SINTERING BEHAVIOR OF HYDROXYAPATITE CERAMICS PREPARED BY DIFFERENT ROUTES

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ABSTRACT

The sintering behaviour of three different HA, i.e. a commercial HA(C) and synthesized HA by wet precipitation, HA(W) and mechanochemical method, HA(M) were investigated over the temperature range of 1000°C to 1350°C. In the present research, a wet chemical precipitation reaction was successfully employed to synthesize highly crystalline, high purity and single phase stoichiometric HA powder that is highly sinteractive particularly at low temperatures below 1100ºC. It has been revealed that the sinterability and mechanical properties of the synthesized HA by this method was significantly higher than that of the commercial material and HA which was synthesized by mechanochemical method. The optimum sintering temperature for the synthesized HA(W) was 1100°C with the following properties being recorded: 99.8% relative density, Vickers hardness of 7.04 GPa and fracture toughness of 1.22 MPam$^{1/2}$. In contrast, the optimum sintering temperature for the commercial HA(C) and synthesized HA(M) was 1300°C with relative density of 98% and 95.5%, Vickers hardness of 5.47 GPa and 4.73 GPa, fracture toughness of 0.75 MPam$^{1/2}$ and 0.82 MPam$^{1/2}$ being measured, respectively.

INTRODUCTION

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ (HA) material has been clinically applied in many areas of dentistry and orthopedics because of its excellent osteoconductive and bioactive properties which is due to its chemical similarity with the mineral portion of hard tissues[1]. Bulk material, available in dense and porous forms, is used for alveolar ridge augmentation, immediate tooth replacement and maxillofacial reconstruction[2]. Nevertheless, the brittle nature and the low fracture toughness (< 1 MPam$^{1/2}$) of HA constraint its scope as a biomaterial in clinical orthopaedic and dental applications[3]. Hence, the development of an improved toughness HA material is required. As a result, various studies have been carried out to improve the mechanical properties of sintered HA[4].

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[4]. 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[1-3]. Among the more prominent methods used to synthesize HA are wet precipitation method, mechanochemical technique, sol-gel technique and hydrothermal. Although numerous studies on HA synthesized via wet precipitation technique and mechanochemical method are carried out, nevertheless, reports on the sinterability of HA synthesized through these technique are rather scarce. Therefore, the primary objective of the present work was to synthesize a well-defined, crystalline, pure hydroxyapatite (HA) phase using two techniques, i.e. wet precipitation technique and mechanochemical technique. The sinterability of both synthesized hydroxyapatite (HA) was evaluated and compared with a commercially available HA (Merck, Germany).

METHODS AND MATERIALS

In the current work, the HA powder used was prepared according to a novel wet chemical method, hereafter named as HA(W), comprising precipitation from aqueous medium by slow addition of orthophosphoric acid (H_3PO_4) solution to a calcium hydroxide $(Ca(OH)_2)$[5]. The HA powder synthesized by mechanochemical method used in the present work, labeled as HA(M), was prepared according to the method reported by Rhee[6]. The starting precursors used were commercially available calcium pyrophosphate, $Ca_2P_2O_7$, and calcium carbonate, $CaCO_3$. In order to evaluate the sinterability and performance of both the synthesized HA, a commercially available stoichiometric HA powder manufacture by Merck, Germany was also studied, hereafter is known as HA(C). The green samples were uniaxial compacted at about 1.3 MPa to 2.5 MPa 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 over the temperature range of 1000ºC to 1350ºC, with ramp rate of 2ºC/min. (heating and cooling) and soaking time of 2 hours 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 HA powders was determined using a standard Micromeritics® SediGraph 5100 X-ray particle size analyzer. The specific surface area of the powder was measured by the Brunauer-Emmett-Teller (BET) method. The morphology of the starting powder was examined using a Philips ESEM model XL30 scanning electron microscope. The phases present in the powders and sintered samples were determined using X-Ray diffraction (XRD) (Geiger-Flex, Rigaku Japan). 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 Mgm^{-3}. The microhardness (H_v) of the samples was determined using the Vickers indentation method (Matsuzawa, Japan). The indentation fracture toughness (K_{Ic}) was determined from the equation derived by Niihara[7].

RESULTS AND DISCUSSIONS

Within the accuracy of the analysis, the results show that the Ca/P ratio of all the powders studied was within the stoichiometric range of 1.67. Ozeki *et al.*[8] have emphasized the importance of the Ca/P ratio since any deviations from the stoichiometric value would have an adverse effect on the sintered properties of the hydroxyapatite body.

