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Influence of temperature and aging time on HA synthesized by the hydrothermal method

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The influence of temperature and aging time on the morphology and mechanical properties of nano-sized hydroxyapatite (HA) synthesized by a hydrothermal method is reported here. The pre-mixed reactants were poured into a stirred autoclave and reacted at temperatures between 25–250 °C for 2–10 h. HA powders thus obtained were examined using X-ray diffraction (XRD), high-resolution field emission scanning electron microscopy (FESEM) and a particle size analyzer. It was found that the aspect ratio of the particles increased with the reaction temperature. The length of the HA particles increased with the reaction temperature below 170 °C, but it decreased when the temperature was raised above 170 °C. The agglomerates of HA particles were formed during synthesis, and their sizes were strongly dependent on reaction temperatures. As the reaction temperature increased, the agglomerate size decreased ($p = 0.008$). The density of the discs pressed from these samples reached 85–90% of the theoretical density after sintering at 1200 °C for 1 h. No decomposition to other calcium phosphates was detected at this sintering temperature. A correlation existed ($p = 0.05$) between the agglomerate sizes of HA particles synthesized at various conditions and their sintered densities. With the increase of the agglomerate size, the sintered density of the HA compact decreased. It was found that both the sintered density and flexural strength increased with increasing aging time and reaction temperature. A maximum flexural strength of 78 MPa was observed for the samples synthesized at 170 °C for 5 h with the predicted average at these conditions being 65 MPa. These samples attained an average sintered density of 88%.

1. Introduction

Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, is idealized as the main mineral or inorganic component of bones and teeth [1, 2]. Combined X-ray diffraction, infrared spectroscopy and chemical analyses demonstrate that bone and tooth apatite is not pure HA but can better be described as carbonate-hydroxyapatite (CHA) approximated by the formula $(Ca, Na, Mg, K)_{10}(PO_4, CO_3, HPO_4)_6(OH, Cl)_2$ [3, 4]. The similarity in composition to bone mineral and the osteoconductivity and bioactivity of HA have made it an excellent biomaterial for bone repair and substitution and for orthopedic and implant coating [1–3, 5, 6]. However, owing to its mechanical weakness and brittleness [7–9], applications of HA have been confined primarily to those involving low mechanical stress.

Hydroxyapatite can be synthesized in a number of ways, including the wet chemical process [10, 11], the hydrothermal method [12], the use of sol-gel procedures [13, 14], the solid-state reaction [15, 16], and emulsion or micro-emulsion routes [17]. Among these methods, the wet chemical process has been used widely. However, it has been reported that the microstructure and properties of the HA prepared using a wet method may vary greatly with pH, temperature and concentration of the reactants [11, 18–21]. The properties of HA powder, such as crystallinity, morphology and particle size, will influence the effectiveness of the powder in its final application [19].

Numerous studies have dealt with the toughening of ceramic matrices by adding whiskers or fibers of SiC and alumina. When this technology is applied to HA, a

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decrease in biocompatibility and bioactivity is observed [18]. The low dislocation density of whiskers generally leads to high tensile properties [22]. This problem can be overcome by synthesizing HA particles with high aspect ratios. The high aspect ratio particles act as self-reinforcing fibers. Hence there is abundant interest in using the hydrothermal method to synthesize HA with high aspect ratios, and consequently possessing the desired strength and thermal stability for application in a variety of biomedical parts.

A wide range of experimental conditions for preparing HA by the hydrothermal method has been reported [19–21], though the HA thus synthesized has exhibited relatively low crystallinity and has possessed other phases. Zhang *et al.* [23] have prepared HA whiskers using varied operation temperatures, soaking times and reactant concentrations in a moderately acidic solution. However, long synthesis periods (70–120 h) were used in the study. Furthermore, the decomposition of HA into various phases of calcium phosphates at relatively low sintering temperatures was observed. Liu *et al.* [12] studied the effect of the pH of the reacting solution and reaction temperature on HA particles. It was found that at pH = 9 and 120 °C, HA crystals with an aspect ratio around 10 were obtained. Unfortunately, the effect of the reaction time on HA particles was not included in this study. In the current study, we systematically examined the effect of reaction temperature and aging time on the particle size and mechanical properties of HA synthesized by the hydrothermal method.

