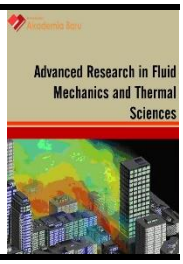
Penerbit Akademia Baru

Journal of Advanced Research in Fluid Mechanics and Thermal Sciences

Journal homepage: www.akademiabaru.com/arfmts.html
ISSN: 2289-7879



Eggshell Derived Calcium Phosphate and Its Conversion to Dense Bodies

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ARTICLE INFO

Article history:
Received 8 January 2020
Received in revised form 30 January 2020
Accepted 30 January 2020
Available online 4 February 2020

Keywords:
Eggshell; Calcium phosphate; Hydroxyapatite; β-Tricalcium phosphate; Sintering

ABSTRACT

Since eggshell waste is one of the many contributors to food waste in Malaysia, recycling activities and proper waste management can help reduce the amount of eggshell waste. The present study discusses the synthesis method of eggshell derived calcium phosphate utilizing recycled eggshell as the calcium precursor and di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$) as the phosphate precursor by a simple hydrothermal reaction when the pH of the solution was adjusted at 9. A rod-like nanostructure of CaP which contains only HA phase was produced following heat treatment at 400 °C using the CaO produced from the recycled eggshell. The effect of sintering temperature ranging between 900 °C and 1250 °C on the dense bodies using the resulting CaP powder was also studied. It was found that the HA phase in the resulting CaP powder was mostly transformed to β-TCP with a trace amount of the HA phase following the sintering process. The increase of sintering temperatures subsequently increased the hardness and density of the sintered bodies. Further, SEM observations showed the formation of denser microstructures by effective pore removal at the higher sintering temperature.

1. Introduction

Nowadays, there is a significant demand in using biomaterial for bone implants or bone grafts in orthopaedic and dental surgeries due to the medical treatments for bone trauma, diseases, bone cancer, ageing and fractures. Calcium phosphate (CaP) bioceramics have commonly been used in biomedical and dental applications given their good biocompatibility, bioactivity, thermodynamic stability in body fluids and osteoconductive properties [1-3]. Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, HA] and beta-tricalcium phosphate [$Ca_3(PO_4)_2$, β-TCP] are the most common phases of CaP which are extensively used as substitute materials for artificial bone grafts given their unique composition and crystal structure which are near to natural bone [4-6].

It is reported that around 8,000 tonnes of food waste are generated each day in Malaysia [7]. Of this amount, egg consumption, especially in the food industry, contributes towards the production

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of about 70,686 tonnes of eggshell waste which needs to be disposed of in landfills [8]. The abundance of this amount of eggshell waste has a significant potential to be converted into calcium phosphate for commercial applications with a lower production cost. Useful products based on calcium phosphate such as bone and dental implants in the form of porous, dense, granules and coatings can be mass-produced for medical applications [9-12]. Moreover, over the last few years, food waste such as eggshell, fishbone, bovine bone, mussel shells, clam, and oyster shells have been utilized as the source of calcium precursor in the production of calcium phosphate [9].

In producing calcium phosphate from eggshell waste, numerous attempts have been made employing using several methods. Abideen *et al.,* [3] produced nano-sized calcium HA with a needle-like shape using eggshell waste via a wet chemical precipitation method. However, a flower-like HA nanostructure was produced using eggshell waste with the help of EDTA as the chelating agent by simple and rapid microwave irradiation [13]. Moreover, several studies have been conducted to investigate the sintering effect of as-synthesized eggshell derived calcium phosphate in the form of compact bodies [14-16]. These studies reveal that HA is the only phase obtained following the sintering process at 1250 °C.

However, limited studies have reported on the formation of β-TCP as the major phase following the decomposition of HA at high sintering temperature. In this study, we report on the formation of β-TCP as the main phase in the sintered dense CaP produced from the eggshell-derived CaP. Moreover, the preparation of the eggshell derived calcium phosphate using eggshell waste as the calcium precursor by a simple hydrothermal reaction is also discussed. The sintering effect on the dense bodies of the as-synthesized CaP is also studied at various temperatures ranging between 900 °C and 1250 °C.

