Preparation of highly concentrated aqueous hydroxyapatite suspensions for slip casting

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This paper reports the preparation of highly concentrated aqueous hydroxyapatite (HA) suspensions for slip casting of dense bone implants. The dispersing behaviour of HA powders in aqueous media was monitored by viscosity and zeta potential analyses as a function of pH of the slurry. The rheological properties of concentrated aqueous hydroxyapatite suspensions have been characterized with varying pH, NH_4PAA concentration and solids loading. The intrinsic pH of the suspension was found suitable for slip casting. The optimum dispersant concentration is 0.75 wt.% for 75 wt.% solid loading. A stable suspension with 75 wt.% solid was suitable for slip casting with viscosity of 0.36 Pa s at 100 s^{-1}. Finally, crack-free and dense microstructures have been obtained successfully with a grain size of 2–5 μm.

1. Introduction

The key step in processing of advanced ceramics is the control of the microstructure of the green bodies with minimized defects so that dense, high strength and reliable products are obtained after sintering [1].

It has been well established that the present agglomerates in the green compacts are difficult to eliminate through the conventional dry powder consolidation process as like uniaxial pressing [2]. Consequently, the wet processing route involving a colloidal dispersion of the fine powder particles in a liquid medium and their consolidation into a homogeneous dense green body with minimum defects (both in number and size) has gained wide acceptance [3, 4]. The colloidal consolidation technique involves the deflocculation and stabilization of micron/sub-micron sized ceramic powders dispersed in an aqueous or non-aqueous liquid medium before their consolidation. The spontaneously formed soft agglomerates due to Van der Waals attractive forces between the powder particles are broken down into individual particles and dispersed by promoting interparticle repulsion by any or both of the following methods: (i) through the control of surface charges either by adjustment of pH of the liquid medium or by adsorption of dispersants (electrolytes) onto the surface of powder particles (electrostatic stabilization) and (ii) through steric separation of individual particles by adsorption of neutral or charged large chain polymers on to the particle surface (steric or electrosteric stabilization) [5–9].

The optimization of colloidal suspensions is important to reach the low viscosity and stable suspension in order to produce homogeneous, defect free pieces. The kind and amount of dispersant have great effect on the preparation of homogeneous, high concentrated ceramic suspensions with low viscosity [10].

Synthetic hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), because of its biocompatibility and chemical and biological affinity with bone tissues, has potential applications as a bioceramic material [11, 12]. Nordstrom and Karlsson [13] found slip casting of the commercial HA powder difficult, because of the lower zeta potential values for the slip. However, those researchers were able to successfully slip cast a well-dispersed slip consisting of a mixture of commercially available tricalcium phosphate (TCP) and calcium hydroxide ($Ca(OH)_2$) containing nonionic deflocculants, and they vacuum-sintered such cast bodies to near the theoretical density of HA. Toriyama *et al*. [14] investigated the dispersion behavior of mechanochemically synthesized HA powders in water, using various dispersing agents. They observed that, although pH modification had a negligible effect, anionic polyelectrolytes at considerably higher concentrations (3 wt.%) effectively stabilized the suspensions through an electrosteric mechanism.

The key point is the preparation of a concentrated suspension with optimised flow behaviour suitable for slip casting. In this paper, HA suspensions with high solids loadings, suitable viscosity and stability were studied. In order to obtain highest green density

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and to reduce the final shrinkage of components, the solids loading of the suspension must be as high as possible while the viscosity should be kept low enough for processing.

2. Experimental

2.1. Powder characterization

A commercial hydroxyapatite powder (Budenheim Company, Germany) with a stoichiometric ratio of Ca/P = 1.67 was used in this study. The mean particle diameter and the specific surface area were 4.9 ± 1.1 μm and 65.2 m^2/g, respectively. The surface area has decreased from 65.2 m^2/g, for the as-received powder to 4.6 m^2/g for the powder calcined at 1000°C.