The HA(W) powder consists of a mixture of fine 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 as shown in Figure 1. 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 which was found to break easily using a very low pressing pressure of 1.3-2.5 MPa during powder compaction to form the green body. Due to the soft nature of the powders, attempts to use higher pressures during uniaxial pressing the samples proved to be futile as powders lamination on the die surface was observed and in some extreme cases, a layer of compacted powders separated immediately from the green body upon ejection from the mould.
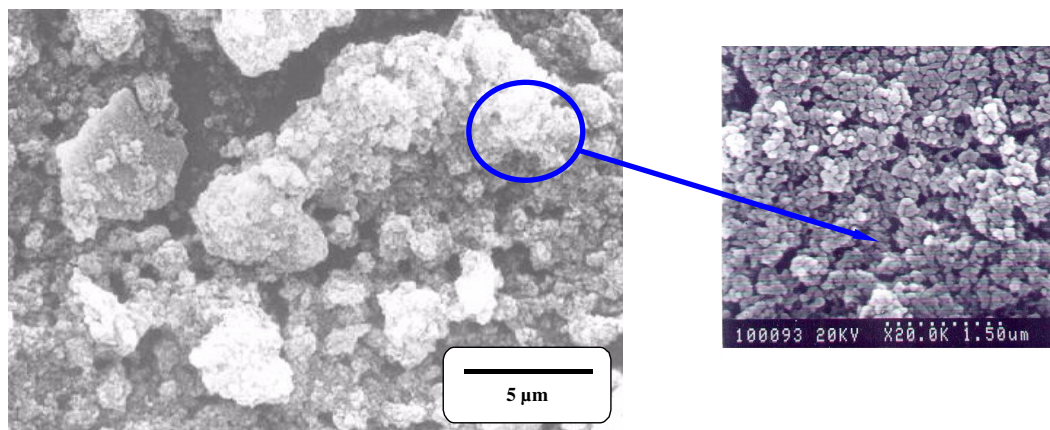
Figure. 1. SEM micrographs of HA(W) revealing the presences of loosely packed particles.

In contrast, although the particle size for powder synthesized by mechanochemical method ranges from 0.5-4 µm diameters, it should be highlighted that the powder consists of hard agglomerates as typically shown in Figure 2. Additionally, "neck" formation could be observed between smaller particles as a result of the heat treatment process carried out on this powder during the synthesis stage.
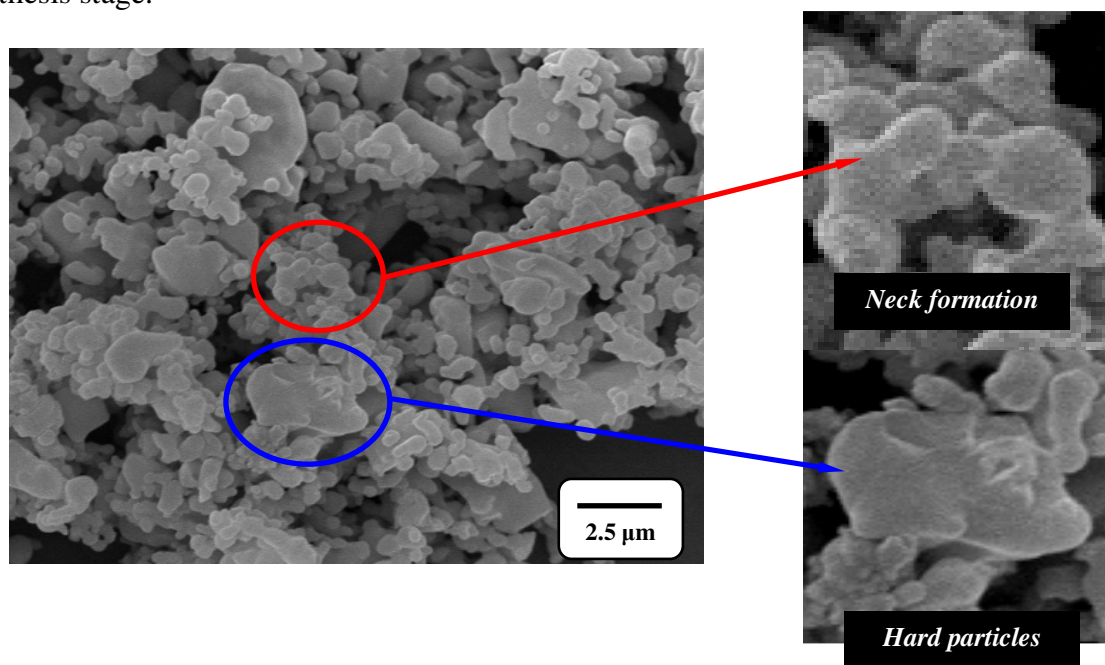

Figure 2. SEM micrographs of synthesized HA(M) revealing neck formation between particles and presences of hard particles.

