

Properties of hydroxyapatite synthesized by wet chemical method

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The sintering behavior of a commercial HA and synthesized HA was investigated over the temperature range of 700 °C to 1400 °C in terms of phase stability, bulk density, Young's modulus and Vickers hardness. In the present research, a wet chemical precipitation reaction was successfully employed to synthesize a submicron, highly crystalline, high purity and single phase stoichiometric HA powder that is highly sinterable particularly at low temperature regimes below 1100 °C. It has been revealed that the sinterability of the synthesized HA was significantly greater than that of the commercial HA. The temperature for the onset of sintering and the temperature required to achieve densities above 98% of theoretical value were approximately 150 °C lower for the synthesized HA than the equivalent commercial HA. Nevertheless, decomposition of HA phase upon sintering was not observed in the present work for both powders.

Key words: Hydroxyapatite, Wet chemical method, Sintering, Mechanical properties.

Introduction

Hydroxyapatite (HA) is one of the most attractive calcium phosphates and is widely used in clinical applications such as restorative dental and orthopaedic implants due to its close resemblance to the natural bones and teeth, excellent bioaffinity and its enhancement in osseointegration [1-3]. These properties have subsequently encouraged persistent efforts in the development of this material in appropriate form for various applications as a biomaterial. Densified HA powders are widely needed for load bearing orthopaedic and dental applications [4]. Nevertheless, dense HA ceramics have always showed a lower tensile strength as compared with the values of human bones [4, 5]. Therefore, the development of bioactive HA that has improved and ultimately bone-like mechanical properties are desirable. As a result, a great number of studies have been devoted to improve the mechanical properties of HA materials [3-6].

The success of HA ceramic in biomedical application is largely dependent on the availability of a high quality, sintered HA that is characterized having refined microstructure and improved mechanical properties [7, 8]. Wang *et al.* have reported that nanosized HA exhibits

much higher bioactivity than the coarser crystals as it provides larger interfaces for osseointegration, thus, making it a promising material in orthopaedic and dental implant applications [8]. Therefore, intensive research in HA involving a wide range of powder processing techniques, composition and experimental conditions have been investigated with the aim of determining the most effective synthesis method and conditions to produce well-defined particle morphology [7-10]. Among the available synthesis methods, wet precipitation technique, which involves aqueous solutions, is most widely used by many researchers [6, 11, 12]. The advantages of this process are that the by-product is almost water and the probability of contamination during processing is reported to be very low [12]. In addition to that, the process is economical and can be easily synthesized at low temperatures ranging from 40 to 100 °C [13].

The sintering temperature and atmosphere are also important as these factors could adversely affect the strength of HA. For instance, sintering at elevated temperatures has the tendency to eliminate the functional group OH in the HA matrix (dehydration) and this would result in the decomposition of HA phase to form α -tricalcium phosphate (α -TCP), β -tricalcium phosphate (β -TCP) and tetracalcium phosphate (TTCP) [14]. It is worth mentioning that decomposition of HA suppresses densification and will be accompanied by a decrease in mechanical properties [14-16].

Therefore, in this work, a wet chemical technique was

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employed to manufacture nanocrystalline HA powder using high purity Ca^{2+} precursor. The sinterability and properties of the sintered product derived from these powders were evaluated and compared with commercial HA.

Experimental Procedures

In the current work, the HA powder used was prepared according to a novel wet chemical method comprising precipitation from aqueous medium by slow addition of orthophosphoric acid (H_3PO_4) solution to a calcium hydroxide ($\text{Ca}(\text{OH})_2$) suspension containing ammonium hydroxide (NH_4OH) in order to maintain the $\text{pH} > 10$. The precipitate is aged overnight and subsequently filtered thoroughly to form a sticky cake, which was then dried overnight and ground to powder [17]. In order to evaluate the sinterability and performance of the synthesized HA, labeled as HA (P):CIP, a commercially available HA powder manufacture by Merck, Germany was also studied, hereafter is known as HA(M):CIP.

