures of the material being used itself [2]. Due to its low cost fabrication, the formation of porous ceramic is widely used through polymeric sponge replication method [3]. The sponge is dipped into ceramic slurry, dried and finally sintered at high temperature [4].

Clay is a well-known type of earthy raw materials that been formed due to erosion and weathering process. It is a type of low cost natural resources that is used as CO₂ adsorbents [5]. The size of clay particles is very small which is about 2µm with various degrees of crystal perfection [6]. Since long time ago, due to its physical and mechanical properties, clay had been great attention in ceramics fabrication [7]. The addition of clay into porcelain based-ceramic composition will generate properties such as good compressive strength and bending strength [8]. Firing of clay greatly contribute to the requirements of ceramics. Various elements contained in the clay is expressed with

respect to their oxides. Limestone is a type of sedimentary rock that contains high percentage of calcium carbonates (CaCO_3). Due to its various physical and mechanical properties, PCC is mainly used in different applications such as based for filler in paper making, rubber, paints and plastics. The objective of this research is to study the flexural strength and crack propagation of porous clay-precipitated calcium carbonates.

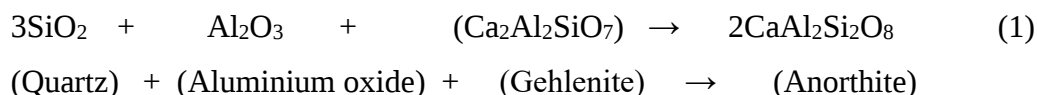
2. Experimental Procedure

The method of this project starts off with preparation of samples. In order to produce ceramic foams, replication method will be used by using polymeric sponge as a template material. Controlled amount of precipitated calcium carbonates (PCC), red clay and distilled water were mixed to form a mixture by using roll mill machine for 24 hours and 48 hours. The polymeric sponge is then immersed into the slurries and pressed the polymeric sponge in order to remove excess slurries. The foam is dried for at 80°C for 24 hours in an oven and finally sintered in a furnace at a temperature of 1250°C for 2 hours. The foam was cut into a rectangular shape with dimension of 30 mm (length) x 8 mm (width) x 6 mm (thickness) after sintering. In order to determine the mineralogical characterization of ceramic foam produced, X-ray diffraction (Bruker D2 Phaser model) is used. The density and porosity of ceramic foam is determined by using Archimedes method using distilled water as liquid media. The mechanical properties of ceramic foam were carried out by conducting flexural test using Universal Testing Machine (Instron 5569 model) in accordance to ASTM C-1161-13 (four-point bending) at a cross speed of 1mm/min. Finally, the morphological analysis of ceramic foam crack propagation produced from flexural test is analysed by using stereomicroscope (SZ61 Olympus model).

3. Results and Discussion

Mineralogical Characterization

Figure 1 shows the mineralogical characterization of porous clay-precipitated calcium carbonates after sintering at 10 wt.% $[\text{CaCO}_3]\text{PCC}$ and 15 wt.% $[\text{CaCO}_3]\text{PCC}$ milled at 24 hours and 48 hours. Sintering of clay based product may causing processes such as formation of new crystalline phases and decomposition. The highest peak of the pattern for all porous ceramic composition is anorthite. After samples were sintered, there are also new crystalline phases such as gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and esseneite (CaFeAlSiO_6) formed. Gehlenite is a non stable intermediate phase formed through metakaolinite and calcium. As for illite phase, it is not noticable due to this mineral phase break down at higher temperature during sintering. It is also found out that there is no mullite phase after sintering of of porous clay-precipitated calcium carbonates which may affected the flexural strength of the porous ceramic. Anorthite is formed from gehlenite due to combination of anorthite with silica, aluminium oxide from the structure break of metakaolinite and fine quartz shown in Eq. 1.



