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The Effect of Calcination Temperature on the Behaviour of HA Powder for Injection Moulding

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Abstract: Hydroxyapatite ($Ca_{10}(PO_4)6(OH)_2$) ceramic bars have been prepared by injection moulding. In this process, calcination treatment was used to reduce the fine fraction of the starting hydroxyapatite powder to improve the packing density and the flowability behaviour. The effect of different calcination temperatures on the powder characteristics, shaping by injection and sintering was investigated. The results show that a higher calcination temperature is beneficial for shaping but delays the sintering. The optimum calcination temperature obtained in this study is 900 °C and that for 50 v/o solid loading feedstock, 43 MPa of 4-point bending strength and a Weibull modulus of 10.62 are obtained. © 1997 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), HA, is the major component found in human hard tissues like bone and teeth and therefore holds great promise as biomaterials.[1–3] Sintered HA has potential for application as artificial tooth roots, a catalyst used for dehydrogenation and dehydration of primary alcohols to aldehydes and ketones[4] and in electrical application like CO_2 sensor,[5] etc.

Most of the studies about HA are devoted to the knowledge of the chemico-physical and biological interaction with the surrounding tissues; in the literature there is a lack of knowledge about the processing parameters and material characteristics of hydroxyapatite.

Powder injection moulding is a manufacturing process capable of producing high performances and complex shaped ceramics, metals in massive form.[6] The method is composed of the following major steps: powder mixing, moulding, debinding and sintering. The process parameters for injection moulding should be optimized to achieve the highest volume loading of ceramic powder in the feedstock to give a high green density and less binder to remove.

Very fine as-received HA powder is difficult for shape forming, no matter press-forming, slip casting[7,8] or injection moulding, etc. In preliminary study, it was found that the feedstock of HA and binder can not be achieved until the solid loading is as low as 30 v/o. The aim of this research is to study the effect of calcination temperature on the HA powder and subsequent injection moulding process.

2 EXPERIMENTAL

Extra pure reagent HA (Hayashi, Japan) was used as a starting material. The HA powder was calcined in an oven with SiC heater at a rate of 5 °C/min to 700, 800, 900 and 1000 °C, respectively, for 4 h. The calcined HA was then sieved through 60 mesh for subsequent use.

The ratio of binder components used for injection are 65:10:10:10:5 for paraffin wax, LDPE, HDPE, EVA and SA, respectively, as listed in Table 1. Mixtures of HA and binders were prepared by using a sigma-type blade kneader rotated at 50 rpm. The HA powder was initially added into the kneader and pre-heated at 150 °C for 30 min to

Table 1. The components of the binder mixed with hydroxyapatite

Binder	Source	Density (kg/m^3)
NA208 (LDPE)	USI Far East Co., Taiwan	895
LS606 (HDPE)	USI Far East Co., Taiwan	924
ELVAX770 (EVA)	Du-Pont Inc., USA	930
YHZG-2 (Paraffin wax)	Nippon Oil Co., Japan	780
Stearic acid	Merck, Germany	941

achieve homogeneous temperature distribution. The binders were then subsequently added and the mixing was continued for 90 min. Granules were obtained by continuously rotating the blade during the cooling process.

Rectangular test bars with dimensions 80×5×4 mm were injection moulded at barrel temperature 140 °C and the die temperature was kept at 30 °C. The test bars were then treated with two stage debinding method which involved immersion in hexane of 50 °C followed by thermal debinding at a heating rate of 1 °C/min to 600 °C for 1 h and then heating to sintering temperature with a heating rate of 5 °C/min for 1 h.

The sintered test bars were ground (1000 grit) on both sides for 4-point bending test. Bending strength measurements were made with a strength testing machine (AGS-500D, Shimadzu, Japan) using 4-point loading at a loading rate of 0.5 mm/min with 30×10 mm span.

The flow behaviour of the powder mixtures was measured with a capillary rheometer (Galaxy III-9052, Kayeness, USA), with capillary die 1 mm in diameter and 30 mm in length at temperatures ranging from 110 °C to 160 °C.

The density of specimens was measured with Archimedes method and the fracture surfaces were observed with SEM.

