Preparation of hydroxyapatite/α-tricalcium phosphate composites by colloidal process

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Abstract

Synthesised hydroxyapatite (HAp)/α-tricalcium phosphate (α-TCP) composites were prepared by colloidal process. Mixed slurries composed of 30 vol% HAp/α-TCP powder and 70 vol% aqueous solution containing a small amount of polymer dispersant were produced. HAp/α-TCP powder was blended with 0, 0.2, 0.4 or 1.0 mass fraction of α-TCP. Rheological behaviour of the HAp/α-TCP mixed slurries depended on the quantity of polymer dispersant and pH. Addition of suitable quantity of polymer dispersant at higher pH resulted in an increase in the stability of colloidal state due to electrostatic stabilisation. The optimum quantity of dispersant for the colloidal process was found to be proportional to the mass fraction of α-TCP. In the dehydration process of the slurries, pressure filtration technique was effective in preventing the gravity segregation of α-TCP. Thus, HAp/α-TCP composites with homogeneous microstructure and high relative density could be prepared by optimising the colloidal process. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Hydroxyapatite; Tricalcium phosphate; Colloidal process; Pressure filtration

1. Introduction

Calcium phosphate (CaP) ceramics of hydroxyapatite (HAp) and tricalcium phosphate (TCP) have been used as a bone substitute because of their excellent biocompatibility [1–3]. They differ in mechanical properties and biocompatibility each other. Therefore, CaP ceramic composites are favourable for development of superior biomaterials with high strength and excellent bio-compatibility. For example, HAp is most stable among CaP ceramics in vivo and can combine directly with a new bone [4,5] while α-TCP dissolves in the body 10 times faster than HAp [5]. A good supply of Ca and P ions from α-TCP is effective in accelerating the formation of new bone. Since HA and α-TCP behave as a seed of bone and a supplier of ions, respectively, the mixture of HAp and α-TCP is expected to assist faster bone growth [6]. In fact, HAp/TCP composites were reported to induce faster bone regeneration than HAp alone [7]. Monma et al. [8] also reported that HAp/α-TCP composites showed higher strength than HAp.

In general, CaP ceramics are prepared by dry powder process. Nevertheless, agglomeration of powder during dry powder consolidation, due to van der Waals force, results in an inhomogeneous microstructure of sintered materials. The colloidal process is known to be effective in avoiding the spontaneous agglomeration by producing a repulsive force between particles either electrostatically, sterically or electrosterically [9–12]. The uniform colloidal state of powder results in a homogeneous consolidated state.

In this study, the colloidal process was applied in the preparation of HAp/α-TCP composites and an optimum condition was sought focusing on the microstructure and rheological behaviour of the mixed slurries.

2. Experimental procedure

Synthesised HAp (HAp-200) and α-TCP (α-TCP-A) powders which were produced by Taihei Chemical Industrial Co. were mixed in ratios of 100–0, 80–20, 60–40 and 0–100 by weight. HAp primary powder of 1 μm long and 1.2 μm wide with a hexagonal shape tended to aggregate and form secondary particles while α-TCP powder particles were as large as a few micron. Slurries were prepared with 30 vol% HAp/α-TCP mixed powder and 70 vol% aqueous solution containing a small amount of polyacrylic acid ammonium (PCAA) as an anion dispersant. These slurries were ultrasonically dispersed for 20 min and then stirred by a magnetic agitator for 5 h. The pH of the slurries was

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adjusted to 8–10 by adding nitric or ammonium solution. Their rheological behaviour was investigated using an automatic rotation viscometer at room temperature. The viscosity of the slurries was measured at shear rates ranging from 3.83 to 383 s⁻¹.

Two types of dehydration technique were selected: slip casting and pressure filtration. In slip casting, the slurries were poured into a plaster mould and remained intact for 24 h to absorb water. Water in the slurries was filtered through a membrane at a uniaxial pressure of 4 MPa with pressure filtration. After the dehydration process, the samples were sufficiently dried at 323 K for 24 h. Density of green bodies was calculated by measuring the weight and size. The consolidated samples were sintered at 1473 or 1773 K for 2 h. The heating rate for sintering was 200 K h⁻¹. The homogeneity of HAp/α-TCP composites was checked by X-ray diffractometry (XRD). The relative density of the sintered samples was measured by Archimedes method, and microstructure of the sintered bodies was observed by a scanning electron microscope (SEM).

3. Results and discussion

3.1. Rheological behaviour of HAp/α-TCP mixed slurries

Fig. 1 shows rheological curves of HAp slurries containing different amounts of dispersant. With a lower quantity of dispersant, the shear stress of the slurries increases linearly with increasing shear rate up to 75 s⁻¹, while a strong shift from the linear relationship to lower shear stress is observed at higher shear rates. Such rheological behaviour is called shear thinning. HAp powder has a tendency to aggregate due to van der Waals force but a polymer dispersant is known to enhance the monodispersion of primary particles electrosterically. However, with a lower quantity of dispersant, the dispersion of primary HAp powder is not sufficient at lower shear rates because of the lack of dispersant. Destruction of the aggregates leads to a decrease in the shear stress at higher shear rates. Moreover, primary HAp powder was not spherical but rod-like. At higher shear rates, rod-like primary particles of HAp were aligned parallel to the shear direction, also resulting in the decrease in a lower shear stress. The rheological curve for the slurry containing 1.0 mass% dispersant, on the other hand, is almost straight. This suggests that well-dispersed HAp slurry with a suitable quantity of dispersant can be regarded as Newtonian fluid.