2. Materials and methods

2.1. Preparation of HA

Calcium nitrate (99% pure, Sigma) and ammonium hydrogen orthophosphate (99% pure, Sigma) solutions were prepared at a concentration of 1.0 g/dL and the pH of each solution was brought up to 12 by adding strong ammonia (Sigma, ACS reagent). The phosphate solution was added to the calcium solution at a rate of 50 mL/min at room temperature and the mixture was poured into an autoclave with the reaction conditions controlled by an external setup. The 1-L stainless steel autoclave featured a stirrer driven by a magnetic coupling and a thermocouple to measure the temperature of the charge. After initial loading, the autoclave was heated with a band heater to the desired temperature at a heating rate of 5 °C/min and then the temperature was kept constant at the desired level. No initial pressure was applied in the autoclave and the air initially present was not flushed out. The parameters investigated were confined to reaction temperature and aging time in the autoclave.

The precipitates were formed in the autoclave from the mixture, which was stirred continuously and maintained at the designed reaction temperature and duration. The mixture was cooled to room temperature by natural cooling, whereupon the precipitates settled to the bottom of the autoclave. The recovered solids were washed with distilled water until all traces of ammonia were removed. The product was dried at 80 °C overnight in an oven and ground into a fine powder using a mortar and pestle. Table I describes the notation used for the HA samples prepared at various temperatures and aging times of operation.

TABLE I Codes and preparation conditions of the samples studied in this work at various conditions

Reaction temperature (°C)	Aging time, (h)		
	2	5	10
25	25-2	25-5	25-10
70	70-2	70-5	70-10
100	100-2	100-5	100-10
130	130-2	130-5	130-10
170	170-2	170-5	170-10
200	200-2	200-5	200-10
250	250-2	250-5	–

2.2. Characterization of HA particles

X-ray diffraction (BRUKER AXS D5005) equipment with a copper target was used to identify the phases produced in the resulting HA powders. A step size of 0.02° and a scan speed of 1.0°/min were used while the voltage and current were held at 40 kV and 40 mA, respectively. Data were collected over the 2θ range from 10–70°. Both the as-prepared and sintered specimens (at 1200 °C) were analyzed using X-ray diffraction. The particle size and morphology of the HA precipitates were investigated using a JEOL JSM-6335F (15 kV) field emission scanning electron microscope (FESEM). Microscopy samples were prepared by dispersing the HA particles in ethanol, and dropping the HA solution onto a copper mesh covered with a thin carbon film. The FESEM images provided the basis for measuring the particle dimensions and hence, aspect ratio. Agglomerate sizes of the particles, which had formed during the powder processing, were obtained using a dynamic light scattering technique (NICOMP 380/DLS Particle Analyzer).

2.3. Preparation of sintered discs

HA powders prepared at different temperatures and reaction times were hydrostatically pressed into 12.5-mm-diameter discs at a pressure of 150 MPa for 1 min and sintered in air at 1200 °C for 1 h with a heating rate of 5 °C/min. Nine discs in each group were prepared, and the average bulk density of each specimen before and after sintering was calculated by measuring its weight and size. XRD was used to examine the composition of the sintered specimens. The biaxial flexural strength of sintered specimens was measured using an Instron testing machine according to ASTM C 1499-03.

3. Results

3.1. XRD patterns of HA particles

Fig. 1 shows an XRD pattern of the HA powder synthesized at the different temperatures and times. The (100), (200) and (300) reflections of the particles perfectly matched with the JCPDS card 9-432 for HA, suggesting that pure HA was obtained for all the

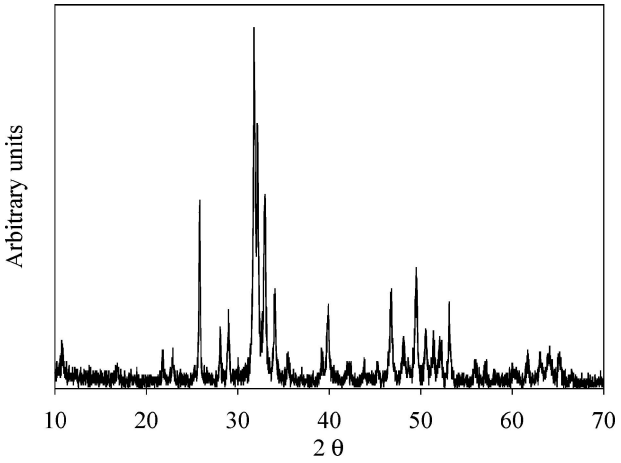

Figure 1 Typical XRD pattern for the HA particles.

samples prepared at varied conditions. After sintering at 1200 °C for 2 h, no decomposition was observed in any of the sintered HA samples.

