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Influence of Tiron concentration on dispersability and sintering behaviors of hydroxyapatite in an aqueous system

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Abstract

Rheological and sintering behaviors of hydroxyapatite slurries with different Tiron concentrations were investigated. It was shown that HAp slurries could be stabilized at pH 11 with 2.25 wt% Tiron concentrations. Results confirmed that well dispersed slurries could be obtained with solid content as high as 50 wt%. Zeta potential measurements were conducted on HAp powders evaluated the influence of dispersant on surface charge properties of the particles. X-ray diffraction technique was used to study the crystalline phase evolution; scanning electron microscopy was used to estimate the particle size of the powder and fracture surfaces of bodies sintered at various temperatures. After sintering process at 1200 and 1350 °C, relative density and bending strength of HAp samples reached 76.67% and 92.18% and 57.77 and 97.36 MPa, respectively.

Keywords: A. Slip casting; A. Sintering; Hydroxyapatite; Rheology; Tiron

1. Introduction

There is an increasing interest in hydroxyapatite ceramics for hard tissue replacement due to its excellent biocompatibility with hard and soft tissues [1,2]. Common applications of HAp ceramics are in repairment of bone defects in dental and orthopaedic sites, immediate tooth replacement, augmentation of alveolar ridges, pulp capping material, maxillofacial reconstruction, etc. [3–6]. In recent years, efforts have been made toward preparing more reliable bioceramic bodies. Colloidal approach has potential for eliminating detrimental heterogeneities, avoiding their reintroduction during successive processing steps, and fabricating complex shapes similar to human bones [7,8]. Various colloidal processes, such as slip casting [9–14], tape casting [15–17], and gel casting [18–20] have been reported for preparation of HAp composites with different sizes and complicated shapes. In these methods, particle dispersion is often the limiting factor, affecting both rheology and homogeneity of suspensions. Addition of polymer dispersant has been effective in preventing the agglomeration of ceramic powder by electrosteric stabilization and enhancing particle stability [21,22].

In the present study, Tiron was introduced as a dispersant for preparation of 50 wt% solid content HAp slurries.

2. Experimental

Hydroxyapatite used in this study was a commercial powder (Budenheim Company, Germany) with stoichiometric ratio of Ca/P = 1.67 and 1.1 ± 0.1 μm mean particle size. The particle size distribution and mean particle size (d_{50}) were determined by the laser diffraction method (Frisch Partical Sizer, model Laborgeratebau type: 22902,Germany). Aqueous suspensions were prepared by adding HAp powders to deionized water in the presence of different amount of dispersant (1.75, 2, 2.25, 2.5, 2.75 wt% solid). The solid content was kept constant at 50 wt% and the dispersant was Tiron ($C_6H_4Na_2O_8S_2 \cdot H_2O$: 1,2-dihydroxybenzene-3,5-disulfonic acid disodium salt hydrate BDH Co.). The suspensions were roll milled in milling jars for 1 h prior to analysis. The rheological characterization of the slurries was performed at 25 °C with a coaxial-cylinders shear rate controlled viscosimeter (Brookfield LV, USA). Once the optimum percentage of Tiron was determined, zeta potential of the HAp particles was then measured through Zeta plus (3000HSA, Malvern Instruments Corporation). HAp suspen-

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sions (0.01 vol%) were prepared in the absence and in the presence of optimum percentage of Tiron at various pH values. The ionic strength of each slurry was adjusted with 0.001 M KCl solution. The slurries were mixed for 12 h to break agglomerates and achieve equilibrium between the powder surface and the dispersant in the suspensions. The pH of suspensions was adjusted by HNO_3 and NaOH in the acidic and basic ranges, respectively. Well stabilized 50 wt% HAp slurries were used for slip casting process. The slurry was degassed under low vacuum (10^{-5} Torr) to eliminate the air bubbles before casting it into a plaster mould. The obtained green body was heat treated at a heating rate of 1 °C min^{-1} to 500 °C to burn out the organic components. Sintering process was conducted in an electric furnace with the heating rate of 10 °C min^{-1} and HAp samples were sintered at 1100, 1200 and 1350 °C for 1 h. Density of the sintered samples were measured using Archimedean method following BS 1902A standard. Phase establishment of samples were identified by X-ray diffractometry (XRD, Siemens, model PW3710, 30 kV and 20 mA). The step size and scan rate were fixed at 0.02° and 0.5° min^{-1}, respectively. Bending strengths were measured at room temperature with a crosshead speed of 0.5 mm/min by three-point bending test. Test specimens with dimensions of 3.5 mm × 5 mm × 35 mm were cut and machined for bending strength tests. The entire specimen surface was ground with an 800-grit diamond wheel and the tensile surface was polished with diamond slurries. Fracture surfaces were observed with a Cambridge scanning electron microscope (SEM, model Stereo Scan s360) operating at 25 kV.