The green samples were uniaxial compacted at about 1.3 MPa to 2.5 MPa into rectangular bar ($4 \times 13 \times 32$ mm) and circular disc (20 mm diameter) samples. The green compacts were subsequently cold isostatically pressed at 200 MPa (Riken Seiki, Japan). This was followed by consolidation of the particles by pressureless sintering performed in air using a rapid heating furnace (ModuTemp, Australia), over the temperature range of 700 °C to 1400 °C, with ramp rate of 2 °C/min. (heating and cooling) and soaking time of 2 hrs for each firing. All sintered samples were then polished to a 1 μm finish prior to testing.

The calcium and phosphorus content in the synthesized HA powder were determined by using the Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) technique. The particle size distributions of the powder were determined using a standard Micromeritics Sedigraph 5100 X-ray particle size analyzer. The phases present in the powders and sintered samples were determined using X-Ray diffraction (XRD, Geiger-Flex, Rigaku Japan). The microstructural evolution of the HA under various sintering temperature was examined by using the scanning electron microscope (SEM) and the grain size was determined from scanning electron micrographs using the line intercept analysis [18]. The bulk densities of the compacts were determined by the water immersion technique (Mettler Toledo, Switzerland). The relative density was calculated by taking the theoretical density of HA as 3.156 Mg m^{-3} . The Young's modulus (E) by sonic resonance was determined for rectangular samples using a commercial testing instrument (GrindoSonic : MK5 "Industrial", Belgium). The instrument permits determination of the resonant frequency of a sample by monitoring and evaluating the vibrational harmonics of the sample by a transducer.

The modulus of elasticity or Young's modulus was calculated using the experimentally determined resonant frequency [19]. The microhardness (H_v) of the samples was determined using the Vickers indentation method (Matsuzawa, Japan). The indentation load (< 200 g) was applied and held in place for 10 sec. Five indentations were made for each sample and the average value was taken.

Results and Discussion

The results of the chemical analysis as well as the particle size analysis that was carried out on the two HA powders are shown in Table 1. It shows that within the accuracy of the analysis, the Ca/P ratio of the commercial HA was slightly higher by $< 1\%$ than that of the synthesized HA. The average particle size of the synthesized HA was slightly smaller than the commercial powder. This was also evident from the SEM micrograph of the two powders as shown in Fig. 1. The synthesized HA powder (Fig. 1(a)) consists of a mixture of small powder particles ranging from 1-3 μm diameter and larger particles of 5-10 μm diameter. The larger particles appear to be large agglomerates of loosely packed smaller particles, resulting in a rough surface. Similarly, the micrograph of the commercial powder (Fig. 1(b)) consists of a mixture of small and large particles. However, the commercial HA powder appeared to produce larger agglomerated particles (up to 10 μm), and these agglomerates appeared to be more compacted compare to those observed for the synthesized HA. The drying of the filter cake of synthesized HA could have resulted in less compaction of the precipitate and, although the dried filter cake was ground and sieved, this probably resulted in the formation of soft agglomerates that breaks easily during compaction.

Table 1. Properties of the starting HA powders.

	Synthesized HA HA(P):CIP	Commercial HA HA(M):CIP
Calcium (as Ca), %w/w	38.9	37
Phosphorous (as P), %w/w	23.2	22
Ca/P ratio	1.677	1.682
Particle size (μm)	3.20 ± 0.54	3.26 ± 1.53
Color	White	White

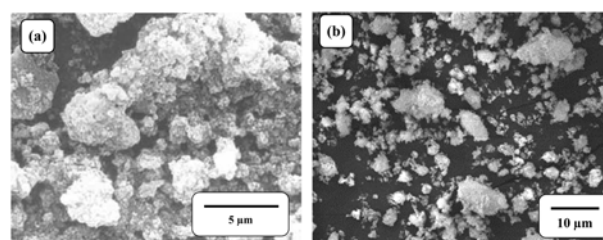


Fig. 1. SEM micrographs of (a) synthesized HA and (b) commercial HA powders.

