The Densification of Hydroxyapatite from Eggshell Waste at Different Sintering Temperature

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ABSTRACT

The outstanding biocompatibility and bioactivity properties of hydroxyapatite (HA) as a bio-implant material have garnered significant attention in prompting its extensive study. However, due to its brittleness and lower strength, its usage as a bone implant in load-bearing regions of biomedical applications is limited. The mechanical performance of the HA bodies is decreased by transformation-induced cracking as well as uncontrolled grain development. However, sintered HA ceramics with superior mechanical characteristics may be created if the prepared powder has better powder attributes including stoichiometry, crystallinity, agglomeration, and morphology from the start. Thus, this research explored the preparation of HA from discarded eggshells as a source of calcium via the dry reaction method and the correlation between its sinterability, densification, and mechanical properties at various sintering temperatures. In this work, the calcined eggshell powder was mixed with Calcium Hydrogen Phosphate Dihydrate (CHPD) via ball milling at 400 rpm speed for 4 hours and subsequently heat treated at 800 °C. The synthesized HA powder was compacted via hydraulic press and then sintered at temperatures of 1100 °C, 1150 °C, 1200 °C, and 1250 °C. The XRD analysis of the sintered HA samples revealed that the phase stability of the HA phase remained unaffected up to 1250 °C. Similar trends of

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average grain size, relative density, and hardness to sintering temperature were observed. HA samples sintered at 1250 °C exhibited the optimum mechanical properties with a relative density of 90.72% and a hardness of 4.34 GPa. It is believed that the grain boundary diffusion through the densification mechanism does not reach a densification level that is conducive to grain growth. Hence, the hardness still increased although the densification was relatively low. It can be concluded that HA densification significantly influences the grain coarsening and mechanical properties of the eggshell-derived HA.

Keywords: *HA; Eggshell; Densification; Mechanical Properties*

Introduction

Calcium Phosphate (CaP) is a compound that contains calcium and phosphorus which can be found naturally in inorganic waste among others such as eggshells, corals, cow bones, chicken bones, and fish bones [1]. One of the many variations of CaP mineral, HA (HA) has gained much interest in the medical and health-related fields as a bone graft alternative due to its mineral composition, which is comparable to teeth and bone besides its excellent bioactivity and biocompatibility. To date, it has been applied in drug delivery systems and bone tissue engineering implants in the form of powders, porous blocks, and hybrid composites. For example, it has been used when extensive bone removal is required or when bone augmentations are necessary (e.g., dental applications) [2].

However, due to its brittleness and lower strength, its application as bone implants in load-bearing regions of biomedical applications is limited [3]. It was reported that grain growth affects its density and hardness which contribute to its strength [4]. Besides that, poor mechanical properties and porosity can affect the biocompatibility of HA whereby the presence of voids or defects can hinder cell attachment, proliferation, and impede the formation of strong bonds between the implant and the surrounding tissue [5]. However, sintered HA ceramics with superior mechanical characteristics may be produced if the prepared powder has better powder attributes from the start including stoichiometry, crystallinity, agglomeration, and morphology. As a consequence, the employment of a suitable processing regimen enables the production of well-crystallized, high-density sintered HA that exhibits enhanced mechanical properties.

Hence, various synthesis methods have been employed to produce synthetic HA powder with significant purity and good mechanical properties [6]. Among the available methods are the hydrothermal method, solid-state reactions, the sol-gel process, emulsion, micro-emulsion, and predominantly chemical precipitation [7]. In addition, the synthesis of HA has also been

conducted using waste materials such as fish bone, eggshell, and coral as calcium precursors [1]. Typically, the eggshell constitutes around 11% of the total weight of an egg and is commonly regarded as a food waste with little commercial value. However, its abundant calcium content can be utilized as a viable source of calcium precursor. Besides that, by deriving HA from a natural source, it becomes feasible to obtain a material that closely matches the stoichiometry of human bone [8]. On another note, this practice not only offers economic advantages but also aligns with a sustainable approach to solid waste management, fostering economic growth and environmentally friendly practices.