3. Results and discussion

3.1. Rheological behavior

The optimal content of dispersant required was determined using 50 wt% HAp slurries at pH 7. Fig. 1 represents suspension viscosity as a function of Tiron concentrations. Minute addition of dispersant considerably decreased the slurry viscosity. A concentration of 2.25 wt% dispersant resulted in stable suspensions. At low Tiron concentration (<2.25 wt%), the suspensions exhibited shear thinning behavior. This could be well correlated to inadequate adsorption of dispersant giving rise to flocculated slurry [22]. Also, at low amounts of dispersant, the electric double layers are not sufficient to achieve an effective inter-particle repulsion and prevails the attraction between them. When the dispersant content increased to 2.25 wt%, the slurry stability improved from shear thinning to near Newton behavior. The viscosity increased at higher amounts of dispersant (>2.25 wt%) due to compression of the electric double layer by excessive electrolyte concentration and insufficient electrostatic repulsion. In general, the surface charge of solid hydroxyapatite is the result of pH and preferential dissolution or adsorption of calcium and phosphate ions, since H^+, OH^- and lattice ions are the potential determining ions. Formation of surface complexes between potential determining ions further complicates the estimation of ion activity product and surface potential [23]. In particular, a solid surface complex $Ca_2(HPO_4)(OH)_2$, formed by HAp hydrolysis mechanism, controls the solubility equilibria, according to the following equations [24,25]:

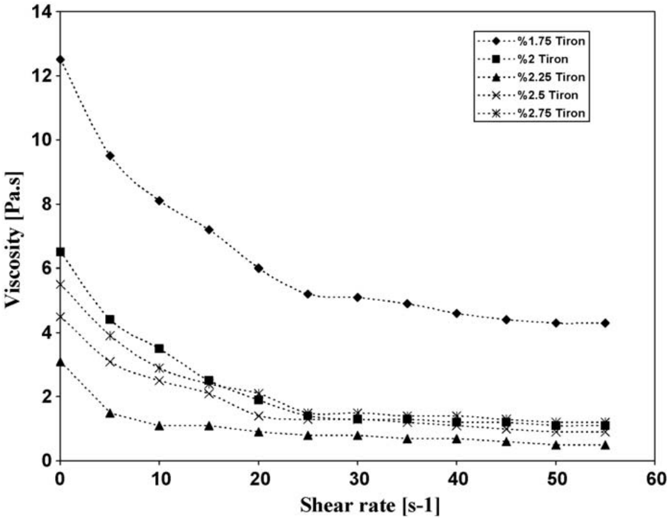

Fig. 1. Viscosity vs. shear rate for 50 wt% HAP slurry as a function of the Tiron dispersion concentrations.

$$Ca_{10}(PO_4)_6(OH)_2 + 6H_2O \rightarrow 4Ca_2(HPO_4)(OH)_2 + 2Ca^{2+} + 2HPO_4{}^{2-} \quad (1)$$