2. Methodology

Calcium phosphate (CaP) in this work was synthesized applying the hydrothermal method using eggshell as the precursor for calcium as published elsewhere [9]. The collected eggshell waste was first washed with distilled water, dried and ground into a powder and calcined in air at a temperature of 1000 °C in order to convert the calcium carbonate ($CaCO_3$) to calcium oxide (CaO) by removing the organic constituents. The resulting CaO powder was ball milled and sieved before used as the calcium (Ca) precursor to prepare the HA powder via hydrothermal synthesis. The obtained CaO was then dissolved in distilled water, continuously stirring with a magnetic stirrer. Next, the diluted di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$, R&M Chemicals) solution was added drop-wise into the CaO slurry. Ammonia solution (NH_4OH, Fisher Scientific) was then added into the mixed solution to adjust the pH to 9 in order to produce an alkaline solution. This was followed by stirring the prepared solution on a hot plate at ~90 °C. Upon completion of the synthesis, a white paste was obtained, and oven-dried overnight before heat treatment at 400 °C.

The dense bodies were prepared using the resultant powder by a uniaxial pressing method using a manual Hydraulic Press (Specac) using a load of 3 tonnes. The compacted bodies were then sintered at 900 °C, 1050 °C and 1250 °C for 2 hours respectively, with the heating and cooling rate set at 5 °C/ min.

The X-ray diffraction (XRD) pattern of the eggshell, as-produced CaO, as-synthesized calcium phosphate and sintered dense calcium phosphate were then analysed using an X-Ray Diffractometer System X'Pert Pro (PANalytical, Netherlands). The microstructure of the as-synthesized calcium phosphate and dense bodies were observed using a Field Emission Scanning Electron Microscope – Energy Dispersive X-Ray (FESEM, JSM-6701F, Jeol). The hardness of the sintered bodies was next determined using Vickers's hardness indentation (Mitutoyo HV-523) with the applied force; F of 0.3

kilogram-force (kgf) with a dwell time of 20 s. A total of five indentations were made on each sintered sample, with the average value recorded. The density of the sintered samples was measured based on the Archimedes technique using an electronic densimeter (MD-300S, Alpha Mirage, Japan) having a resolution of ± 0.001 g/m^3. The test was conducted at ambient room temperature, using distilled water as the immersion liquid.

3. Results

3.1 Characterisation of Calcium Phosphate Synthesized from Eggshells

Figure 1 shows the XRD patterns of the raw eggshells, calcined eggshells and as-synthesized calcium phosphate. Figure 1(a) depicts that the raw eggshells were recognized as $CaCO_3$ (JCPDS, 01-072-4582). The heat treatment of the raw eggshell at 1000 °C converted the $CaCO_3$ into CaO and another complementary phase of calcium hydroxide, $Ca(OH)_2$, as shown in Figure 1(b). From the analysis, the obtained $Ca(OH)_2$ in the eggshell-derived CaO samples developed from the reaction towards the moisture in the surroundings is known as a hydration process [17]. Moreover, the study by Othman *et al.,* [18] reported using $Ca(OH)_2$ as the precursor to produce calcium phosphate, which was β-TCP. Figure 1(c) reveals that the obtained calcium phosphate is matched well with JCPDS no. 09-0432, indicating that the resultant powders were mainly from the HA phase. The crystallite size of the obtained powders was calculated as 58.92 nm using Scherer's equation from the most prominent peak; (211) plane.