3.2. Particle size and shape

FESEM images of selected samples are shown in Fig. 2. It was observed that the morphology of HA crystals was dependent on the reaction temperature. These images also provided the basis for subsequent particle size distribution analysis. Table II summarizes the average particle dimensions of HA synthesized at various conditions. It can be inferred from Table II that at a constant aging time, as the reaction temperature increased, the particle size and aspect ratio also increased.

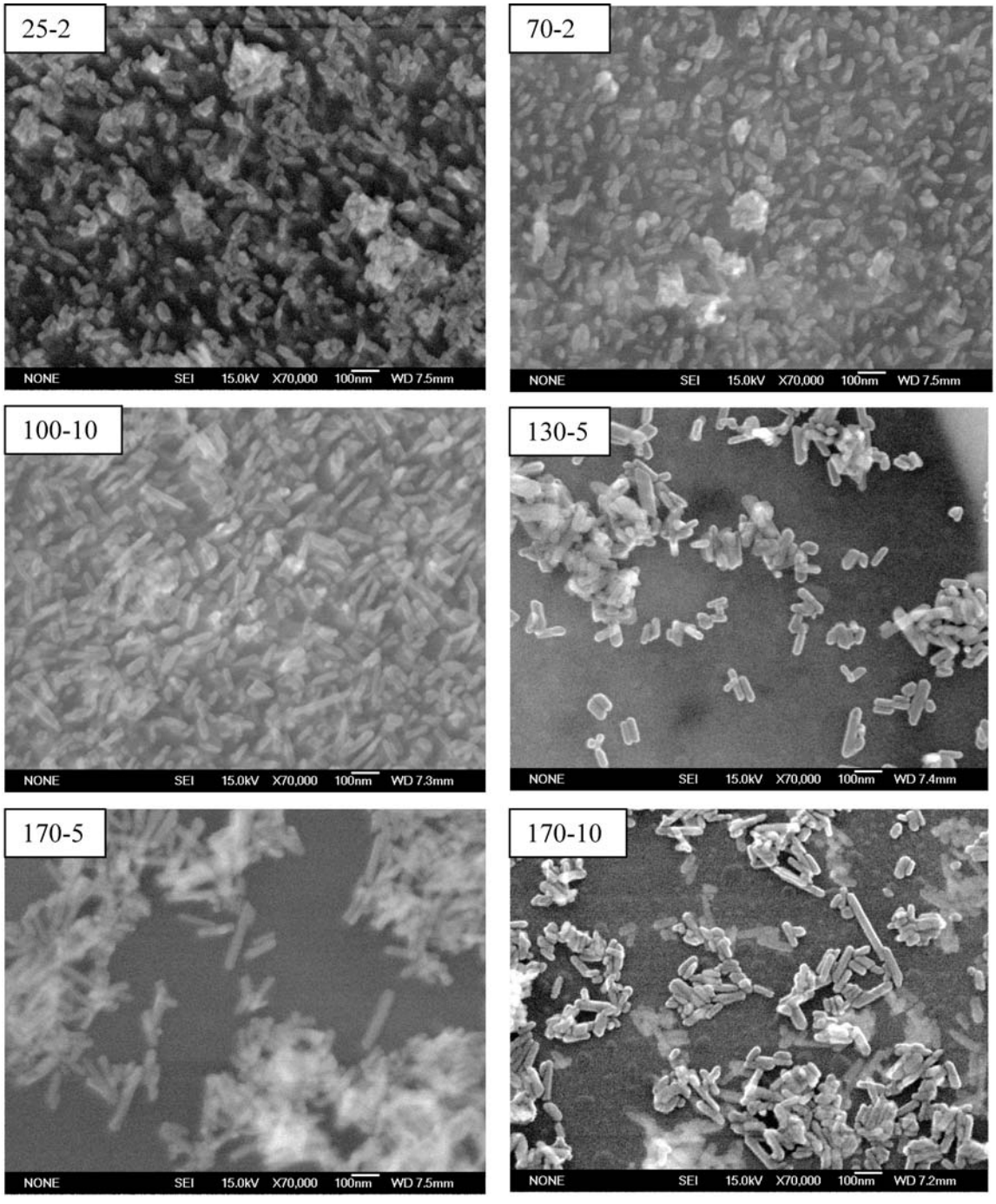

Figure 2 FESEM images of the particles.

TABLE II HA particle size and aspect ratios based on FESEM images of the particles

Time (h)	2			5			10		
Temp (°C)	Length (nm)	Breadth (nm)	Aspect ratio	Length (nm)	Breadth (nm)	Aspect ratio	Length (nm)	Breadth (nm)	Aspect ratio
25	50	20	2.5	60	20	3	85	40	2.125
70	60	20	3	60	20	3	90	30	3
100	60	20	3	70	30	2.33	90	20	4.5
130	60	25	2.4	70	20	3.5	110	25	4.4
170	100	20	5	150	25	6	100	30	3.33
200	70	20	3.5	100	20	5	70	30	2.33
250	100	30	3.33	50	20	2.5			

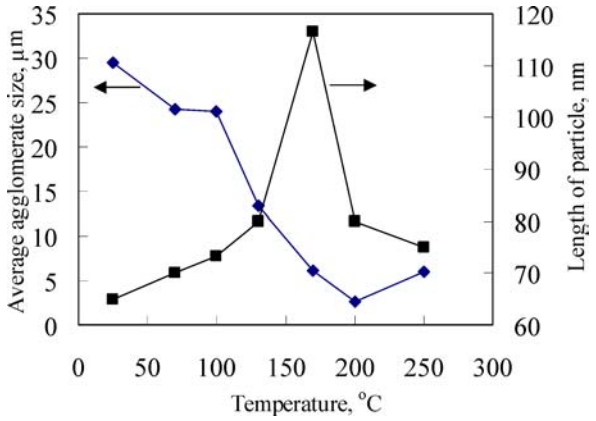

Figure 3 Agglomerate size variation of HA particles with aging time and temperature.

3.3. Agglomerate size