$$4Ca_2(HPO_4)(OH)_2 \rightarrow 8Ca^{2+} + 4HPO_4{}^{2-} + 8OH^- \quad (2)$$

The resulting non-stoichiometric Ca/P ratio in solution (1:1 for Eq. (1) or 2:1 for Eq. (2)) depends on which dissolution reaction occurs. If HAp is prepared in water, the surface is, presumably, just covered with surface complex $Ca_2(HPO_4)(OH)_2$ and subjected either to the equilibrium shown in Eq. (2) or to adsorption phenomena of ionic species present in solution [26]. On dispersion into aqueous media, the HAp particles might have various ions on their surfaces (such as Ca^{2+}, $CaOH^+$, $PO_4{}^{3-}$, $HPO_4{}^{2-}$, $H_2PO_4{}^-$, and $CaH_2PO_4{}^+$). However, HAp slurries can be stabilized by the anionic polyelectrolytes as well as by a polyphosphate. Therefore, it can be concluded that the surface of HAp is positively charged. The positive charge is attributed to the specific adsorption of Ca^{2+} ions or to the preferential dissolution of phosphate ions from the apatite surface [27–29]. As shown in Fig. 2, in the absence of dispersant, the slurry is stable in pH > 10 range, at which the HAp powder is stabilized electro statically due to the high surface charge. In low pH region (<9), the slurries are not stable due to dissolution of HAp. In the pH range 5–10, the instability is due to the low surface charge of HAp particles (near the isoelectric point, pH 9). In the presence of optimum amount of Tiron, the slurry can be stabilized even in neutral region. This might be due to the adsorbed polymers, which modify the surface charge behavior of HAp particles and lead to the shift of the isoelectric point toward more acidic region (isoelectric point, pH 5). The effect of pH on the rheological characteristics of suspensions is reported in Fig. 3 for the 50 wt% solid slurry with optimum dispersant. The viscosity for

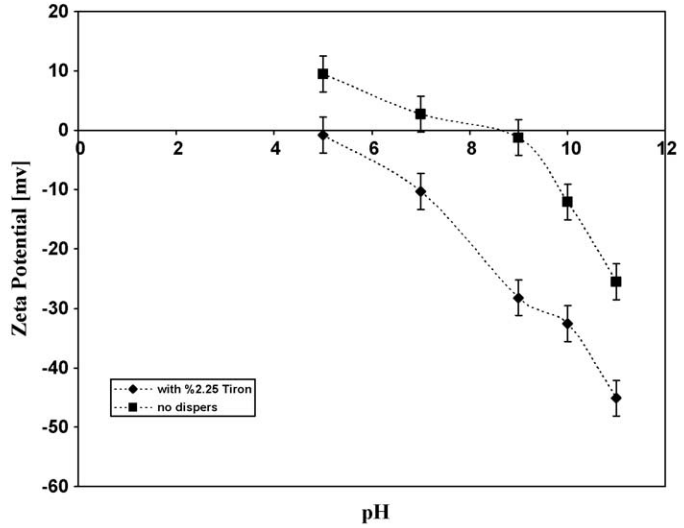

Fig. 2. Zeta potential of HAP particles in the absence and in the presence of optimum Tiron dispersant concentration.

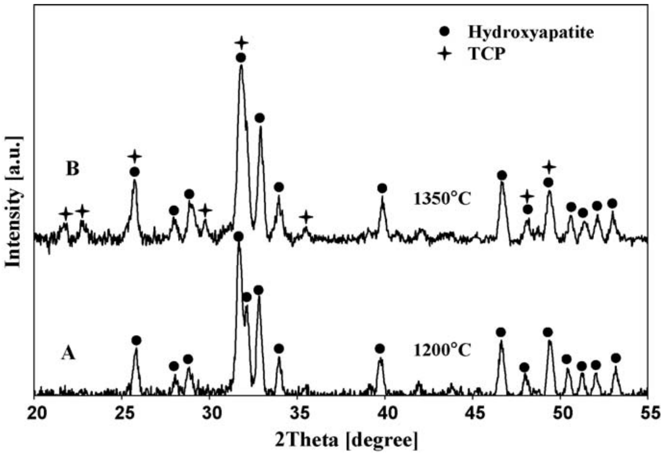

Fig. 4. XRD pattern of HAp samples sintered at different temperature (A) 1200 °C for 1 h and (B) 1350 °C for 1 h.

the given solids volume fraction, decreases with increasing pH value reaching an equilibrium situation of Newtonian suspension. The shear thinning character for a given solid decreases with increasing pH. The results presented above showed that rheological properties and deagglomeration were promoted by increasing pH. However, this is a long duration process and hydrolysis reaction of the HAp powder in water may increase the amount of OH^- in the powder surface.