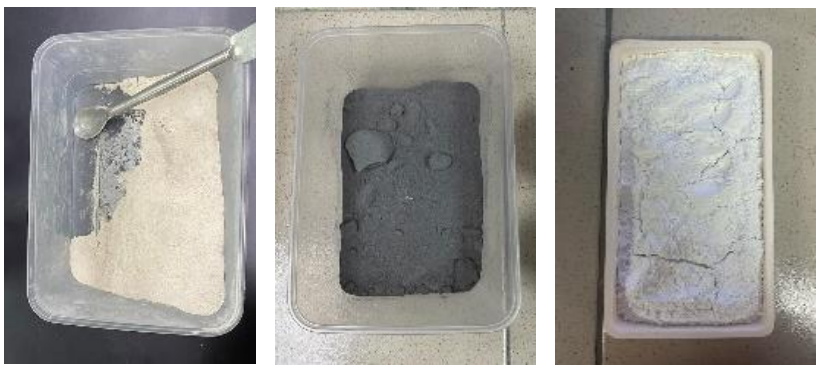
Among the conventional techniques employed for the synthesis of eggshell-derived HA are wet precipitation, hydrothermal processes, low-temperature synthesis, solid-state reactions, and sol-gel methods [9]. Among these different techniques, wet chemistry methods, such as precipitation and sol-gel, are widely preferred due to their ability to provide precise control over particle morphology and size. However, these methods can be laborious and need more reproducibility. On the other hand, dry methods, such as mechanochemical and solid-state methods, offer a straightforward and highly reproducible synthesis process, as they do not require stringent control conditions [10].

One of the methods, mechanical milling, has been used to produce HA derived from eggshells. However, this dry-state reaction method has been claimed to increase the possibility of contamination in the final HA powder. In previous research, the solid-state reaction was used to study the eggshell-derived HA powders through the attrition milling method [11]. In that research, with a proper processing regime, it has been proven that it did not produce any contaminations which resulted in good mechanical properties [11]. Ball milling is a widely utilized technique that involves the use of ceramic balls placed in a milling jar with the material to be milled. By rotating the jar, the balls collide with the material, resulting in size reduction through impact and abrasion. This process effectively breaks down particles and achieves the desired particle size distribution, making ball milling a popular method for producing fine powders with precise sizing [12]-[13]. To date, no work has been reported on the production of HA using calcium carbonate from eggshells through the ball milling method.

Hence, this study aims to produce HA using eggshell as the source of calcium precursor in the form of calcium carbonate through the solid-state reaction method and to determine its sinterability at various sintering temperatures. Subsequently, the influence of different sintering temperatures will be examined to ascertain the correlation of densification on the mechanical properties of eggshell-derived HA.

Methodology

In this work, the waste eggshells were cleaned with distilled water to remove the protein membrane layer. Then, they were dried in the oven before being crushed using a mortar and pestle into a fine powder. Afterward, the eggshell powder was calcined at 700 ℃ for two hours to obtain pure calcium carbonate ($CaCO_3$) (Figure 1a). This pure $CaCO_3$ was then used as the source of calcium (Ca) in the synthesis and mixed with a phosphate (P) precursor, Calcium Hydrogen Phosphate Dihydrate (CHPD), at a Ca/P molar ratio of 1.67 via ball milling for 4 hours milling time at 400 rpm speed (Figure 1b). Following that, the powder mixture was sieved with a 212 µm mesh sieve and then heat treated at 800 °C (Figure 1c) to obtain pure HA powder.



(a) (b) (c)

Figure 1: The HA powder preparation: (a) crushed eggshell, (b) eggshell calcined at 700 °C, and (c) ball-milled mixture calcined at 800 °C

Subsequently, the synthesized eggshell-derived HA powder was pressed into disc samples (26 mm diameter) (Figure 2) via uniaxial pressing and followed by a sintering regime in an air atmosphere at temperatures varying from 1100 to 1250 °C for 2 hours in a box furnace at a rate of 5 °C/min which will induce densification to the prepared eggshell-derived HA powder. The physical change due to densification was shown clearly in Figure 2 by the shrinkage in the sample dimension after sintering. These sintered samples were later addressed as ES-1100, ES-1150, ES-1200, and ES-1250, concerning its sintering temperature.