The particle size distribution and mean particle size (d_{50}) were determined by the laser diffraction method (Coulter LS230, USA). The specific surface area of HA powder was determined by the BET method (Areameter; Model Strohlein, Germany).

2.2. Preparation and characterization of HA slip

The slips were prepared by dispersing the calcined HA powder at 1000°C in deionized water, using mechanical stirring. The dispersion behavior of the HA particles was studied as a function of the pH of the slurry and with the addition of ammonium polyacrylate (NH_4PAA) solution (Dispex A40, Allied Colloids, Bradford, UK). The amount of NH_4PAA used here is expressed as a dry weight of the powder basis, equivalent to the wt./wt. basis of the hydroxyapatite powder.

Zeta potentials were measured for 180 ml, 3.33 wt.% suspensions with the variation of pH and added dispersant, using a zetasizer (Matec MBS-8000, USA) by measuring the electrophoretic mobility of the particles. The pH value of the slurries was adjusted through addition of 1 m KOH and 1 m HCl.

The rheological characterization of the slurries was performed with a coaxial-cylinders shear-rate-controlled viscosimeter (Haake VT 550, Germany). Measurements were performed at 25 °C. Flow curves were obtained under continuous shear conditions by changing the rate of shear from 0 to 500 s^{-1}. The shear rate was subsequently reduced to 0 s^{-1} repeating the cycle three times, in order to determine viscosity and flow behaviour.

2.3. Slip casting, sintering, and characterization of HA

The HA slips were prepared in deionized water, with optimum amounts of dispersing agent milled in plastic jars for 12–24 h, using Al_2O_3 milling media; and then casted into plaster molds, to obtain green bodies in disc shapes of 20 mm diameter. The green bodies were air-sintered in the temperature range of 1000–1300°C for 2–3 h, in an SiC furnace. The green and sintered density of parts were determined by weight and dimensional measurements and Archimedes' method, respectively.

The sintered bodies, polished successively with 400 and 600 grit SiC emery and 2 μ Al_2O_3, were etched with 0.1 M acetic acid for 2 min and HCl for 15 s. The microstructural features of the polished, etched parts were obtained by scanning electron microscopy (SEM; Model Camscan CS4, UK).

3. Results and discussion

Fig. 1 shows the isoelectric point (IEP) at pH 9.5 and 10.2 for the 3.33 wt.% hydroxyapatite suspension with and without dispersant, respectively. At low pH, the curve shows that particles were highly positively charged. The intrinsic pH of the suspension without dispersant was 12.2 with a zeta potential value of −27 mV (Fig. 1). The addition of dispersant NH_4PAA to the suspension caused the zeta potential to become more negative, from −7 mV to around −27 mV, showing the very good dispersing effect. Also, the decrease of IEP while adding dispersant indicates a weak acid property of NH_4PAA.

NH_4PAA is an anionic polyelectrolyte and can dissolve in aqueous solution, producing negatively charged carboxyl groups [shown in Equation 1], which are very easily adsorbed on the positively charged HA surface. Consequently the powder is negatively charged and this results in a shift of the isoelectrical point to a lower value. The dissociation of NH_4PA in water can be described as follows [15]:

$$RCOONH_4 \rightarrow RCOO^- + NH_4^+ \tag{1}$$

Polyacrylates have proved to be effective dispersing agents for both clay- and nonclay-based ceramics [16, 17], through an electrosteric mechanism of dispersing action. On dispersion into aqueous media, the HA particles could have on their surfaces various ions such as Ca^{2+}, $CaOH^+$, $PO_4{}^{3-}$, $HPO_4{}^{2-}$, $H_2PO_4{}^-$, and $CaH_2PO_4{}^+$, depending on the dissolution and the hydrolytic reactions in solution, bringing into play a set of complex flocculating/deflocculating mechanisms. However, because HA slips could be dispersed and