On the other hand, the HA(C) powder consisted of a mixture of small and large particles as shown in Figure 3. The presences of soft agglomerates could not be observed in the commercial powder but instead the particles appeared to be large, up to 10 µm, and seemed to be more compacted when compared to those observed for the HA powder synthesized by the wet chemical method.
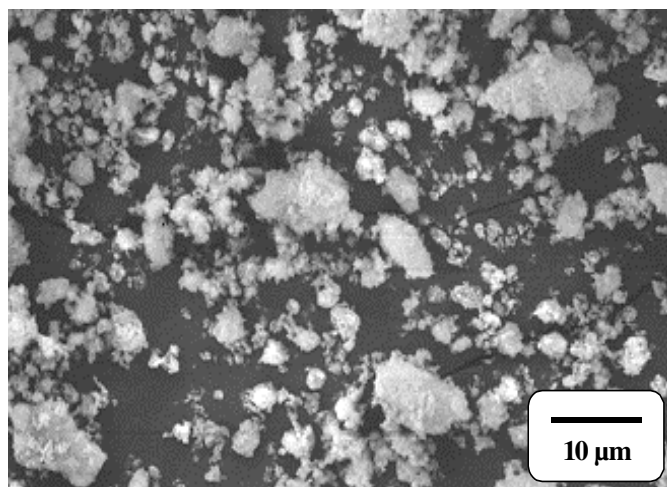
Figure 3. SEM micrographs of commercial HA(C) powders.

X-ray diffraction (XRD) analysis of the synthesized HA(W) and HA(M) powders produced only peaks which corresponded to the standard JCPDS card no: 74-566 for stoichiometric HA as shown in Figure 4 and Figure 5, respectively. The only difference in the XRD patterns of HA(W) and HA(M) powders before sintering was in the degree of crystallinity. The HA(W) XRD patterns indicated the powder was poorly crystalline as shown by the broad diffraction peaks, which is a characteristic of HA prepared by an aqueous precipitation route. This observation is in agreement with that reported by Gibson *et al.*[9] who found that calcination at higher temperature, as in the present case for HA(M) powders, would exhibit a narrower diffraction peaks and not a broad one as observed for the HA(W) powder in the present work.
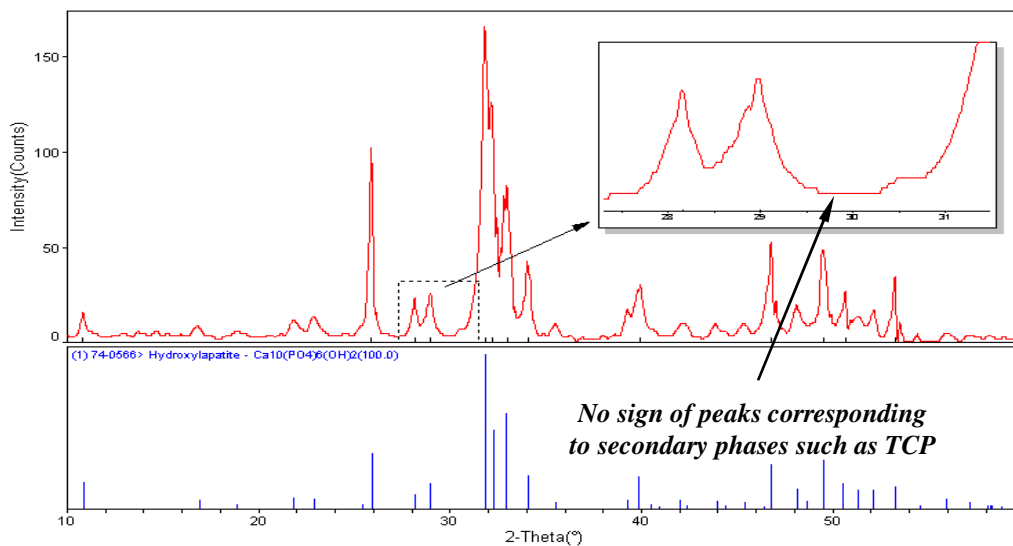