Phase stability evaluation of the sintered HA dense ceramics was determined using X-ray diffraction (XRD) (Rigaku Ultima IV) to observe any phase transformation corresponding to sintering temperature with standard reference to the International Centre for Diffraction Data (ICDD). Meanwhile, the morphological characterization was evaluated using a Field Emission

Scanning Electron Micrograph (FESEM). Subsequently, the grain size of the sintered sample was determined from the FESEM image based on the line intercept method [11]. Archimedes' principle was used in the bulk density measurement for the sintered samples with distilled water as an immersion medium. The relative density of the sintered sample was calculated by taking the theoretical density of HA as 3.156 g cm^{-3}. Meanwhile, the hardness of all the green compacted samples was measured via the Vickers indentation) using an applied load of 100–200 grams with a dwell time of 10 seconds and repetitive indentation to get an accurate reading.

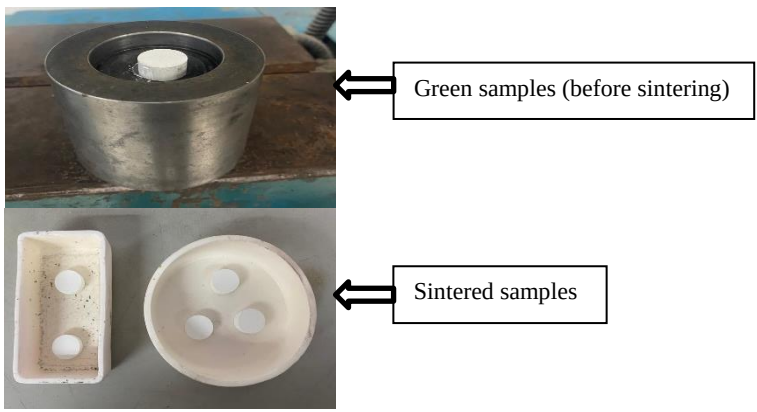


Figure 2: As-prepared dense and sintered eggshell-derived HA samples

Results and Discussion

Figure 3 presented the XRD pattern of the powder mixture (eggshell powder and CHPD) after heat treatment at 800 °C. It could be observed that all the XRD peaks matched those in the ICDD 01-076-8436 for HA; thus, indicating that a pure HA phase was successfully obtained. Besides that, sharper peaks that are visible in the XRD pattern denote the high crystallinity of the synthesized powder.

Meanwhile, Figure 4 depicts the phase stability of the sintered HA samples at various temperatures. All XRD peaks in Figure 4a to Figure 4d perfectly matched those found in the ICDD 01-076-8436 for HA; thus, demonstrating that the stability of the HA phase was not compromised when sintered between 1100 °C and 1250 °C. Nonetheless, HA phase decomposition may happen due to further sintering at 1300 °C and 1350 °C, forming minute amounts of α-tricalcium phosphate (α-TCP) and tetracalcium phosphate (TTCP) [11]. In addition, it was observed that the intensity of the highest peak for HA corresponding to the (211) lattice plane (~2θ = 31.96°- 32.07°)

increased as the sintering temperature increased from 1100 °C to 1250 °C. This indirectly reveals that a highly crystalline HA structure has been formed. A similar XRD pattern of HA at different sintering temperatures has been reported in previous studies [14]-[15].