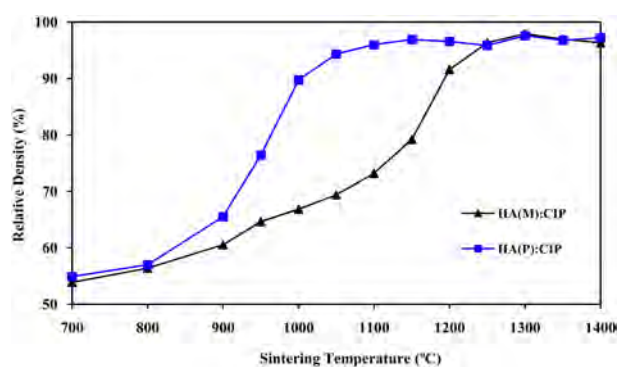


Fig. 2. Effect of sintering temperature on the sintered densities of synthesized hydroxyapatite (HA(P):CIP) and commercial ceramic (HA(M):CIP).

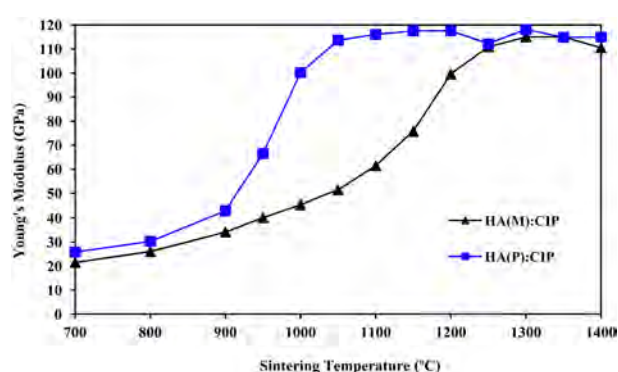


Fig. 3. Young's modulus variation with sintering temperature of synthesized HA(P) and commercial HA(M).

X-ray diffraction (XRD) analysis of the synthesized HA powder produced only peaks which corresponded to the standard JCPDS for stoichiometric HA and compared very favorably with the XRD signatures of commercial HA powder as shown in Fig. 2.

In the present work, it is evident that the synthesized filtered crystals of synthesized HA were mainly single-phase HA. Estimates of crystal size from peak broadening using the Scherrer's formula [20] for the synthesized powder gives about 11 nm from the (211) reflection and about 30 nm from the (002) reflection.

The sintering of both the synthesized HA and commercial HA compacts revealed the presence of only HA phase as typically shown in Fig. 2. The formation of secondary phases such as tricalcium phosphate (TCP), tetracalcium phosphate (TTCP) and calcium oxide (CaO) was not detected throughout the sintering regime employed. The result shows that the phase stability of HA was not disrupted by the initial pressing conditions, sintering schedule and temperature employed.

The effects of sintering temperature and pressing condition on the sintered densities of compacts of the two HA powders are shown in Fig. 2. In general, the results indicate that the synthesized HA exhibited better sinterability than the commercial HA. The bulk density increases with increasing sintering temperature regardless of pressing condition. The onset of densification, indicated by

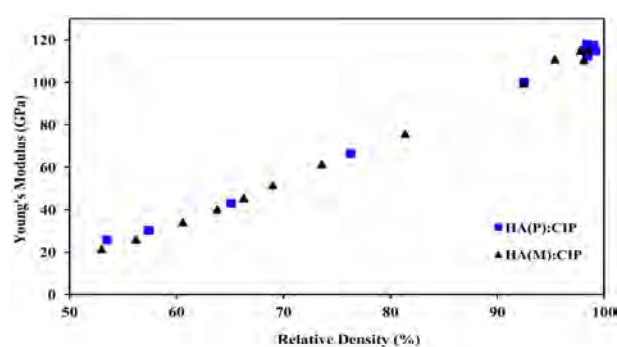


Fig. 4. A linear relationship exists between the sintered density and the Young's modulus of hydroxyapatite ceramics.