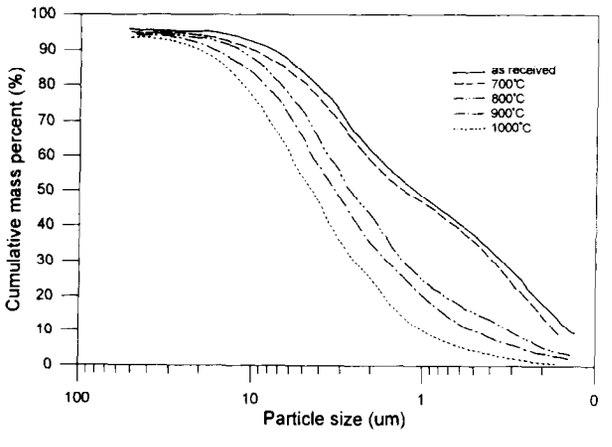

Fig. 1. Particle size distribution of hydroxyapatite as-received and calcined at different temperatures.

3 RESULTS AND DISCUSSION

Figure 1 is the particle size distributions of HA powders with mean particle sizes 1.0, 1.1, 2.5, 3.0 and 4.2 mm for as-received and calcined at 700, 800, 900 and 1000 °C for 4 h, respectively. Because no significant phase transformation is detected by XRD, the increases of particle size are mainly the result of the necking of particles during calcination process. Figure 1 also indicates that the particle size distributions become narrower as calcination temperature increases, which is beneficial for particle packing as shown in Table 2. The tap density of as-received HA powder is only 14.0% of theoretical density, whereas it reaches 25.1% for 1000 °C calcination treatment, almost twice that of raw powder.

Figure 2 (a)–(e) shows the effect of calcination on the morphologies of HA powders. A lot of very fine crystals smaller than 0.1 μm can be seen in as-received HA powder agglomerates. These fine crystals coalesce when the powder is calcined especially as calcination temperature increases.

The agglomerate formed by Van der Waals force is thought to be "soft agglomerate" and can be easily broken by mixing. Greater surface area needs more binder to form a fluidized feedstock. The agglomerate formed by calcination is due to diffusion bonding of particles and this type is called "hard agglomerate" or aggregate, which is difficult to breakdown during mixing binder and HA powder thus a higher powder loading feedstock can be achieved.

Figure 3 shows the flow behaviour of feedstock with 40 v/o solid loading for different temperatures at shear rate 600 s^{-1}. It has been suggested that for ceramic injection moulding, the shear rates can vary from 100 to 1000 s^{-1} and the flow rate during moulding requires a viscosity less than 1000 Pa·s.[9]

Table 2. Tap densities of HA calcined at different temperatures

Calcine	r.t.*	700	800	900	1000
Relative	14.0	15.8	16.7	19.8	25.1

*r.t. express the as-received HA without calcination treatment.

Viscosities of mixtures used in this study are all in this range.

Figure 3 also indicates that a lower calcination temperature results in higher viscosity, because of smaller particle size and greater surface area of powders. Higher viscosity may increase the probability of defect occurring during injection moulding.

Figure 4 shows the sintered bulk densities of injection moulded HA samples for the powders calcined at different temperatures. It is evident that HA specimens calcined at 1000 °C have a lower sintered density than others indicating that 1000 °C is too high a temperature for calcining HA powder for subsequent sintering although a better packing can be achieved. However, the sintered densities for the powders calcined at 700, 800 and 900 °C are on a similar level as the sintering temperature is over 1300 °C. It is also noted that the densities are increasing even when the sintering temperature is above 1400 °C. It indicates that the green densities of the injection moulded HA are too low because of only 40 v/o solid loading for the feedstock. A low green density means longer diffusion path and higher temperatures are needed to eliminate the residual porosities.

Figure 5 (a)–(d) shows the fracture surfaces of HA sintered at 1350 °C for powders calcined at different calcination temperatures. The average 4-point bending strength of specimens sintered at this temperature are 29, 33, 40 and 25 MPa for the powders calcined at 700, 800, 900 and 1000 °C, respectively. As described above, there is only a small difference in the sintered density for the powders calcined at 700–900 °C. The grain size for 700 °C calcined HA is coarser than that calcined at 800 and 900 °C so the strength is lower. For the sintered HA calcined at 1000 °C, many large pores can be observed showing incomplete sintering and resulting in the lowest strength.