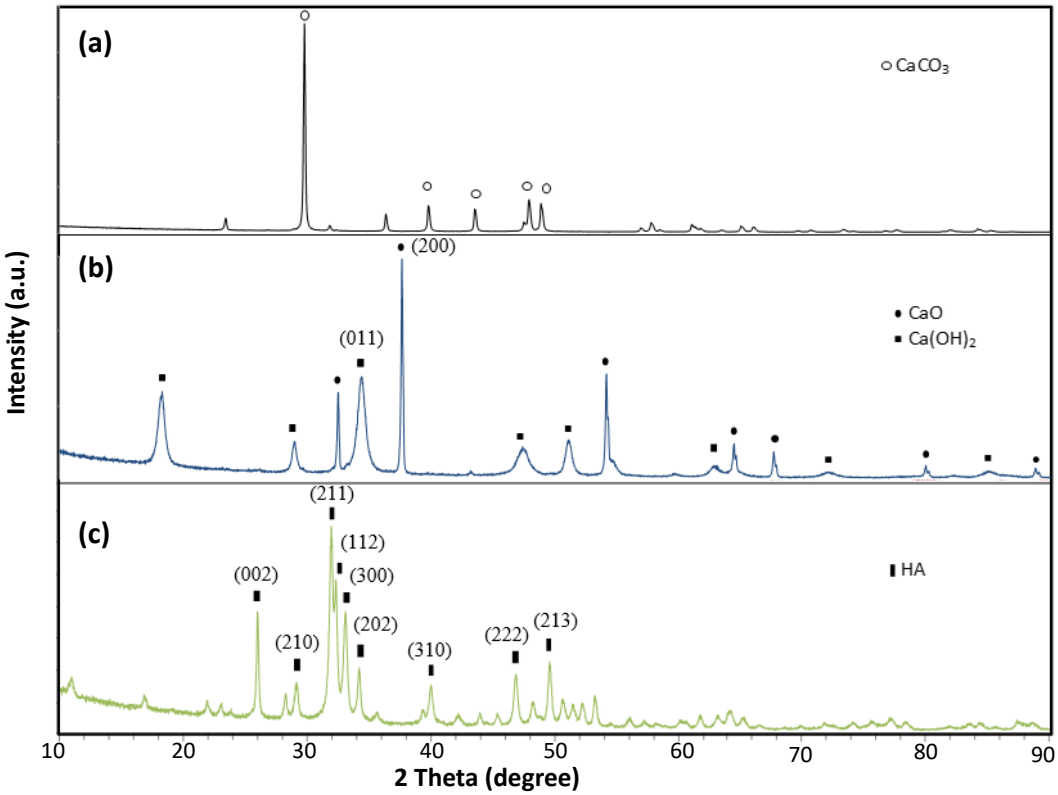

Fig. 1. XRD patterns of (a) crushed eggshell powders, (b) eggshell powders calcined at 1000 °C and (c) eggshell derived calcium phosphate after calcined at 400 °C

The morphology of the calcium phosphate derived from the waste eggshell is presented in Figure 2. Here, the SEM images show that the obtained calcium phosphate consisted of agglomerated powders of elongated rod-shaped particles having an average length of 200 nm and a width of 65

nm, as shown in Figure 2(b). Kamalanathan *et al.,* [14] reported that rod-shaped particles are normally used in human hard tissue. Moreover, the EDX results showed the Ca/P ratio of 1.48 for the as-synthesized powder [14]. Apatites with Ca/P of 1.4 to 1.7 were categorized as HA or, more specifically, as calcium-deficient hydroxyapatite (CDHA) [19]. Some studies have reported that CaPs with Ca/P < 1.5 would be less stable given higher Ca deficiency, and the higher exposure to disorder and imperfection of the structure. Piccirillo *et al.,* [20] reported that a synthetic CaP-based material with the Ca/P ratio smaller than 1.67 leads to the formation of TCP only. The same study also revealed the formation of biphasic calcium phosphate (BCP) consisting of HA and β-TCP following the annealing process using codfish bones as starting materials. Thus, the sintering effect on the dense bodies prepared from the eggshell derived calcium phosphate was studied.

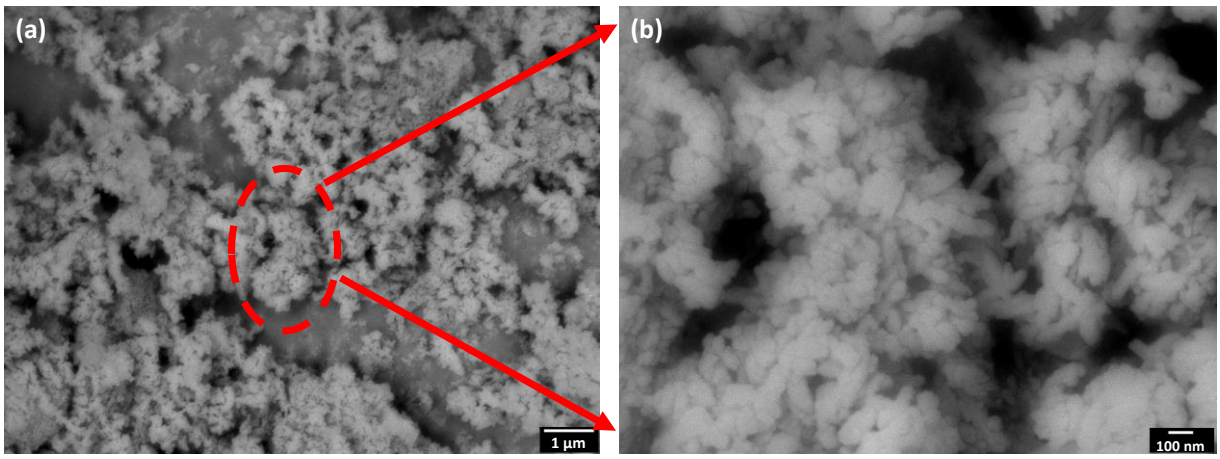

Fig. 2. SEM image of eggshell derived calcium phosphate at a different magnification of (a) 10 000 X and (b) 50 000 X