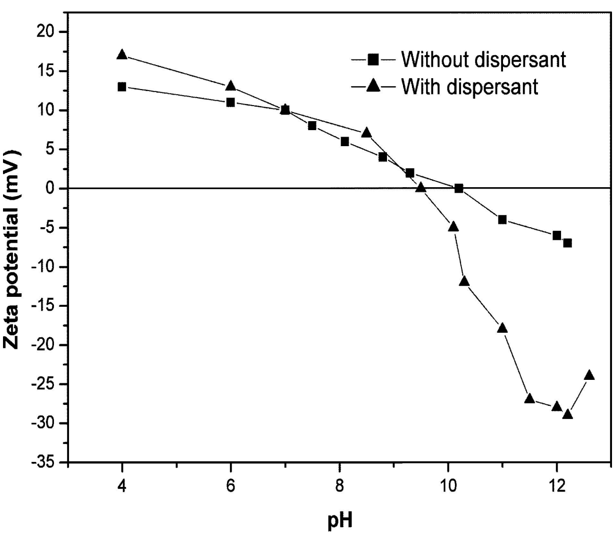

Figure 1 Zeta potential vs. pH of 3.33 wt.% HA suspension with and without dispersant.

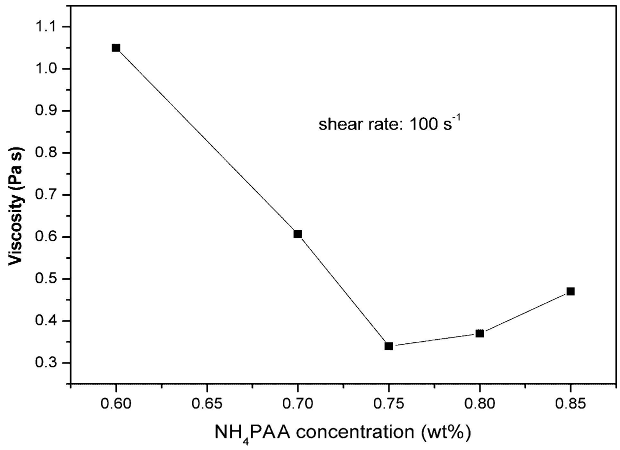

Figure 2 Viscosity vs. NH_4PAA concentration of 75 wt.% HA suspension at shear rate of 100 s^{-1}

stabilized by the anionic polyelectrolytes, as well as by a polyphosphate, it can be concluded that the surface of HA is positively charged and the positive charge attributed to the specific adsorption of Ca^{2+} ions or to preferential dissolution of phosphate ions from the apatite surface [18–20].

The correlation between viscosity and dispersant content is illustrated in Fig. 2 for a slurry with 75 wt.% solid loading. Initially viscosity decreases remarkably with increasing dispersant content and reaches a minimum value at 0.75 wt.% of dispersant concentration. The viscosity data were recorded at a constant shear rate of 100 s^{-1}.

Fig. 3 shows the change of viscosity of suspension with 75.0 wt.% solid loading with decreasing the pH. The lowest viscosity at pH 12.2 (the intrinsic pH of slurry) corresponds with the highest negative zeta potential (Fig. 1).

NH_4PAA has been used to provide the electrosteric stabilization energy to powders in the suspension. When the pH value is changed, the ionisation of NH_4PAA absorbed on the surface of the particles will be affected, as well as the structure of the double-electrical layer. Thus, electrostatic repulsion energy and the zeta potential will be changed. Meanwhile, the steric stabilization energy is also affected by the pH

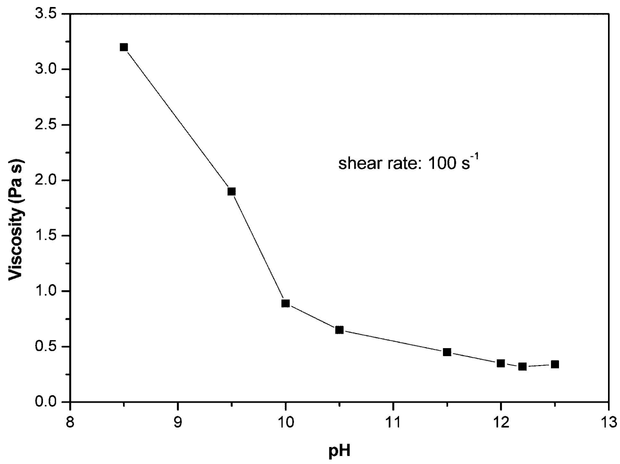

Figure 3 Viscosity vs. NH_4PAA concentration of 75 wt.% HA suspension at shear rate of 100 s^{-1}