3.2. Characterization of ceramic bodies

Fig. 4 depicts the X-ray diffraction patterns of samples sintered at 1200 and 1350 °C. As shown, the TCP phase was only presents in samples sintered at 1350 °C. This was attributed to the dehydroxylation behavior of HAp, which led to the formation of a non-stoichiometric phase [30–34] as considered in the following reaction:

$$\mathrm{Ca_{10}(PO_4)_6(OH)_2 \rightarrow Ca_{10}(PO_4)_6O_{\mathit{x}}(OH)_{2(1-\mathit{x})} + \mathit{x}H_2O} \qquad (3)$$

Water is gradually liberated from hydroxyapatite giving rise to the formation of and hydroxyl-oxyapatite $\mathrm{Ca_{10}(PO_4)_6O_{\mathit{x}}(OH)_{2(1-\mathit{x})}}$ (HOA). The gradual decrease in the content of OH^- groups occurs before oxyaptite formation. This dehydroxylation process is reversible in the temperature range <1200 °C. If temperature exceeds this range, complete and irreversible dehydroxylation process takes place, resulting in the decomposition of HAp to anhydrous TCP. Fig. 5 shows the relative density and flexural strength of sintered plate samples fabricated from 50 wt% solid-loaded slurries dispersed with two different amounts of Tiron (2 and 2.25 wt%). A direct relationship between the efficiency of the dispersant and relative density of HAp bodies was observed. It has been shown that slurries with lower viscosities could result in bodies with

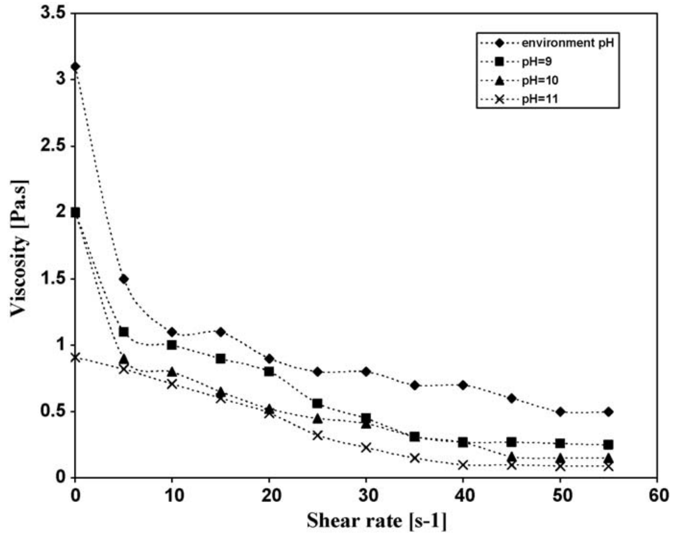

Fig. 3. Viscosity vs. shear rate for 50 wt% HAP slurry with optimum Tiron dispersant concentration as a function of the pH.

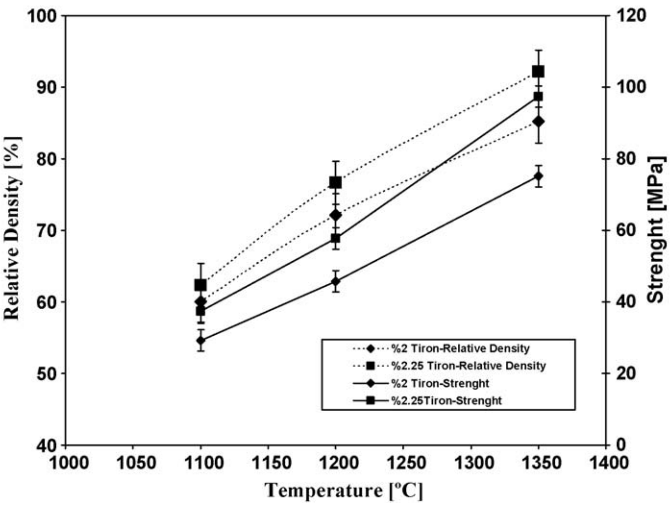

Fig. 5. Variation in the relative density and strength of HAp samples sintered at 1100, 1200, and 1350 °C for 1 h as a function of the quantity of Tiron dispersant.

higher densities [35]. Fig. 5 also shows that higher relative density and strength values were achieved by increasing the sintering temperature. Sintering progresses at higher temperatures resulted in a notable increase in grain size, joining of the particles, density and consequently a decrease of porosity. Fig. 6 shows SEM micrographs of HAp fracture surface containing the optimal dispersion concentration (2.25 wt% Tiron) sintered at 1100, 1200 and 1300 °C for 1 h. The homogenous microstructure composed of equiaxed grains was formed in three samples although some voids were observed at grain boundaries of HAp. The average grain size of HAp sintered at 1100, 1200 and 1300 °C were 1.1, 1.75 and 3.97 μm, respectively. It was shown that the particle size increased with rising sintering temperature, in a good agreement with the literature [36].