3.2 Effect of Thermal Treatment on Sintered Dense Bodies of Calcium Phosphate

The XRD patterns of the sintered eggshell derived calcium phosphate at various temperatures are displayed in Figure 3. The result indicates that most of the HA phase was transformed into β-TCP, even at the lowest sintering temperature, of 900 °C. In comparison, the sintering of dense calcium phosphate prepared from eggshell waste by previous studies [14,15] showed that there was only a single phase of HA observed following sintering at a temperature of 800 °C and above. In the present study, the decomposition of the HA phase into β-TCP may occur due to the formation of the as-calcined CaP in the form of CDHA. Moreover, some studies reported that the decomposition of CDHA synthesized via the hydrothermal method into BCP might occur when the powders were sintered above 700 °C [19,21].

Accordingly, the finding of this work suggests the formation of BCP instead of only HA using eggshell as the starting material following sintering at high temperature. Basically, two processes are involved during the phase transformation of HA, which is dehydroxylation and decomposition [21]. Dehydroxylation occurs due to the gradual loss of OH radicals forming oxyhydroxyapatite or oxyapatite (OHA). This OHA composition is stable in dry conditions while it can retransform to HA in moisture surroundings [22]. The dehydroxylation stage was succeeded in three steps: (1) reversible dehydroxylation at low temperatures (< 800 °C), (2) accelerated dehydroxylation between 800 – 1350 °C temperatures and (3) irreversible dehydroxylation at elevated temperatures (> 1350 °C) [22]. When OHA decomposes, secondary phases as β-TCP, α-TCP, TTCP and CaO are formed [22,23] which explains why β-TCP was formed as the dominant phase in the sintered bodies produced in this study. However, TTCP was not identified since the sintering temperature did not exceed 1300 °C [22]. As

such, the existence of β-TCP in these ceramic bodies can be profited for its good solubility and degradation rate, which is usually used as bioabsorbable bone graft [24,25].