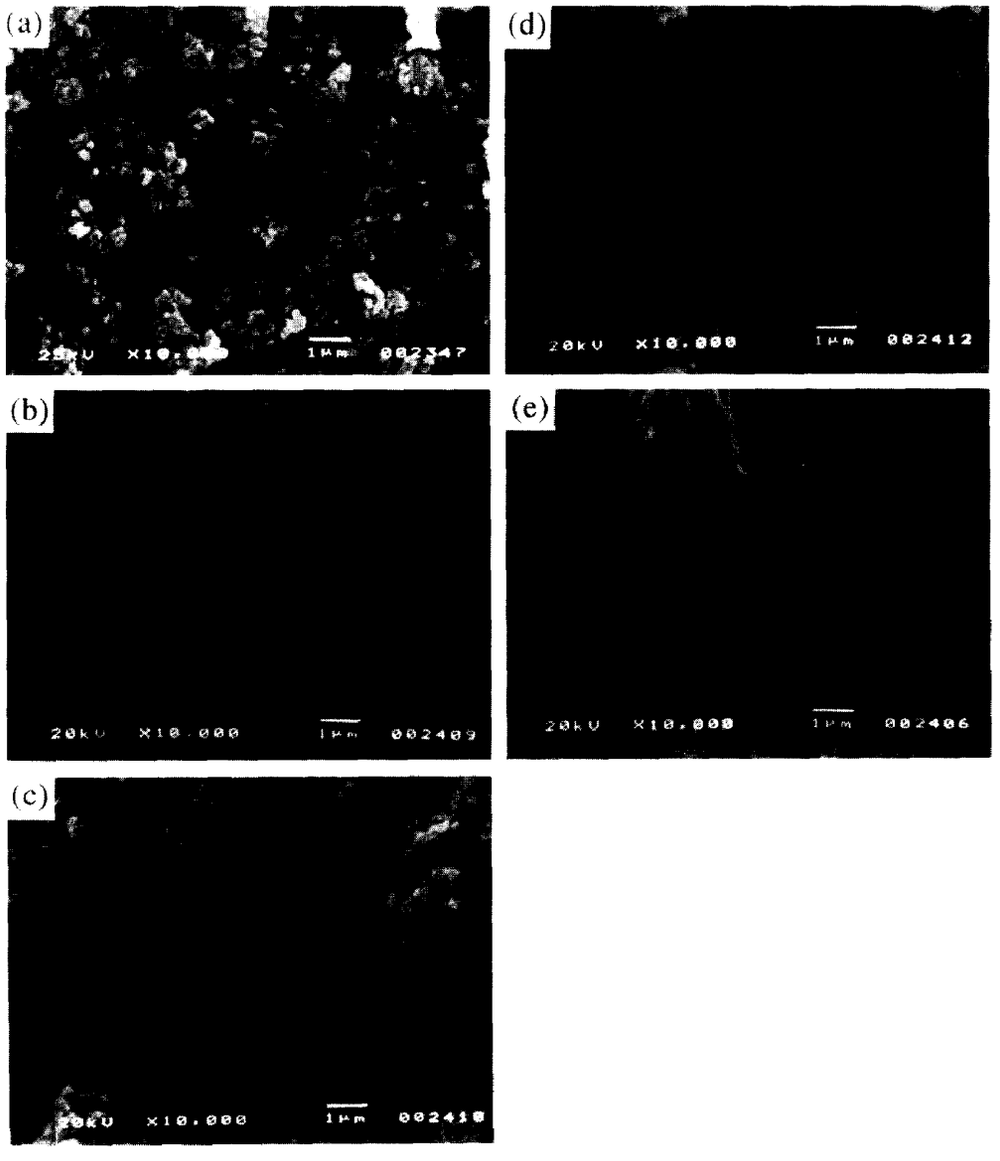

Fig. 2. Morphologies of HA powders as-received and calcined at different temperatures.

From the results of sintered properties of specimens, 900 °C is considered as the optimum calcination temperature in this study. However, 40 v/o solid loading is too low for sintering and specimen distortion occurs easily. From the rheological measurements the viscosity of HA calcined at 900 °C is far lower than requirements for injection moulding which reveals that more solid loading feedstock is possible. Therefore, 50 v/o HA feedstock of viscosity 890 Pa·s at 150 °C and shear rate 600 s^{-1} is prepared and shaped by injection moulding as described previously.