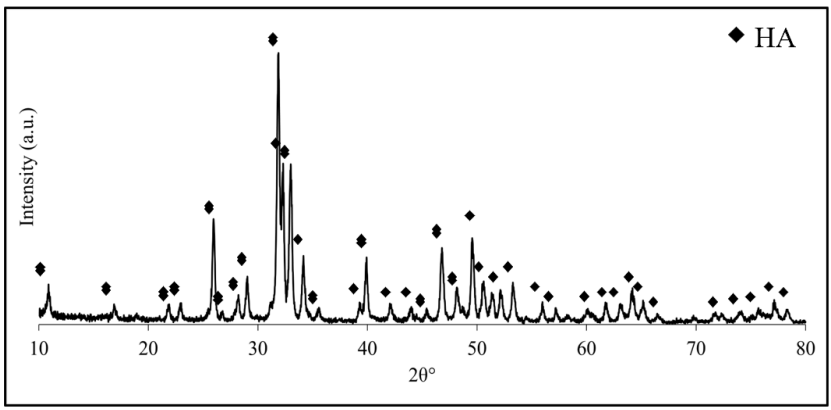


Figure 3: XRD pattern of eggshell-derived HA powder heat treated at 800 °C

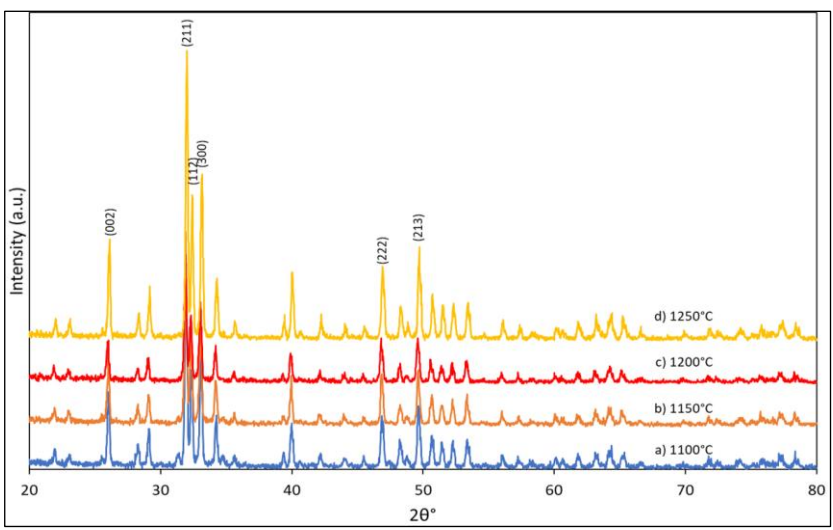


Figure 4: XRD patterns of eggshell-derived HA samples sintered at temperatures ranging from 1100 °C to 1250 °C

The FESEM images showing the microstructural evolution of the samples sintered at various temperatures are presented in Figure 5. Generally,

globular particles are visible in all sintered samples. It was observed that at 1100 °C (Figure 5a), necking formation between the grains has taken place. These phenomena correspond to the first stage of sintering [11]. Besides, with increasing sintering temperature beyond 1100 °C, densification started to occur and formed agglomerated particles. It was found that samples sintered at 1200 °C (Figure 5c) and 1250 °C (Figure 5d) exhibited a more densely packed microstructure with less amount of porosity. The smaller pore sizes exhibit a higher strength and better mechanical properties [15].

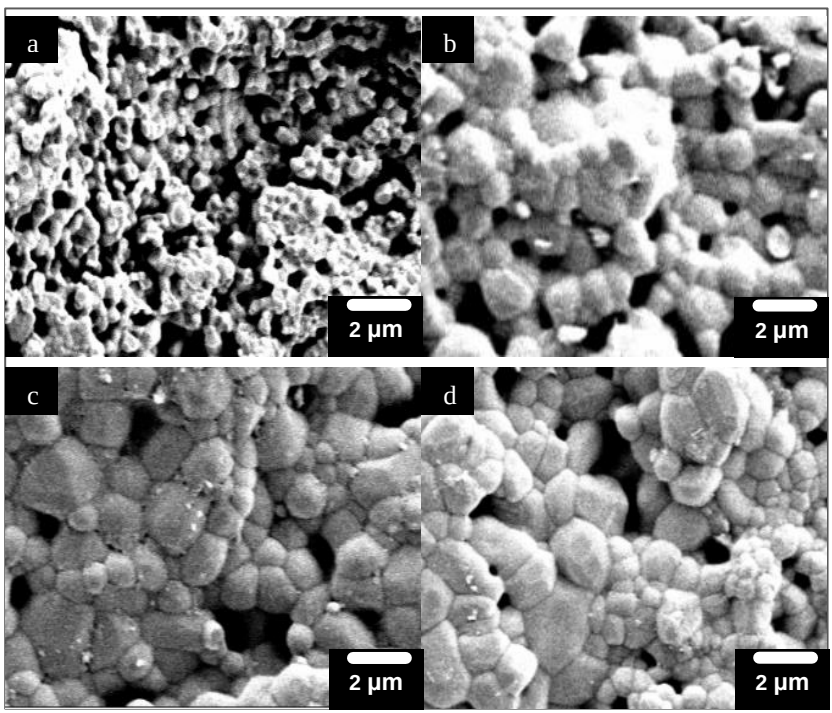


Figure 5: FESEM images of eggshell-derived HA samples sintered at; (a) 1100 °C, (b) 1150 °C, (c) 1200 °C, and (d) 1250 °C