Figure 4. Comparison of XRD patterns of synthesized HA(W) with the standard JCPDS card for stoichiometric HA.
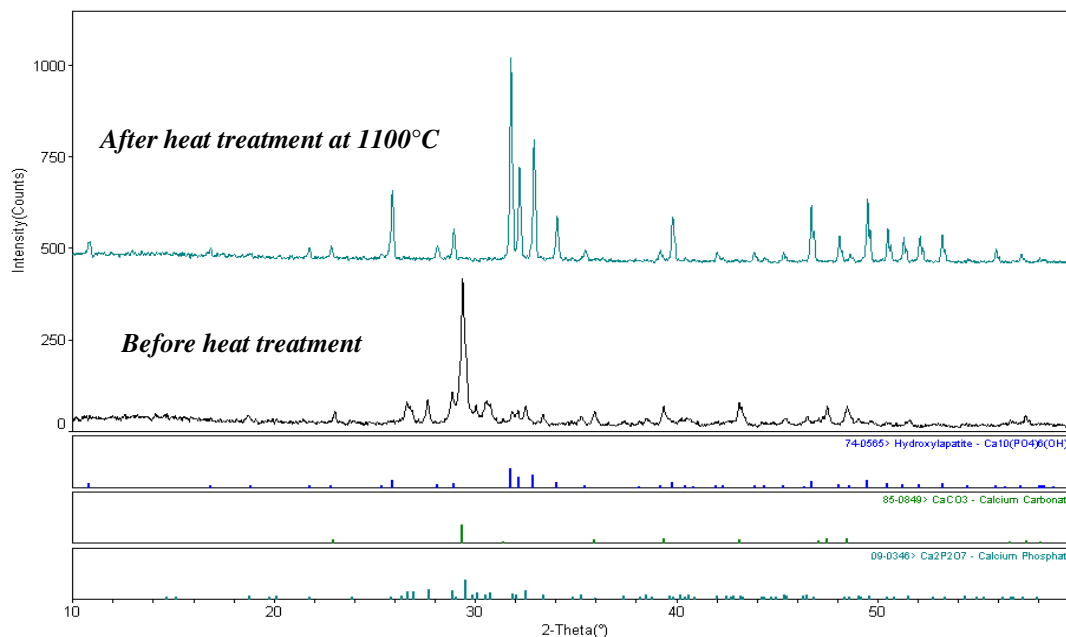
Figure 5. Comparison of XRD patterns of synthesized HA(M) powder before and after heat treatment at 1100°C.

In contrast, powders prepared by mechanochemical process produced a diffraction pattern that indicated a highly crystalline material, with narrow diffraction peaks as a result of heat treatment as typically shown in Figure 5. It should be noted that HA could only be obtained in this powder upon heat treatment at 1100°C. This is shown clearly in Figure 5 where the XRD trace of the prepared powder before heat treatment produced peaks that corresponded to the starting precursors (calcium carbonate and calcium pyrophosphate). Similarly, X-ray diffraction analysis of the commercial powder, HA(C), produced only peaks which corresponded to the standard JCPDS card no: 74-566 for stoichiometric HA.

After sintering in air atmosphere, the commercial HA compacts were observed to have a distinct colour change, i.e. from white (as-received powder) to blue (as-sintered). The intensity of the blue colour was also observed to increase with increasing sintering temperature, i.e. from light blue (1000ºC) to dark blue (1350ºC). It has been reported by Yubao *et al.* [10] that most commercial HA powders contained small additions of impurities and the origin of the apatite blue colour was due to the presence of Mn^{5+} or MnO_4^{3-} ions at the PO_4^{3-} sites in the apatite crystal structure. According to these authors, sintering at high temperature not only increases the intensity of oxidation in the oxidizing atmosphere, but also provides enough energy for the oxidized manganese ion (Mn^{2+} to Mn^{5+}) to migrate within the crystal lattice. This colour change, however was not observed in both the synthesized HA(W) and HA(M) compacts. These materials remained white regardless of sintering temperature.