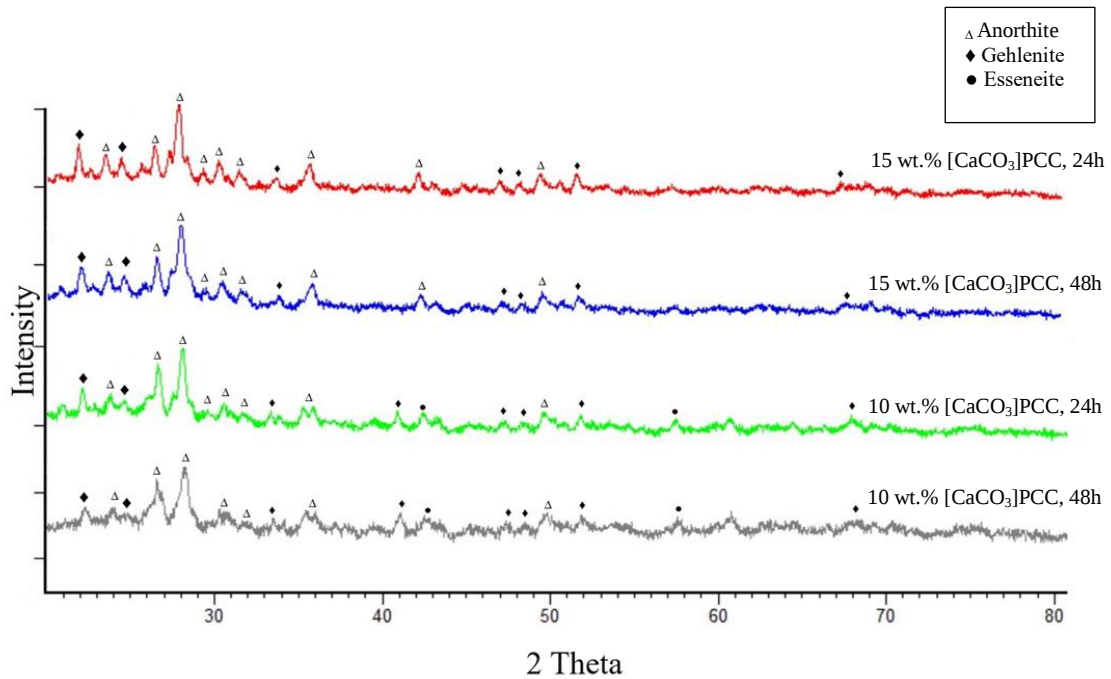


Fig. 1. Mineralogical characterization of porous clay-precipitated calcium carbonates after sintering for 10 wt.% [CaCO₃]PCC and 15 wt.% [CaCO₃]PCC.

Density and Porosity Analysis

Both density and porosity of porous clay-precipitated calcium carbonates were determined by using Archimedes principle method. Figure 2(a) shows the density analysis of porous clay-precipitated calcium carbonates. As the samples with different composition of precipitated calcium carbonates (PCC) were milled at longer time, their density tends to decreased. This is due to pores elimination between agglomerates and aggregates. During sintering, a fast grain growth occurred causing the density of the samples to be reduced too. Longer milling time causing the particles of the slurry to be smaller compared to shorter time. According to Rahiman et. al [9] reported that larger crystals in slurry milled at longer time have higher tendency to be impacted and reduced in smaller size thus causing the density to be reduced. Thus, it can be said that the particle size distribution of the slurry great affected the density of the porous ceramic structure. However, a research made by Kłosek-Wawrzyn et. al [10] reported that density of the porous ceramic tend to decrease due to calcite is added together with the clay.

An increasing trend of porosity analysis of porous clay-precipitated calcium carbonates is shown in Figure 2(b). In can be seen that as more addition of precipitated calcium carbonates (PCC) and longer milling time, the porosity of the porous ceramic increased ranging from 81.00% to 91.40%. The highest porosity achieved by 15 wt.% [CaCO₃]PCC causing it to generate pores to the structure of the porous ceramic as compared to 10 wt.% [CaCO₃]PCC.

During sintering of porous ceramic, the calcium carbonates transformed into calcium oxide and the release of carbon dioxide causing vacant leads to formation of pores. This result is also supported by Kaur, Bulasara, & Gupta [11] proved that calcium carbonates separated into carbon dioxide and calcium oxide at a high sintering temperature. Thus, formation of pores were developed due to release of carbon dioxide.

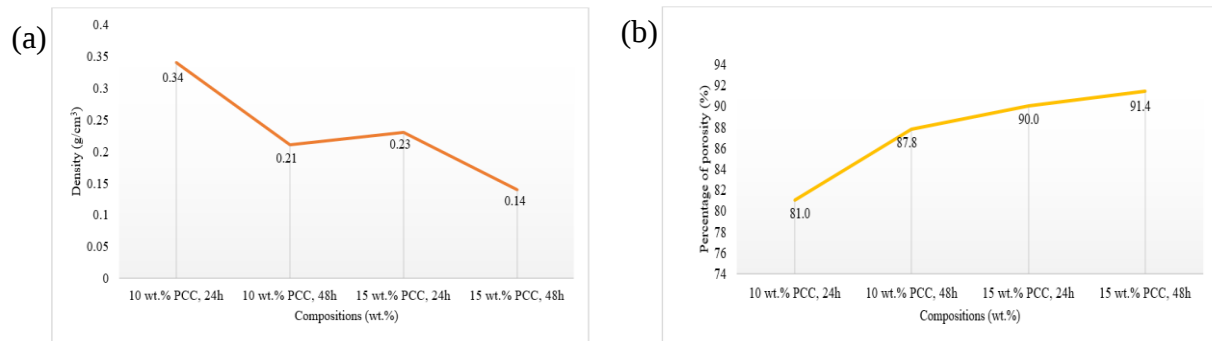


Fig. 2. (a) Density analysis of porous clay-precipitated calcium carbonates; (b) Porosity analysis of porous clay-precipitated calcium carbonates.