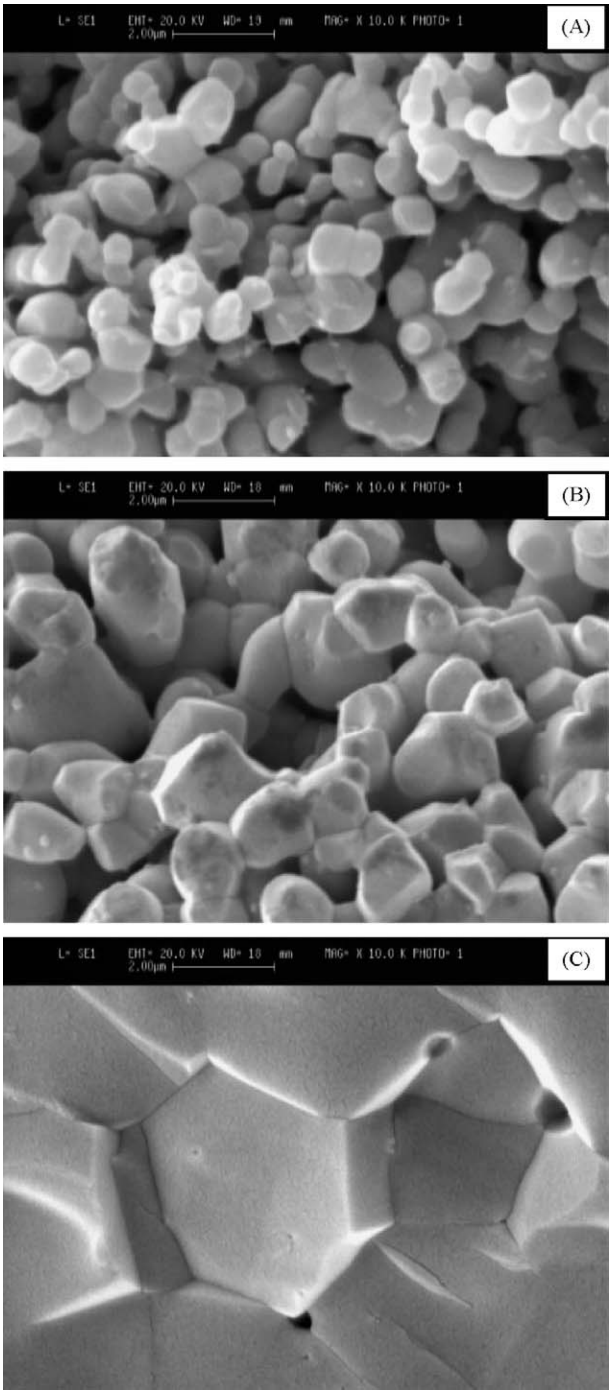

Fig. 6. Microstructure of the fracture surface of HAp samples containing the optimal dispersion concentration sintered at different temperature (A) 1100 °C for 1 h, (B) 1200 °C for 1 h, and (C) 1350 °C for 1 h.

4. Conclusions

The type and amount of dispersing agent added revealed an important factor that determines the rheological behavior of the slips, and the densities of sintered shaped bodies. The rheological behavior of HAp slurry depends strongly on the amount of dispersant used. Addition of 2.25 wt% dispersant induces low viscosity slurries. An appropriate amount of dispersant suppresses agglomeration of HAp powder and enhances the uniform dispersion in the colloidal state. The isoelectric point of HAp is at pH 5 in the presence of 2.25 wt% Tiron. Results showed that 50 wt% HAp slurries can be stabilized at pH 11 with optimum Tiron content 2.25 wt%. The bending strength of sintered HAp is maximum at an optimum amount of dispersant because of its low porosity and uniform microstructure. Also, higher density and strength values are observed with the increase of sintering temperature.

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