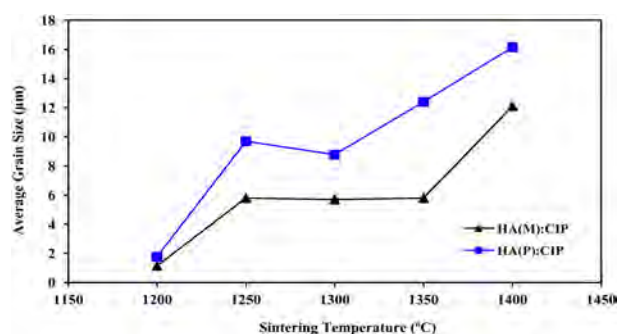


Fig. 5. Average grain size variation with sintering temperature for commercial HA and synthesized HA.

a sharp increase in the sintered density for synthesized HA was between 900 °C and 1000 °C whereas the commercial HA required a higher temperature of between 1150 °C and 1200 °C. Sintering temperatures above this range result in very small increases in density which is associated with the final stages of sintering where small levels of porosity are removed and grain growth begins. The synthesized HA achieves a final sintered density of 97-99% of the theoretical density at 1050-1100 °C, whereas the commercial HA requires a sintering temperature of 1250-1300 °C to reach a similar density.

The relationship between the Young's modulus (E) of both the sintered HA compacts and sintering temperature is shown in Fig. 3. Generally, regardless of pressing condition, it was found that the Young's modulus of the HA gradually increase with increasing sintering temperature up to about 1350 °C. Comparison between both HA indicates that the synthesized HA sinters better at lower temperatures than the commercial HA as depicted in Fig. 2. The results showed that the synthesized HA sintered compacts could achieve a Young's modulus above 100 GPa at approximately 1000 °C, whereas the commercial HA samples require a higher sintering temperature of approximately 1200 °C to reach a similar E value. The maximum E value attained for the commercial HA was approximately 115 GPa when sintered at a higher temperature of 1300-1350 °C.

Attempts to correlate the Young's modulus with bulk density of both the sintered synthesized HA and commercial HA revealed a linear relationship exist as

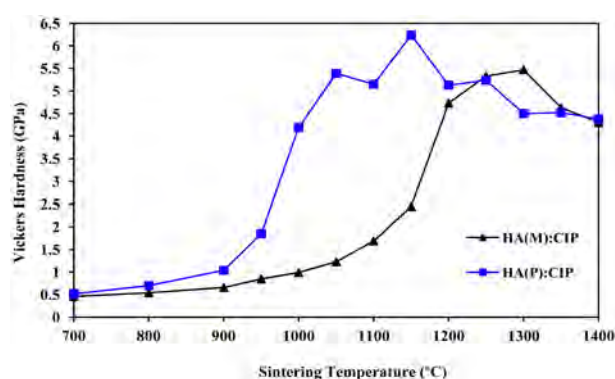


Fig. 6. Effect of sintering temperature on the Vickers hardness of the synthesized HA and commercial HA.

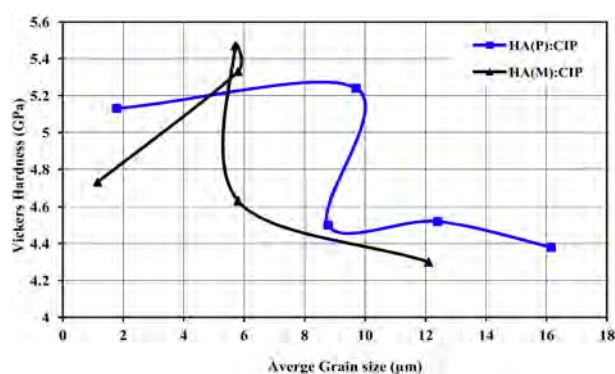


Fig. 7. Vickers hardness dependence on the grain size of hydroxyapatite.

shown in Fig. 4. It is evident that the Young's modulus is governed by the bulk density of HA ceramics.

This result is in agreement with the work of Liu [21] who observed that the Young's modulus of HA was controlled by the pore volume fraction in the sintered body. The author found that the E value decreased from ~ 120 GPa for a dense body to ~ 25 GPa for HA compact containing about 55 vol% porosity. Similarly, Rodríguez-Lorenzo *et al.* [7] also found that flexural modulus of elasticity decreased linearly with a fall in bulk density, i.e. from a high value of 84 GPa for compacts having a porosity of 0.06% to as low as 12 GPa for a porous HA body having a porosity level of 0.69%.