Flexural Strength

The flexural strength of porous ceramic may be controlled by factors such as density, porosity and phase presented after sintering. The most influential factor that control the strength of porous ceramic is the porosity due to the fact that the pores produced were intergranular thus affected the flexural strength. In addition, porous ceramic structure, does not undergo plastic deformation due to it is a type of brittle material.

Porous ceramic sample with the lowest porosity percentage has the highest flexural strength. This is due to the addition of precipitated calcium carbonates into this sample is much smaller thus generation of pores is lower. Addition of calcite greatly affected the porosity of porous structure and its strength [12].

The lowest average flexural strength is 15 wt.% $[\text{CaCO}_3]\text{PCC}$ milled at 48 hours with the highest porosity as shown in Figure 3. Kitouni & Harabi, [12] reported that two ways porosity affected the strength of porous ceramic materials was porosity reduced the load-bearing area since the mechanical properties of the structure depends on the minimal contact of solid area. Secondly, stress concentrations near to the pores under mechanical loading contributes to the lowest average flexural strength of 15 wt.% $[\text{CaCO}_3]\text{PCC}$ milled at 48 hours.

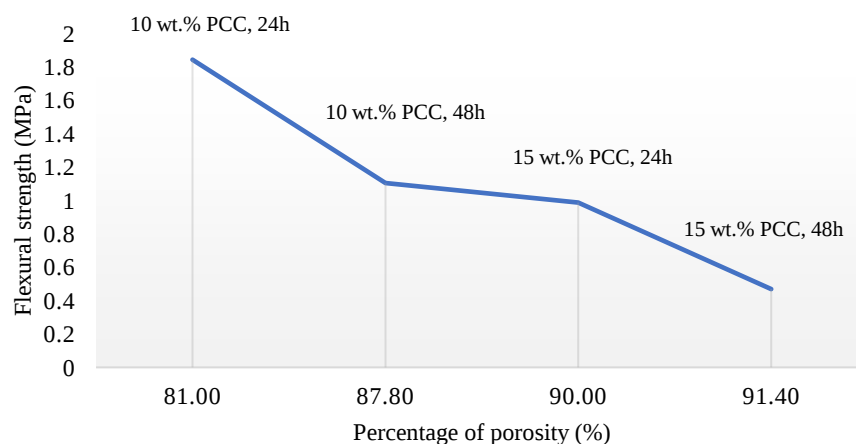


Fig. 3. Flexural strength (MPa) vs percentage of porosity (%) of porous clay-precipitated calcium carbonates.

Morphology and Crack Propagation of Porous Clay-Precipitated Calcium Carbonates

Structure of the ceramic foam after sintering is spherical and polyhedral-shaped cells as shown in Figure 4. Yasmin et. al [13] found out that the ceramic foam is a hierarchical type of structure which consists of open pores and closed pores. The structure of the ceramic foam has similar reticulated structures due to polymeric sponge was used as template [14]. Due the porous ceramic samples were made via polymeric replication method, its open cell size depends on the size of the polymeric sponge template used during the replication method. In order to control the pore size of porous ceramic, proper selection of polymeric sponge template is important [15].

Figure 4(a) which is 10 wt.% $[\text{CaCO}_3]$ PCC shows that the pores formed has a thicker struts and elongated pores due to lower addition of precipitated calcium. Thicker struts and small size of window of porous ceramic foams is due to low degrees of expansion (Peng *et al.*, 2000). From Figure 4(b) with 15 wt.% $[\text{CaCO}_3]$ PCC shows that the struts is the thinnest and more struts were not connected to each other and collapsed. Thus, it is proved the reason this sample has the lowest flexural strength. Nor, Akil, & Ahmad [16] reported that the strength of the structure reduced due to inhomogeneous coating of slurry during replication method thus contribute holes or voids formation in the structure after sintering. More blurred region were noticed due to collapsed of the struts. The figures also shows that the colour for 15 wt.% $[\text{CaCO}_3]$ PCC samples were dull and brownish due to lack of iron oxide content.