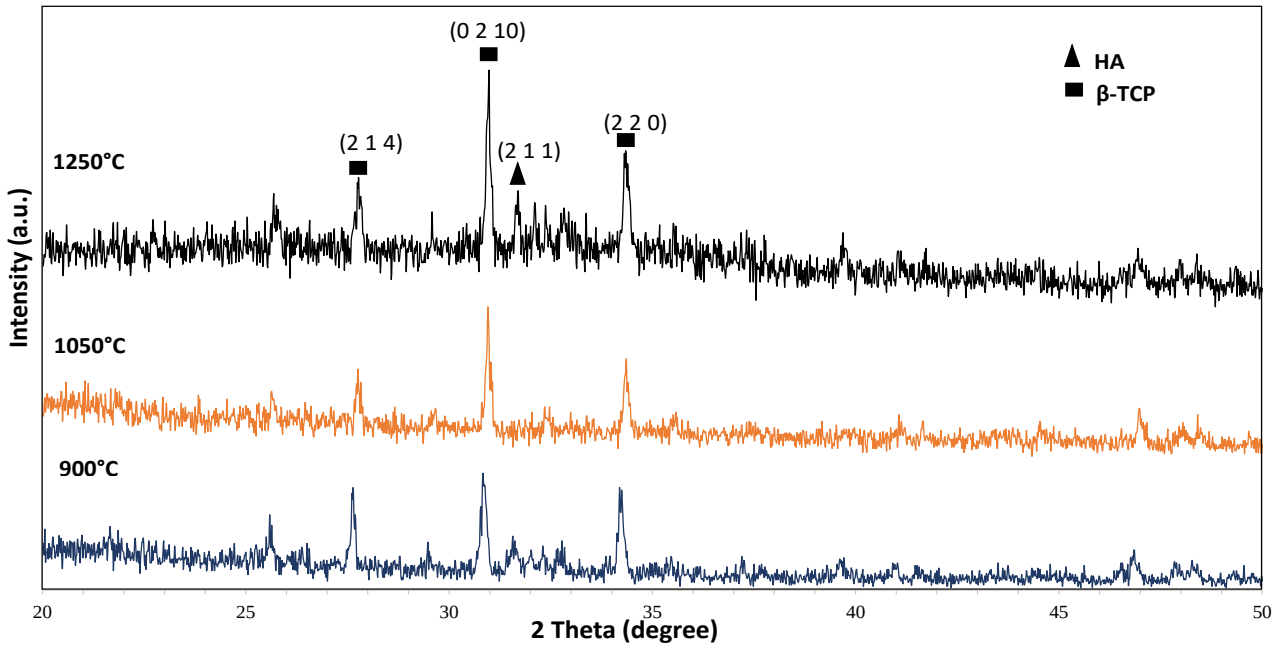

Fig. 3. XRD patterns of eggshell-derived CaP at different temperatures ranging between 900 °C and 1250 °C

Figure 4 shows the microstructural evolution of the sintered dense bodies prepared from eggshell derived CaP. The results reveal that when the sintering temperature was increased to 1250 °C, progressive densification occurred due to effective pore removal. Moreover, the volume of open pores was observed to decrease when the sintering temperature was increased, suggesting increasing necking formation, resulting in grain coarsening [14]. A significant increase in grain size was also reported elsewhere [15,16].

Figure 4(d) presents the EDX analysis for the eggshell derived CaP, sintered at 1250 °C, where Mg was found as the minor elements in the eggshell derived CaP. A study conducted by Adeogun *et al.,* [3] and Kumar *et al.,* [13] also reported the presence of trace elements in the synthesized CaP which originated from the starting materials, eggshell waste. The trace elements contribute to the formation of non-stoichiometric HA in which is also found in human bone [9].

Figures 5(a) and 5(b) depict the difference in density and porosity as a function of sintering temperature for the eggshell-derived CaP. It can be seen in the figure that the highest density was 2.67 g/ cm^2, which was achieved for dense CaP sintered at 1250 °C. This result also shows that an increase of sintering temperature improved the densification, leading to a steady increase in density of the sintered CaP through the reduction of porosity as revealed in Figures 5(a) and 5(b). This result is in good agreement with the SEM images as shown in Figure 4 which illustrates the complete removal of pores present in the sintered CaP at 900 °C to become almost fully dense CaP which was sintered at 1250 °C with the porosity (%) value reduced from 56.94% to 5.88%, respectively.

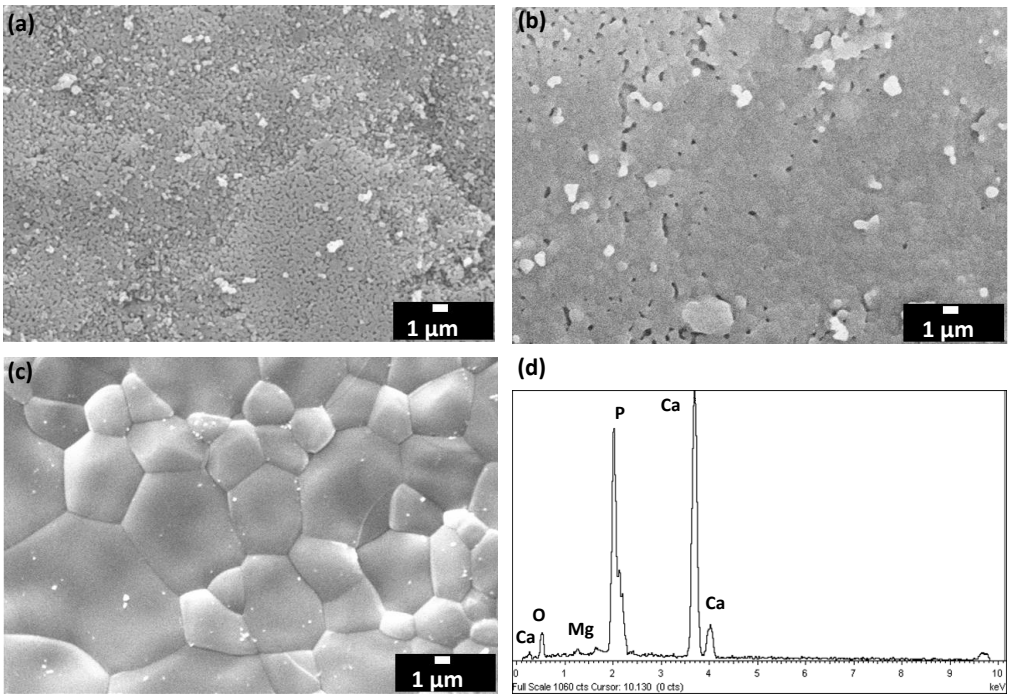

Fig. 4. SEM micrographs of eggshell-derived CaP sintered at (a) 900 °C, (b) 1050 °C and (c) 1250 °C

As presented in Figure 5(c), an increase of the sintering temperature noticeably enhanced the hardness of the sintered dense eggshell derived CaP. The highest value of hardness was measured at 3.78 GPa for dense bodies sintered at 1250 °C. On the increase of sintering temperature, the density continued to increase by the densification of particles which produced a densely packed microstructure, in turn, eliminating the pores existence in the dense bodies and contributed towards increasing the hardness value.