The hydrothermally prepared HA particles formed into agglomerates during the drying process. The agglomerate sizes of the particles synthesized at varying aging times were averaged for each temperature; these averages are plotted in Fig. 3. As the reaction temperature increased, the agglomerate size decreased ($p = 0.008$). It can also be observed that the length of the HA particles increased till the reaction temperature reached 170 °C, but after that it decreased.

3.4. Bulk density

The average bulk densities of HA discs after sintering at 1200 °C for 2 h are plotted in Fig. 4. Though a curvature seemed to have existed with all the significant parameters, more experiments need to be done to confirm the systematic influence of temperature and aging time on the sintered density. Results suggest that the sintered density increased with increasing aging time ($p = 0.005$) and reaction temperature ($p = 0.017$). While the bulk density of the discs pressed from all samples possessed 43–52% of the theoretical density (3.16 g/cm^3) before sintering, the density reached 85–90% of the theoretical density after sintering at 1200 °C. It is evident from Fig. 4 that the samples 100–10 exhibited the maximum sintered density, i.e., 2.85 g/cm^{3}while the samples 25-2 showed the lowest density among all the samples tested. Fig. 5 shows the agglomerate size of HA particles synthesized at various conditions and their sintered densities, which demonstrated a weak relationship between the agglomerate size and synthesizing conditions. The