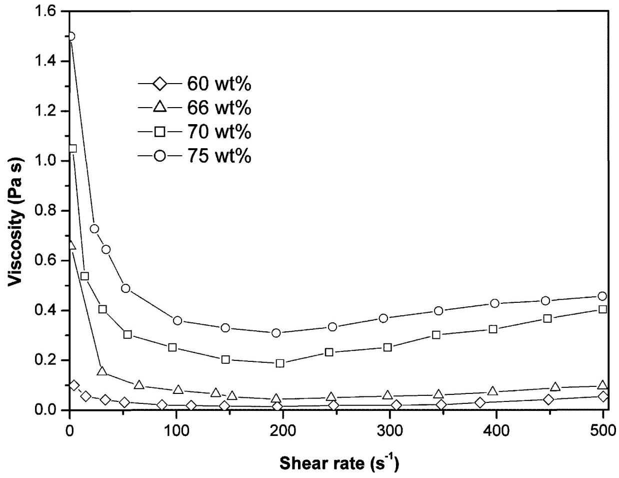

Figure 4 Flow behaviour of HA suspensions with 0.75 wt.% NH_4PAA of different solids loading.

value. Therefore, for further studies, there is no need to adjust the pH of the suspension since the viscosity of the intrinsic pH is suitable to slip casting.

Fig. 4 show viscosities of different solid loaded suspensions with 0.75 wt.% NH_4PAA. These suspensions show a slight shear-thinning behaviour for a lower range of shear rates (up to 200 s^{-1}) whereas at higher shear rates (500 s^{-1}), they show slight shear thickening.

This initial shear thinning, followed by a shear-thickening phenomenon, is a well-known characteristic of colloidally stable suspensions at higher solids loadings [21].

In terms of solid loading for slip casting, the 75 wt.% suspension with 0.75 wt.% of NH_4PAA dispersant seems very suitable for processing with a viscosity of 0.36 Pa s at the shear rate of 100 s^{-1}. Slurries casted into plaster molds to produce green bodies have densities in the range of 56.6% th. d. (3.16 $g \cdot cm^{-3}$).

The slip-cast HA samples were sintered in the temperature range of 1000–1300°C for 2–3 h. The typical density values of the sintered products are plotted versus the sintering temperatures for 2 h soaking time in Fig. 5. The increased densification observed as a func-

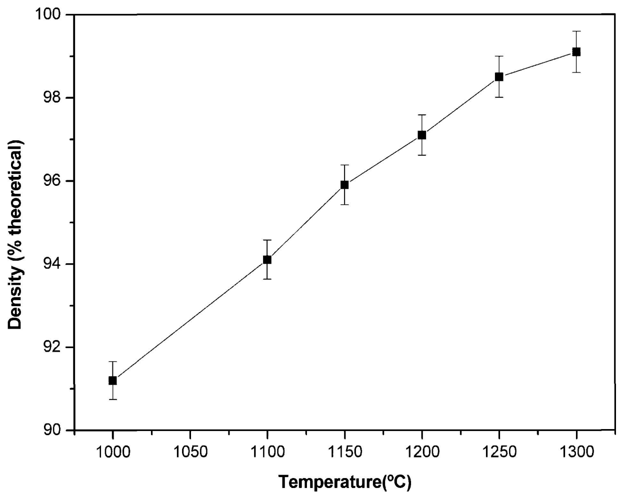

Figure 5 Sintered density of slip-cast HA, as a function of sintering temperature.