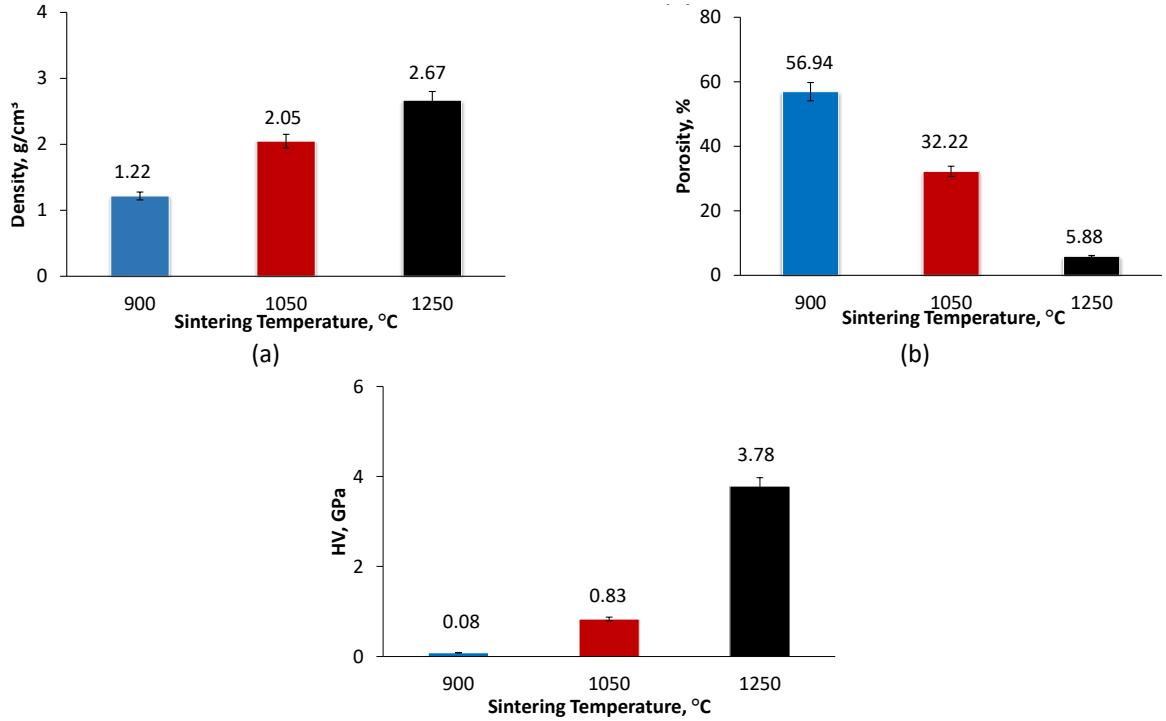

Fig. 5. The effect of sintering temperature on the (a) density, (b) porosity and hardness of dense CaP

4. Conclusions

Calcium phosphates were successfully obtained from the calcium precursor derived from the eggshell waste and ammonium hydrogen phosphate as the phosphate precursor by a simple hydrothermal reaction. The obtained calcium phosphate consisted of pure HA following the calcination at 400 °C. Studying the effect of the sintering temperature showed the decomposition of the initial HA phase in the dense green bodies being mostly transformed into a β-TCP phase which might due to the Ca/P ratio of the as-synthesized CaP being smaller than the stoichiometric ratio for HA which was 1.67. With increasing sintering temperature, it was found to promote densification and elimination of porosity in sintered dense bodies, which led to improvement in the hardness and density of the calcium phosphate. This study explored the potential of converting the eggshell waste into beneficial calcium phosphate for biomaterial application.

Acknowledgement

The authors would like to thank the Universiti Teknikal Malaysia Melaka for laboratory facilities and financial assistance under Short Term Research Grant PJP/2018/FKP (3A)/S01583

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