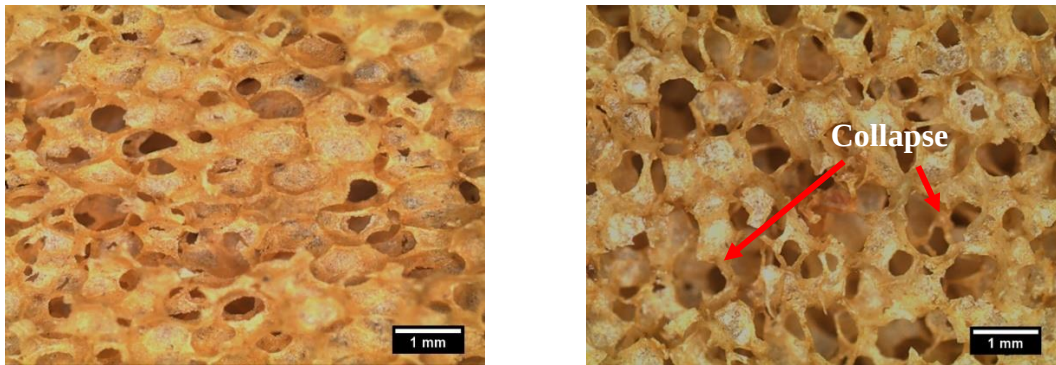


Fig4. Morphology of porous clay-precipitated calcium carbonates:
(a) 10 wt.% $[\text{CaCO}_3]$ PCC and (b) 15 wt.% $[\text{CaCO}_3]$ PCC.

The crack begins to propagate at the weakest spot of the sample such as pores. A research made by Meille et. al [17] have reported that damage due to compressive testing consist of fracture between pores for porous ceramic structure above 50% porosity. Based on Figure 5(a) the fracture shows that the crack produced through the pores and the surface of crack is uneven thus produced the blurred region. The crack propagates through the center of the sample from one side to other side of the sample. Since porous ceramic is a type of brittle material, the crack propagation propagates through the grains or pores thus it is an intergranular type of fracture [18]. Based on Figure 5 (b), there is a large size of pore formed at the structure of the sample. As expected, the pore formed due to this sample has higher addition of precipitated calcium carbonates (PCC). It is also expected that the struts of the structure collapsed thus the pore is produced.

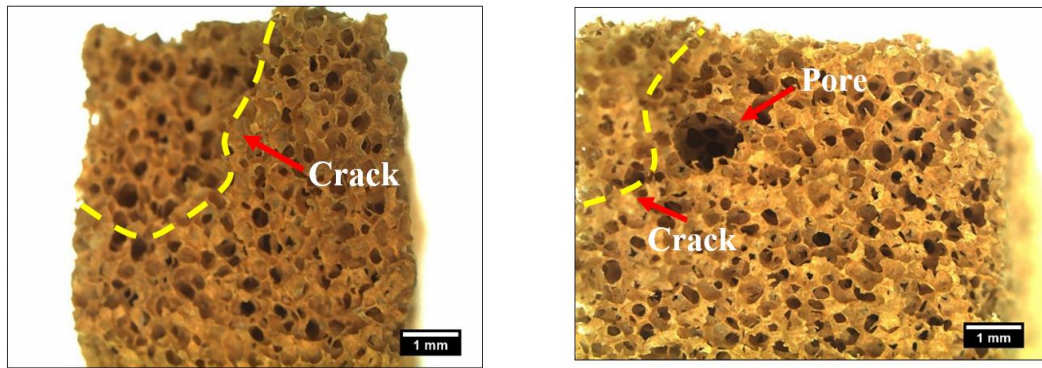


Fig. 5. Crack propagation of porous clay-precipitated calcium carbonates:
(a) 10 wt.% [CaCO₃]PCC and (b) 15 wt.% [CaCO₃]PCC.

4. Conclusions

Based on the mineralogical characterization, flexural testing and morphological analysis for both 10 wt.% [CaCO₃]PCC and 15 wt.% [CaCO₃]PCC, few findings can be concluded as follow:-

- i. The highest flexural strength obtained of porous ceramic were 10 wt.% [CaCO₃]PCC milled at 24 hours with the lowest percentage of porosity. The struts thickness of the porous ceramic becomes thinner and higher percentage of porosity as more addition of precipitated calcium carbonates were added due its function as a pore generating agent.
- ii. After sintering at 1250°C, the major phases formed were anorthite (2CaAl₂Si₂O₈), gehlenite (Ca₂Al₂SiO₇) and esseneite (CaFeAlSiO₆) which affected the colour and strength of the porous ceramic. The crack propagates at the middle and the weakest point of the porous ceramic structure with intergranular type of fracture mode.

5. Acknowledgements

The author gratefully thanked Universiti Malaysia Perlis (UniMAP), the Dean of School of Materials Engineering and technicians for providing the equipment and apparatus to carry out this project.

6. References

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