Although this densification was accompanied by grain coarsening, it can be seen that the rate of grain coarsening was not primary when compared to that reported in other works where the grain size of HA increased from approximately 2 to 8 mm as the sintering temperature increased from 1200 °C to 1250 °C [16]. An increase in grain size was not favoured as induced strength deterioration of the sintered samples. Moreover, accelerated grain growth at high sintering temperatures is a typical result of conventional pressureless sintering due to the uncontrollable presence of moisture in the sintering

atmosphere [17] but this was not observed in this work. Thus, it is believed that the grain boundary diffusion through the densification mechanism does not reach a densification level that is conducive to grain growth [18].

The influence of sintering temperature on the average grain sizes of HA is presented in Figure 6a. The graph illustrates a linear relationship between average grain size and sintering temperature. The smallest average grain size of the sintered HA was 0.83 ± 0.02 µm, which was obtained at 1100 °C as shown in Figure 6a, while the largest average grain size of the sintered HA was 2.29 ± 0.02 µm, which was obtained at 1250 °C.

In studying mechanical properties, the ability of the material to densify is used to evaluate the material's structure as well as porosity predictions [19]. Figure 6b and Figure 6c depict the relative density and Vickers hardness of HA as a function of sintering temperatures, respectively. A steady increase in density is observed with an increase in sintering temperature up to 1250 °C. These findings align with the compacted arrangement of the sintered HA microstructure, which becomes denser as the sintering temperature increases, as demonstrated in Figure 6a. The relative density exhibited an increase, starting at 89.42% at 1100 °C and reaching a peak of 90.72% at 1250 °C. Nevertheless, based on the previous study, higher relative density values were obtained ranging from 96% - 97% [6], [11], [15]. The lower relative density values obtained in the current work could also possibly be due to insufficient pressing pressure applied during the compaction of the green samples. This is shown in Figure 5 whereby the presence of porosity between the grains was still observed at 1250 °C. Hence, it can be generalized that pressing pressure applied during the preparation of green samples also plays a vital role in their densification. Nevertheless, a study by Ramesh et al. [11] acquired a similar trend for the result of sintered HA samples from 1100 °C to 1250 °C although a different processing method (attrition milling) was used.

It is noteworthy that in Figure 6b, the Vickers hardness also exhibited a similar trend to that observed for relative density. It was also observed that grain size imparted a significant impact on the sintered sample hardness. The Vickers hardness values ranged from 1.59 GPa at 1100 °C to a maximum of 4.34 GPa at a sintering temperature of 1250 °C. It was reported in a previous study that the value of hardness for 1100 °C to 1250 °C temperature ranged from 1 GPa to 5 GPa but via a two-step sintering method [11], [14]. Besides that, the significant increase in hardness up to 1250 °C can be attributed to the concurrent increase in relative density, as depicted in Figure 6a. It is widely acknowledged that the hardness of HA tends to increase with relative density. In addition, hardness is also governed by grain growth [6], [11]. In this work, although the grain growth was observed to gradually increase with sintering temperature, the comparative value of hardness to the previous study that worked on eggshell-derived HA via the different source of Ca and method was obtained. This could be attributed to the hardness of the material which will increase if the indentation is smaller [20] as observed on the indented sintered

sample. Overall, it was observed that sample ES-1250 demonstrated the best mechanical properties compared to all other samples in this study.