To evaluate the stability of injection moulding process, the Weibull's statistics is used to analyse the mechanical properties of injection moulded parts.[10] The Weibull modulus m as shown in Fig. 6 is obtained by calculating the gradient of the curve for the value of 10.62. The average strength is about 43 MPa which is higher than those of 40 v/o HA specimens.

Figure 7 is the fracture surface of 50 v/o HA specimen calcined at 900 °C and sintered at

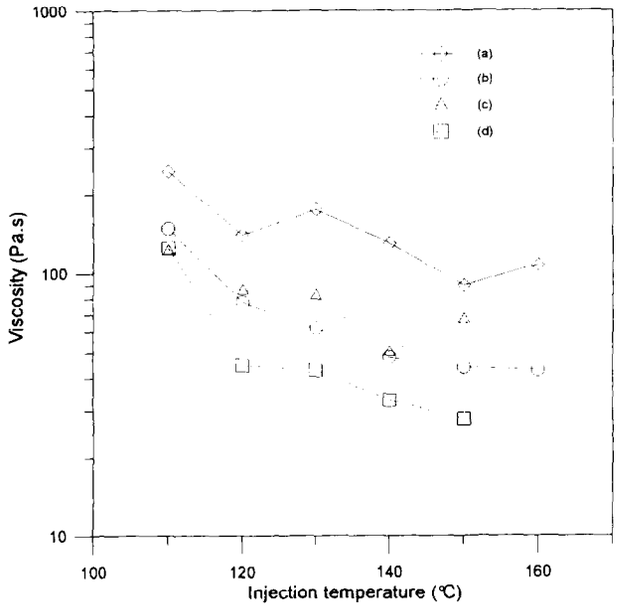

Fig. 3. The viscosities of binder and HA calcined at (a) 700 °C, (b) 800 °C, (c) 900 °C and (d) 1000 °C, with 40 v/o solid loading at shear rate 600 s^{-1}.

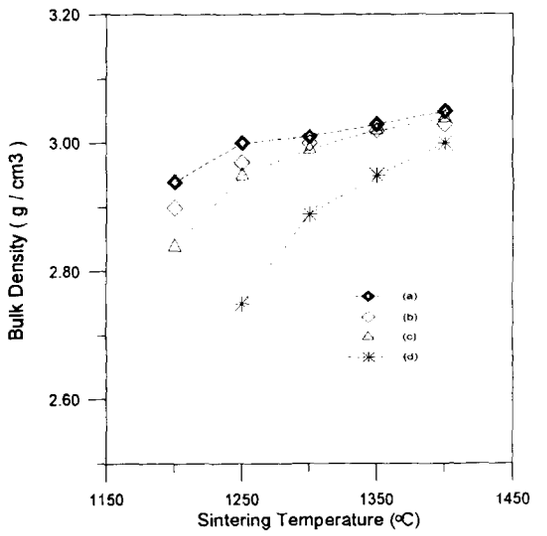

Fig. 4. Bulk densities of injection moulded HA calcined at (a) 700 °C, (b) 800 °C, (c) 900 °C, (d) 1000 °C and sintered at 1350 °C.