The effect of elemental impurities on the sinterability of the powders could not be confirmed by this study alone. The change in colour in commercial HA was found to have negligible effect on the HA phase stability as confirmed by XRD phase analysis of the sintered HA in the present work. The sintering of the synthesized HA(W) compacts revealed the present of only HA phase as shown in Figure 6. Similar results were observed for HA(C).
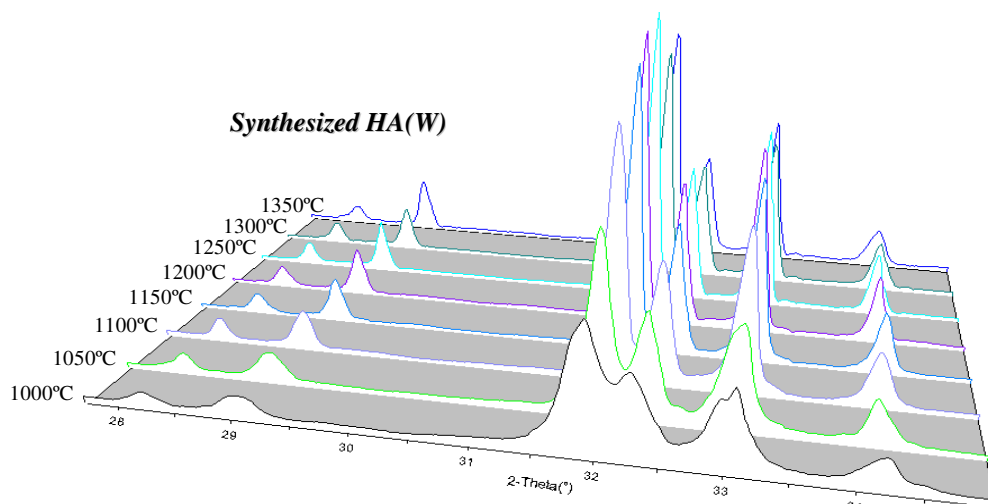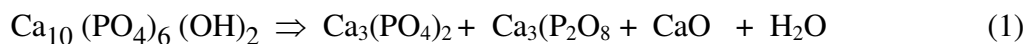
Figure 6. XRD patterns of synthesized HA(W) sintered at various temperatures. All the peaks corresponded to that of stoichiometric HA.

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. Similarly, Liao *et al.*[11] described that HA ceramics would only start to decompose into secondary phases upon sintering beyond 1350ºC.

The present results however are not in agreement with other workers who found that decomposition of HA synthesized by wet precipitation method starts at about 1300ºC [12]. Kothapalli *et al.*[13] have reported that sintering at 1200°C would caused the HA to decomposed into α-TCP {$Ca_3(PO_4)_2$}, β–TCP {$Ca_3(P_2O_8)$} and calcium oxide (CaO) according to Equa.1.

$$Ca_{10}(PO_4)_6(OH)_2 \Rightarrow Ca_3(PO_4)_2 + Ca_3(P_2O_8 + CaO + H_2O \qquad (1)$$

In the present work, decomposition of HA(W) was not observed throughout the sintering regime employed. Additionally, no attempt was made to control the sintering atmosphere and the sintering atmosphere was just plain air (not moisturized). The high local humid atmosphere (i.e. the mean monthly relative humidity falls within 70% to 90% all year around) could have played a role in hindering dehydroxylation in the HA matrix even at 1350ºC. In addition, as the HA was produced by wet chemical route and were not calcined prior to sintering, a significant amount of absorbed water would probably remained in the structure. However, it is not clear if the loss of water during sintering plays a role in suppressing dehydroxylation.

The XRD traces of hydroxyapatite synthesized via the mechanochemical technique also revealed the present of only HA phase as indicated in Figure 7. The present results obtained for the sintered HA(M) samples contradicted the findings of Mostafa[14]. In general, the author reported that the powder which was synthesized using the same technique as the present HA(M) transformed partially