In Fig. 5, the variation in average grain sizes with sintering temperature is presented. Both the HA exhibited a similar grain size trend with increasing temperature, with the synthesized HA exhibiting higher rate of grain growth and larger grain sizes, although the composition determined by XRD was 100% HA phase. For instance, the average grain sizes of compacts sintered at 1200 °C and 1400 °C were 1.78 μm and 16.15 μm for the synthesized HA, as compared to 1.15 μm and 12.10 μm for the commercial HA, respectively. In general, the grain sizes of both the commercial HA and synthesized HA increases by a factor of ~ 5 when the sintering temperature increases

from 1200 °C to 1250 °C, and then remained almost constant between 1250-1250 °C for synthesized HA and between 1250 °C-1300 °C for commercial HA before increasing rapidly with further increased in temperature as shown in Fig. 5.

The effect of sintering temperature on the Vickers hardness of synthesized HA and commercial HA is shown in Fig. 6. It can be noted that the synthesized HA(P) exhibit a large increase in hardness from 900 °C to 1050 °C and reached at maximum value of ~ 6.24 GPa at 1150 °C. On the other hand, the hardness of commercial HA(M) start to increase sharply between 1100-1250 °C and attained a maximum of ~ 5.47 GPa at 1300 °C.

In comparison with the data obtained for the effect of sintering temperature on the sintered densities (Fig. 2), the relative density of HA(M) increased from 53.8% at 700 °C to 98.6% at 1300 °C. This increase in density is clearly reflected in the improved hardness with increasing sintering up to 1300 °C as shown in Fig. 6. However, sintering beyond 1300 °C, the hardness started to decrease although the densities of these compacts above this temperature range was still high, i.e. above 96% of theoretical density as shown in Fig. 2. This decreased in hardness is believed to be associated with a grain size effect as shown in Fig. 7.

Analysis of the results indicated that the hardness of HA increased with grain size and reached a maximum value at a certain grain size limit (d_c). Thereafter, the H_v started to decrease with increasing grain size resulting from sintering at higher temperature. A similar trend was observed for the synthesized HA(P).

Based on the results presented, it is hypothesis that below some critical grain size of d_c the hardness is governed by bulk density (or porosity). In contrast, above d_c the bulk density is not the controlling parameter but rather grain growth. This is evident from Fig. 7, where the d_c for the HA(M) and HA(P) in the present work was found to coincide at about ~ 6 μm and ~ 10 μm respectively. However, more work is in progress to elucidate the actual mechanism controlling the grain size effect on the hardness of HA.

Conclusions

The following conclusions can be drawn from the present work:

1. The sinterability of a high purity, single-phase HA powder produced in this study by a wet chemical precipitation reaction, was significantly greater than for a commercial HA powder.
2. The X-ray diffraction signatures of the synthesized HA compared very favorably with that of a stoichiometric HA. Decomposition of HA phase to form tri-calcium phosphate, tetra tri-calcium phosphate and calcium oxide was not observed in the present work for both powders.

3. The temperature for the onset of sintering and the temperature required to achieve densities above 98% of theoretical value were approximately 150 °C lower for the synthesized HA than the equivalent commercial HA. Accordingly, the maximum density was found at 1300 °C with value of 3.11 Mgm⁻³ (~98.6% relative density) for commercial HA and at 1150 °C with value of 3.12 Mgm⁻³ (98.9% relative density) for synthesized HA.
4. In general, the synthesized HA was harder than the commercial HA, i.e. the maximum Vickers hardness measured was 6.36 ± 0.53 GPa for HA (S) when sintered at 1150 °C as compared to 5.57 ± 0.25 GPa for the HA (C) when sintered at a higher temperature of 1300 °C.
5. The effect of sintering temperature on the sintered densities of the two materials was reflected in the Vickers hardness values up to the point where the material has attained >97% of theoretical density. Sintering beyond this point, i.e. 1150 °C and 1300 °C for the synthesized HA and commercial HA, respectively, the hardness was not governed by density effect but believed to be associated with a grain size effect.

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