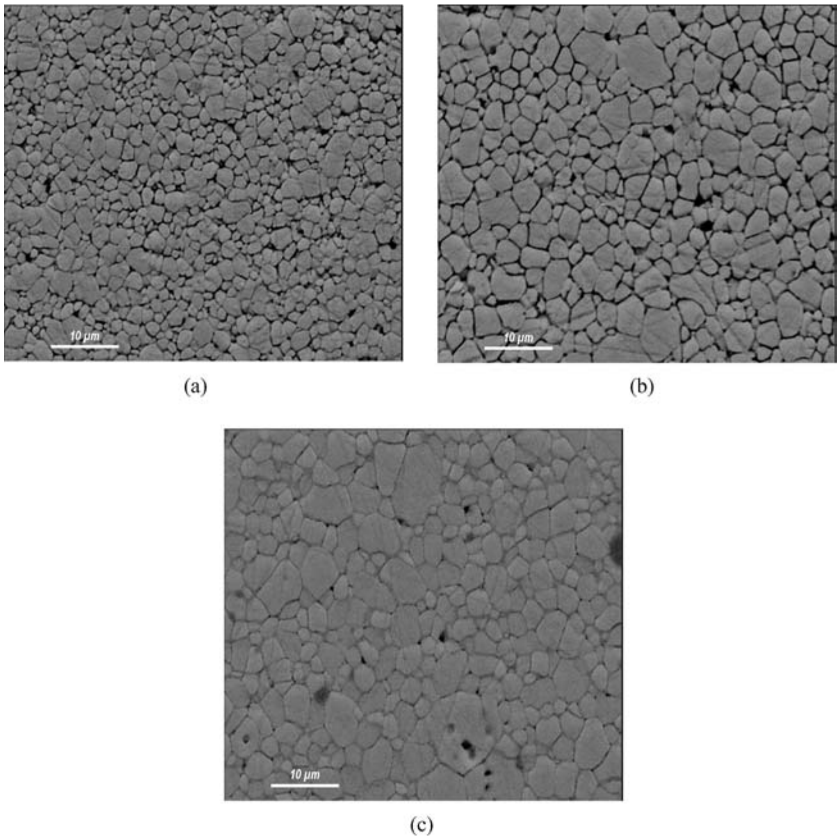

Figure 6 SEM images of polished and etched surface of the HA samples sintered at (a) 1250°C for 2 b, (b) 1300°C for 2 h and (c) 1300°C for 3 h.

tion of temperature reached a maximum of 99.1% th. d. at 1300°C.

The highest solid loading of the HA suspension leads to crack-free parts and dense microstructures.

Scanning electron micrographs of the polished and etched surfaces of sintered bodies are presented in Fig. 6a–c. The figures show a uniform grain-size distribution of 2–5 μm. A comparison of Figs. 6a–c reveals that some grain growth occurs with sintering at higher temperature and longer soaking time.

4. Conclusion

The rheological properties of highly concentrated aqueous suspensions of hydroxyapatite have been characterized with regard to pH, solids loading and dispersant concentration. The isoelectrical point of the HA powder in deionized water without a dispersant is near pH 10.2. However, the isoelectrical point of HA powder shifts to a more acidic condition with the addition of NH_4PAA dispersant.

NH_4PAA is very effective as a dispersant for this colloidal system by introducing electrosteric stabilization energy to prevent the agglomeration, with 0.75 wt.% being the best concentration for the 75 wt.% solid loading systems. pH value also has strong influence on the stability of the high solid loading suspension and flocculation happens while the pH shifts from the intrinsic point to the acidic region, indicating the intrinsic pH is suitable for slip casting.

The suspensions generally exhibited a transition from shear thinning to shear thickening flow as shear rate exceeded a certain critical level.

A stable and easily processable suspension has been achieved with a viscosity of 0.36 Pa s at a shear rate of 100 s^{-1} for solid loading of 75.0 wt.% with NH_4PAA dispersant of 0.75 wt.%. Such a slurry is suitable for the fabrication of dense components with density of 99.1% th. d. that was sintered at a temperature of 1300°C.

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