into β-TCP upon sintering at 1100ºC. In another work, Yeong *et al.*[15] has also confirmed that the HA powder synthesized using mechanochemical method transformed partially into TCP when sintered beyond 1200ºC. The difference in the results reported in the literatures as compared to the present work could be attributed to the milling medium used, the milling time and probably due to the high purity of the starting powders. The milling medium used in the current work was water with a milling time of 8 h. Rhee[6] has emphasized the importance of having 100% water content in the milling medium during the mechanochemical synthesis process. Yeong *et al.*[15] have synthesized their HA powder using ethanol as the milling medium and this could be the reason for obtaining secondary phases upon sintering due to insufficient H_2O present in the medium to suppress decomposition activity in the HA structure. Additionally, the milling time employed is another important factor that could influence the sintering behaviour of HA. Kim *et al.*[16] synthesized HA powder by mechanochemical method using water as the milling medium and the milling time was set at 60 minutes. Nevertheless, the authors observed secondary phases in their HA matrix upon sintering.
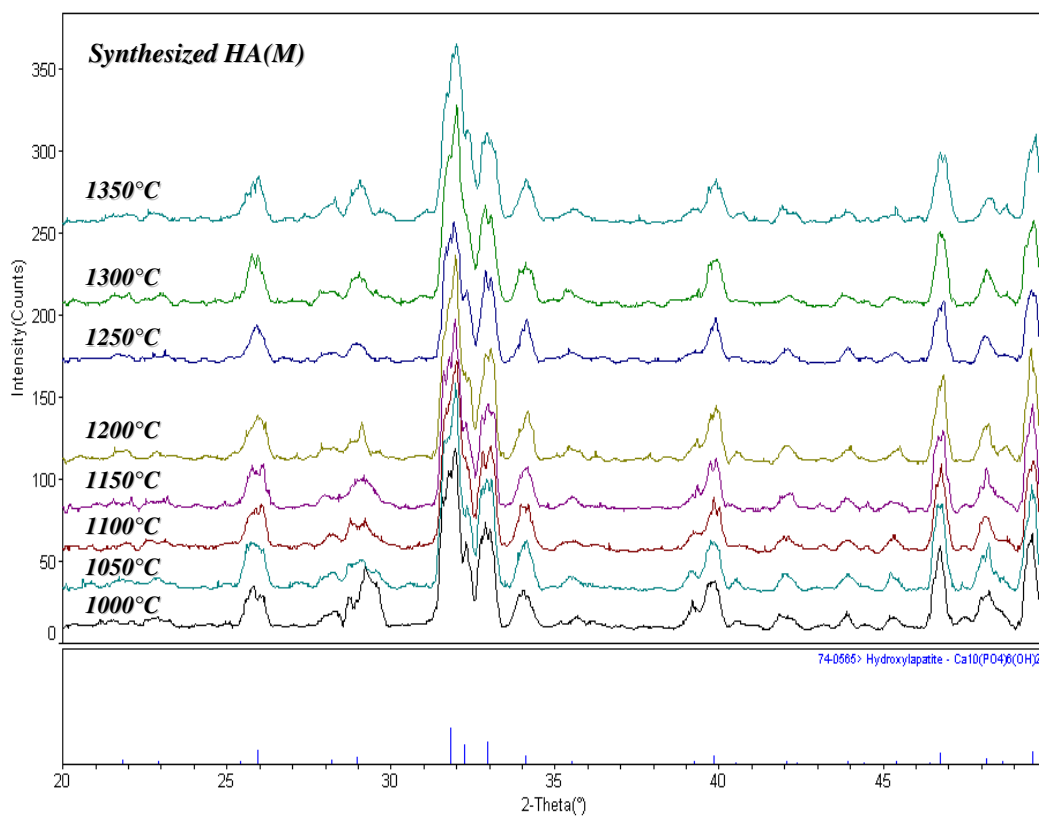

Figure 7. XRD patterns of synthesized HA(M) sintered at various temperatures. All the peaks corresponded to that of stoichiometric HA.

The effects of sintering temperature on the sintered densities of the three HA compacts are shown in Figure 8. All samples were heated to the chosen sintering temperature at 2ºC/min. and, after a dwell time of 2 h, cooled to room temperature at 2ºC/min..

In general, the bulk density increases with increasing sintering temperature regardless of the type of powder studied. A small increase in density is observed before the onset of densification and this corresponds to the first stage of sintering, where necks are formed between powder particles. The second stage of sintering corresponds to densification (onset of densification) and the removal of most of the porosity. The onset of densification, indicated by a sharp increase in the sintered density, for HA(M) and HA(C) was between 1100ºC and 1200ºC. In the case for HA(W) samples, sintering were carried out from 700ºC so as to determine the onset densification temperature. As shown in Figure 8, this temperature was found to be between 900ºC and 1000ºC. Generally, sintering above this range resulted in very small increased in density which is associated with the final stages of sintering where small levels of porosity are removed and grain growth begins.
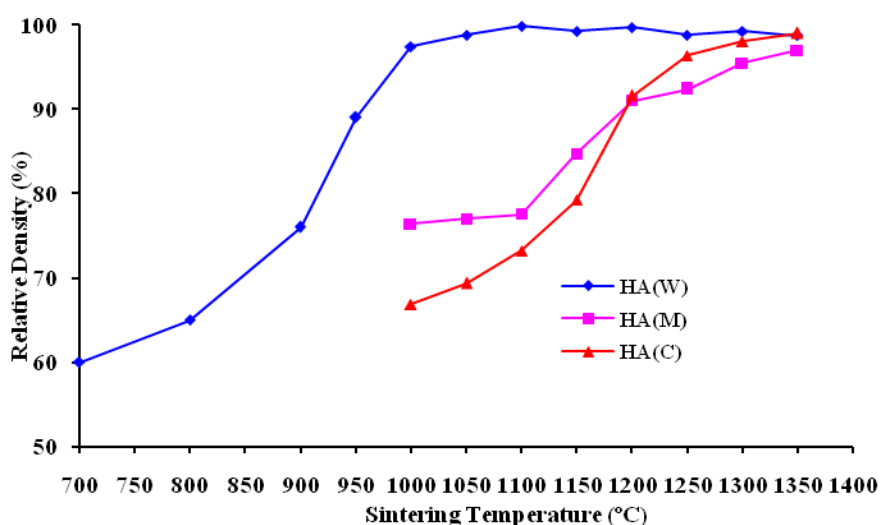