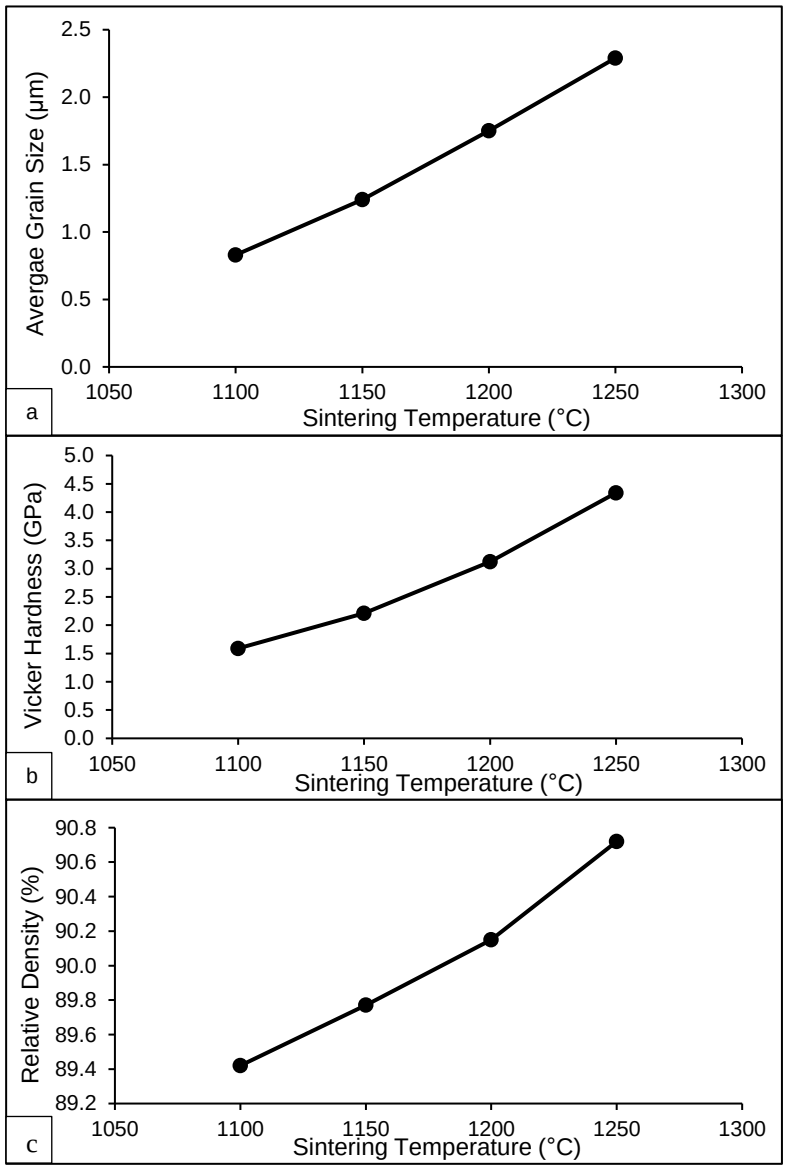


Figure 6: The effect of sintering temperature on; (a) average grain size, (b) Vickers hardness, and (c) relative density of eggshell-derived HA samples

Conclusion

Ultimately, highly crystalline and phase-pure HA from bio-waste eggshells were successfully produced via a combination of mechanical alloying and sintering methods. The HA powder was obtained after pre-heat treatment of calcined eggshell and CHPD at 800 °C. Throughout the sintering regime, the phase stability of the HA samples was not disrupted at all sintering temperatures as shown in the XRD analysis. The resulting sintered HA samples, which have globular agglomerated particles as their microstructure, were found to increase in grain size with sintering temperature as the first stage of sintering took place at 1100 °C. However, in this work, it is believed that the grain boundary diffusion through the densification mechanism did not reach a densification level which is conducive to grain growth as the presence of porosity between the grains was still observed at 1250 °C. A similar trend was also observed for both densification and hardness of the sintered HA samples with increased sintering temperature. Similarly, it can be concluded that lower grain growth by these samples indicates the lower-level densification obtained. Although the densification was comparatively low, the measured hardness of these sintered samples still increased as the resulting diamond indentation on the sample was smaller. Overall, it was observed that sample ES-1250 demonstrated the best mechanical properties compared to all other samples from this study with the highest relative density of 90.72% and a hardness of 4.34 GPa. On top of that, the usage of this natural waste as a precursor in synthesizing HA is not only sustainable and cost-effective but would also be beneficial to environmental waste recovery.

Contributions of Authors

The authors confirm the equal contribution in each part of this work. All authors reviewed and approved the final version of this work.

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Conflict of Interests

One of the authors, Natasha Ahmad Nawawi, is a Section Editor of the Journal of Mechanical Engineering (JMechE). The author has no other conflict of interest to note.

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