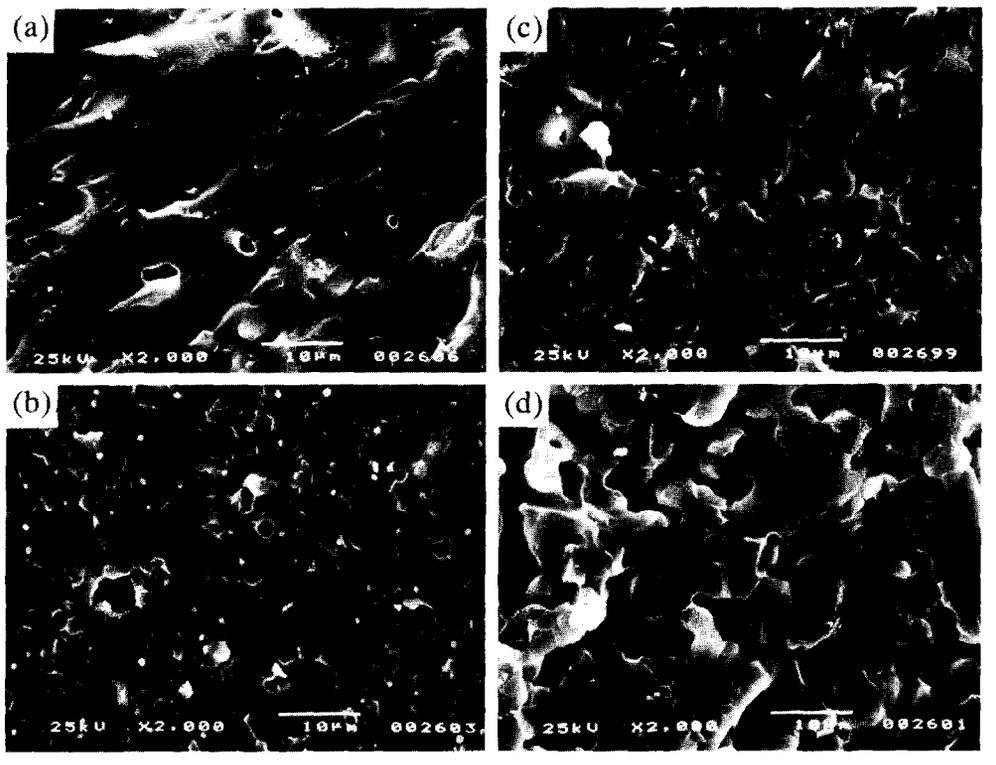

Fig. 5. The fracture surfaces of HA sintered at 1350 °C with 40 v/o solid loading for the powder calcined at (a) 700 °C, (b) 800 °C, (c) 900 °C and (d) 1000 °C.

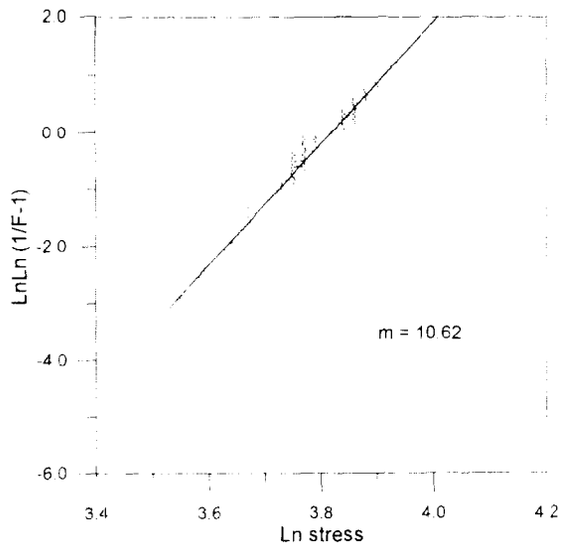

Fig. 6. Weibull distribution of bending strength for HA sintered at 1350 °C with 50 v/o solid loading.

Fig. 7. The fracture surface of HA sintered at 1350 °C with 50 v/o solid loading for the powder calcined at 900 °C.

1350 °C. Compared with Fig. 5 there is less porosity and density is higher. The results indicate that increase of solid loading is necessary.

4 CONCLUSIONS

By calcination treatment at 700–1000 °C the HA powder can be mixed with polymer binder with 40 v/o solid content and shaped by injection moulding. The results can be summarized as follows:

1. Increase of calcination temperature results in a coarser powder, higher tap densities and lower viscosity of HA feedstock, which indicate a better fluidity and packing capacity.
2. Although a higher calcination temperature is beneficial for shaping process, the sintering is delayed and a higher sintering temperature is needed. For the HA powder calcined at 1000 °C, the density is much lower than others indicating that 1000 °C is too high for calcination in this study. 900 °C is the optimum calcination temperature in this study from the viewpoint of a better flow behaviour and the highest bending strength as sintered at 1350 °C because of the smallest grain size.
3. From the results of preliminary study of dilute formulation (40 v/o), the 50 v/o HA solid loading feedstock is prepared and also injection moulded successfully with the bending strength of sintered HA 43 MPa and Weibull's modulus 10.62.

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