Figure 8. Effect of sintering temperature on the relative densities of HA(W), HA(M) and HA(C) samples.

The synthesized HA by wet precipitation method achieved a final sintered density of 97-99% of theoretical density at 1050-1100ºC, whereas the commercial HA required a sintering temperature of 1250-1300ºC to attain a similar density. In general, these results indicate that HA synthesized by wet precipitation method are more sinteractive than the commercial HA. The fact that HA(W) shows improved relative density as compared to HA(C) could be attributed to the physical basis of the Herring law of sintering that suggest sintering rate at a given temperature is inversely proportional to the square of the powder particle size. In the present study, the particle size measured using particle size analyzer for HA(W) and HA(C) are 1.78 ± 0.22 µm and 3.26 ± 1.53 µm respectively. Thus, the smaller the particle size, the easier would be for the powder to achieve high density when sintered at the same temperature.

As for HA(M), the highest relative density of 98% could only be attained when the material was sintered at 1350ºC. In general, the densification behaviour of HA(W) was more superior to that of HA(M). This could be attributed to the higher surface area of 60.74 m^2/g for HA(W) which promoted a large driving force for densification as compared to a low 2.68 m^2/g for HA(M). Furthermore, the spherical nano particles of HA(W) as observed within the larger agglomerates (Figure 1) would have a

higher heat transfer area and thus accelerate densification upon sintering. In contrast, HA(M), which consists of hard agglomerates (Figure 2), could have led to a lower packing density in the green state and hence poor sintering behaviour.

The effect of sintering temperature on the Vickers hardness of the three HA is shown in Figure 9. Throughout the sintering temperature range studied, it can be noted that HA synthesized by the wet chemical precipitation method displayed superior hardness as compared to HA synthesized by mechanochemical method and commercial HA. The hardness for HA(W) increased as the sintering temperature was increased and reached a maximum value of about 7.24 GPa when sintered at 1150ºC. Further sintering above 1150ºC resulted in deterioration in the hardness. On the other hand, the hardness of HA(C) started to increased sharply between 1100-1250ºC and attained a maximum of 5.47 GPa at 1300ºC as shown in Figure 9. This trend is similar for HA(M) which achieved a maximum hardness of 4.73 GPa when sintered at 1300ºC. Nevertheless, a decreased of hardness was observed for both HA(C) and HA(M) samples when sintered beyond 1300ºC.
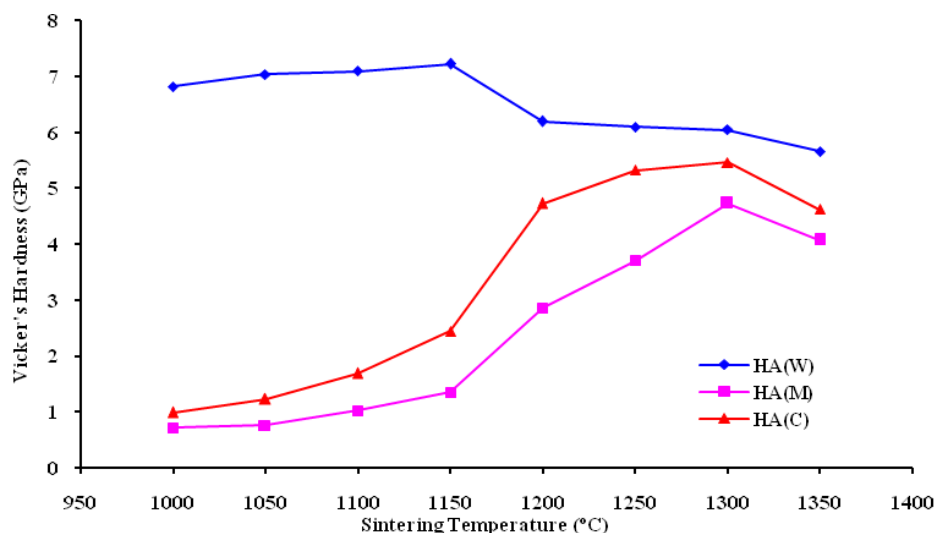