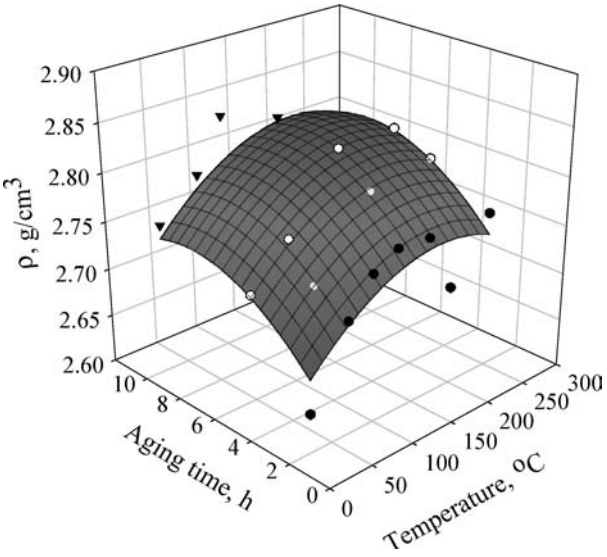

Figure 4 Bulk density of HA samples after sintering as a function of aging time and temperature.

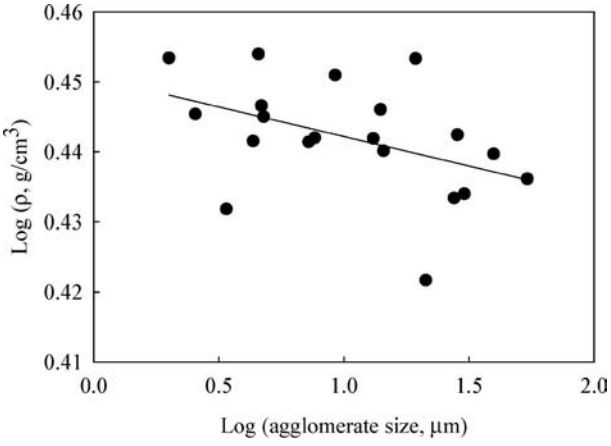

Figure 5 Correlation between density and agglomerate size of HA particles synthesized at various conditions.

powder with a small agglomerate size compacted more efficiently than large agglomerate sized powders, so the former had a relatively higher sintered density than the later at the same sintering temperature. Higher sintering temperatures, such as 1300 °C, might result in more dense compacts, provided the HA does not decompose at this temperature.

3.5. Biaxial flexural strength

The biaxial flexural strength of the HA discs sintered at 1200 °C was plotted as a function of aging time and

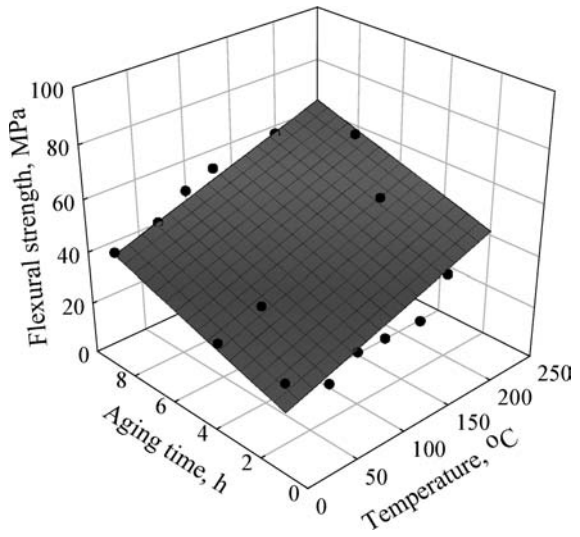

Figure 6 Flexural strength of the sintered HA samples as a function of aging time and reaction temperature.

reaction temperature as shown in Fig. 6. It was found that as both the reaction temperature and aging time increased, the strength of HA discs increased ($p = 0.007$ and $p = 0.006$ respectively). The observed maximum flexural strength of 78 MPa for the sample 170-5 was consistent with that reported by Ruys *et al.* [28] who also used ring-on-disc method to measure the flexural strength of HA.

4. Discussion

The flexural strength of HA has been measured by many research groups [7–14]. Among these studies, the HA powders were either commercially available or synthesized by different approaches, such as wet synthesis [10, 24–26], hydrothermal synthesis [12] and solid-state reaction [15, 16]. The HA powders were formed into shapes by various techniques, such as injection molding [27], uniaxial pressing [28], cold isostatic pressing [30] or hot isostatic pressing [31]. Two major testing methods—three-point bending [25] and ring-on-disc [29]—have been used to measure the flexural strength of HA. Due to the difference in particle size, powder synthesizing methods, shaping methods before sintering, sintering temperatures, and mechanical testing methods, a broad range of flexural strengths have been reported, ranging from 13 MPa for injection molded HA to 250 MPa for hot isostatically pressed HA [31].