Figure 9. Effect of sintering temperature on the Vickers hardness of hydroxyapatite.

The effects of sintering temperature on the fracture toughness of compacts of three different HA powders are shown in Figure 10. In general, HA(W) exhibited better fracture toughness values as compared to both HA(M) and HA(C) throughout the sintering temperature range studied. The synthesized HA(W) by wet precipitation method achieved maximum K_{Ic} value of 1.22 MPam$^{1/2}$ when sintered at 1100ºC. Further sintering at higher temperature would cause a decreased in the toughness as shown in Figure 10. In comparison, both HA(M) and HA(C) could only achieved maximum K_{Ic} of 0.82 MPam$^{1/2}$ and 0.77 MPam$^{1/2}$, respectively when sintered at 1300ºC.
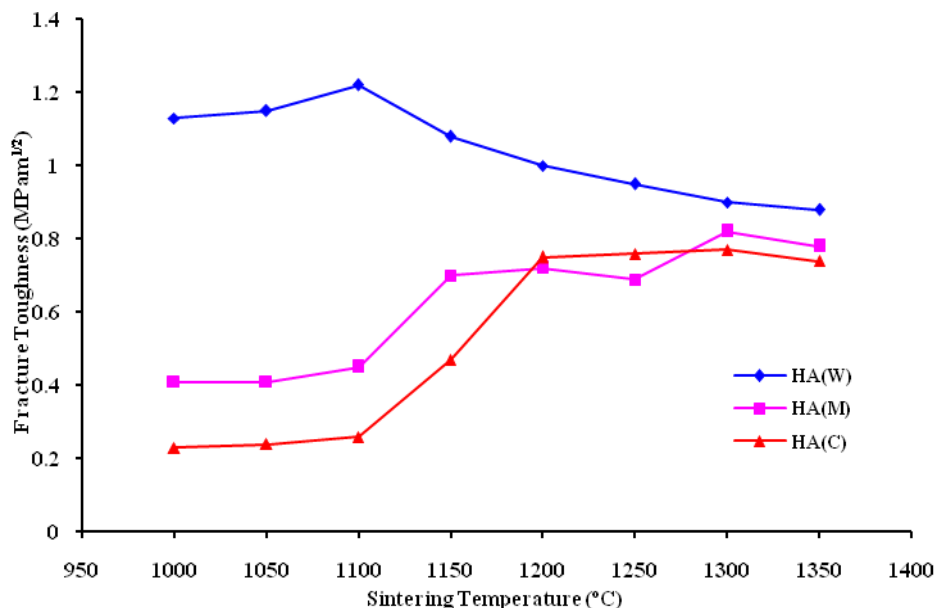
Figure 10. Effect of sintering temperature on the fracture toughness of HA.

In general, the maximum K_{Ic} values for most HA reported in the literature varied between 0.96-1.0 MPam$^{1/2}$ [17-19]. Thus, the high value of 1.22 MPam$^{1/2}$ obtained in the present work for HA(W) when sintered at 1100ºC is very encouraging. It is believed that this improvement in fracture toughness in the present HA(W) could be attributed to the improved properties of the starting synthesized HA powder.

Generally, although the chemical and phase compositions of the powders studied were similar, the powder morphology and particle size distribution are very different. It is believed that the different powder characteristics are largely a result of the different powder processing methods used and these differences are evident in the sintering characteristics of the powders.

CONCLUSION

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 powder synthesized via mecahnochemical technique and a commercial HA powder. The X-ray diffraction signatures of both the synthesized HA studied 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 all the powders. It has been revealed that the sinterability in terms of density, Vickers hardness and fracture toughness of the synthesized HA via precipitation method was significantly greater than that of the synthesized HA using the mechanochemical method and the commercial HA.

ACKNOWLEDGEMENTS

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