In the current study, a hydrothermal method was used to prepare HA powders under different reaction conditions. The powders were uniaxially pressed, and tested by a ring-on-disc method. These procedures are similar to those employed by Ruys *et al*. [28], who achieved a sintered density of 95% and an average flexural strength of 80 MPa at 1150 °C. An equivalent average strength of 78 MPa was obtained in the current study while the sintered density of the corresponding samples was only 90%. Liu *et al.* [12] synthesized HA hydrothermally using $Ca(OH)_2$ and $Ca(H_2PO_4)_2{\cdot}H_2O$, and calcium-deficient HA was formed. They observed a sintered (at 1200 °C) density of 98% and a flexural strength of 120 MPa using a three-point bending test. It is apparent that a higher flexural strength would be obtained if a higher sintered density were achieved in the current work.

It was found in our study that the sintered density was inversely proportional to the agglomerate size of the HA particles. The powder with smaller agglomerate size had higher sintered density at the same sintering temperature. This is in accord with the basic Frenkel theory of glass sintering [32] which predicts that:

$$x/a = [3\gamma t/2a\eta]^{1/2} \quad (1)$$

where degree of sintering is expressed as the ratio of radius of the inter-particle interface (x) and initial particle size (a) depends on: the surface tension (γ), viscosity (η, which is only slightly dependent on temperature) and the time of sintering (t). Assuming constant surface tension and viscosity at a given temperature, the inverse square root dependence on particle size suggests that small particles achieve higher theoretical densities.

It has been reported that less agglomerated HA powders can be prepared using dispersant agents, such as cationic and anionic surfactants [33]. The sintered density might also be improved using different powder-shaping techniques before sintering and programmed heat-treatment settings during the sintering. However, Gibson *et al.* [34] reported that compaction pressure, sintering time, sintering rate only affected the sintered density of calcined HA powders, and had no influence on the density of uncalcined HA. Sintering temperature was the only factor that had significant impact on the sintered density of HA. In general, HA decomposes at a sintering temperature of 1200–1400 °C, according to the reaction:

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 3Ca_3(PO_4)_2 + CaO + H_2O \uparrow \quad (2)$$

The reaction product, tricalcium phosphate, is more resorbable *in vivo* than HA. In order to control the bioabsorption rate, we need to monitor the composition of the implant. To achieve pure HA, the samples have to be sintered below the decomposition onset temperature. However, the density of HA does not increase appreciably until the sintering temperature reaches approximately 1000 °C. It is known that the smaller the HA agglomerates used, the lower the sintering temperature required to achieve a high sintered density, and the less likely to induce the decomposition of HA. Thus, using nano-sized HA may lead to high sintered density at a relatively low sintering temperature. Nano-sized HA particles were obtained in the current study, but they agglomerated during the later powder processing. It was found that the smaller precipitates formed relatively larger agglomerates. This is consistent with the finding of Kothapalli *et al*. [18] for the HA powders synthesized by a wet process.

5. Conclusions

The effect of the two crucial experimental parameters, aging time and reaction temperature, on the morphology and mechanical properties of HA has been studied.

HA particles with varying sizes and aspect ratios were successfully synthesized using the hydrothermal method. As the reaction temperature increased up to 170 °C, the length of the HA particles increased and the corresponding agglomerate size of the particles decreased. The sintered density and flexural strength increased with increasing aging time and reaction temperature. The density reached 85–90% of the theoretical density after sintering at 1200 °C. It was found that the powder with smaller agglomerate size had higher sintered density at the same sintering temperature, which is in accord with the Frenkel's theory of sintering. A maximum flexural strength of 78 MPa was observed for the sample synthesized at 170 °C for 5 h with the predicted average at these conditions being 65 MPa. It can be concluded that the HA thus synthesized can be used in applications involving load-sharing applications due to its high flexural strength.

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