![Fig. 1. Rheological curves of HAp slurry with various quantities of dispersant.](image1)

In contrast, α-TCP slurries demonstrate dilatancy at a lower quantity of dispersant as shown in Fig. 2. In dilatant fluid, shear stress increases as shear rate rises. α-TCP primary particles are so large that the shear of fluid leads to the thickening of the slurries resulting in dilatancy. Addition of an appropriate quantity of 6.0 mass% dispersant, however, results in the Newtonian flow of α-TCP slurries.

![Fig. 2. Rheological curves of α-TCP slurry with various quantities of dispersant.](image2)

Fig. 3 shows changes in shear stress of HAp-20 mass% α-TCP mixed slurries as a function of shear rate. At 1.0 mass% dispersant, the mixed slurries show dilatancy similar to α-TCP single slurry. The rheological behaviour of the mixed slurries is closely related to that of HAp and α-TCP single slurries. The dilatancy in the mixed slurries is believed to reflect that in α-TCP single slurries. However, the mixed slurries also exhibit Newtonian fluid by doping a suitable quantity of dispersant.

The shear stress at a shear rate of 383 s⁻¹ for α-TCP, HAp, HAp-20 mass% α-TCP and HAp-40 mass% α-TCP slurries is plotted against the quantity of dispersant in Fig. 4. In every slurry that was tested, the shear stress decreased gradually with an increase in the quantity of dispersant. After reaching minimum, addition of further dispersant
increases the shear stress. The minimum in the shear stress dispersant curves for HA, α-TCP and the mixed slurries is well dispersed. Therefore, the quantity of dispersant corresponding to the minimum shear stress can be regarded as the optimum dispersant concentration for each slurry.

Fig. 5 shows change in the optimal quantity of dispersant ($W_{\text{PCAA}}$) as a function of mass fraction of α-TCP ($f_{\alpha\text{-TCP}}$). $W_{\text{PCAA}}$ and $f_{\alpha\text{-TCP}}$ obviously have a linear relationship and the following equation is derived

$$W_{\text{PCAA}} = (1 - f_{\alpha\text{-TCP}})W_{\text{HAp}} + f_{\alpha\text{-TCP}}W_{\alpha\text{-TCP}}$$

Eq. (1) strongly suggests that HA, and α-TCP have their own optimum quantity of dispersant ($W_{\text{HAp}}$ and $W_{\alpha\text{-TCP}}$) depending on their surface area and surface charge. Thus, using Eq. (1), a suitable colloidal process can be applied to HA/α-TCP mixed slurries containing any amount of α-TCP.

The pH of slurry is one of the important factors in optimising a colloidal process. Fig. 6 shows variation in the shear stress of HA-40 mass% α-TCP slurries at the optimum dispersant at 383 s$^{-1}$ as a function of pH. The shear stress at pH 10 is much lower than that at pH 8 and 9. Decrease in the shear stress of slurry indicates the stable dispersion of the particles. PCAA dispersant is known to be dissociated into A COO$^-$ and NH$_4^+$ (A = $\text{HC}^\text{-CH}_2\text{-}$). The dissociated polycarboxylic acid may cover the surface of the powder resulting in the monodispersion of powder due to electrosteric stabilisation. The dissociated fraction of PCAA in the solution may influence the stability of the colloidal state, but the PCAA can be entirely dissociated at pH of more than 8 [12]. So, the effect of dissociation of PCAA on the shear stress is therefore negligible. On the contrary, zeta potential of powder is known to depend strongly on pH. For example, HA in water has an isolectric point of about 7. The zeta potential of HA decreases from $-10$ to $-20$ mV with increasing pH from 8 to 10 [13]. The larger absolute value of zeta potential at pH 10

![Fig. 3. Rheological curves of HAp-20 mass% α-TCP with various quantities of dispersant.](image)

![Fig. 5. Relationship between optimum quantity of dispersant and α-TCP content.](image)

![Fig. 4. Variation in shear stress of HAp, α-TCP, HAp-20 mass% α-TCP and HAp-40 mass% α-TCP slurries with various quantities of dispersant.](image)

![Fig. 6. Variation in shear stress of HAp-40 mass% α-TCP slurry with pH.](image)
results in enhancement of the electrostatic stabilisation of the colloidal state.

3.2. Consolidated and sintered states

HAp/α-TCP mixed slurries were dehydrated by slip casting or pressure filtration. Fig. 7 shows XRD profiles of upper and lower green bodies of HAp-40 mass% α-TCP composites obtained by slip casting. A gravity segregation is confirmed to occur in the slip casted samples. HAp and α-TCP powders were preferentially located at upper and lower bodies, respectively. The α-TCP primary particle is heavier than HAp because of its larger size, although specific gravity of α-TCP is lighter than that of HAp. Slip-casted slurries were absorbed water in a plaster mould. Absorption of water in a plaster mould takes a long time and results in the promotion of the gravity segregation. In contrast, pressure filtration takes only 2 h to dehydrate and may suppress the segregation. After the pressure filtration, XRD profiles of the upper and lower bodies were almost the same as shown in Fig. 8. Therefore, pressure filtration is effective in producing homogeneous green bodies of HAp/α-TCP composites. The green density of HAp-20 mass%-TCP composites is plotted against quantity of dispersant in Fig. 9. The stability of colloidal state is reflected by the green density. The maximum green density is obtained at the optimum dispersant concentration of 1.5 mass%. Higher green density results in higher relative density of sintered bodies.

Following the dehydration process, α-TCP and other samples were sintered at 1773 and 1473 K for 2 h, respectively. Fig. 10 shows changes in the relative density of these sintered samples with the quantity of dispersant. In all cases, the relative density shows a maximum at their optimum quantity of dispersant. α-TCP was hard to be sintered even at 1773 K, while HAp/α-TCP composites exhibited a relative density of around 90% at the most suitable quantity of dispersant.

SEM micrographs of HAp-20 mass% α-TCP composites with different quantities of dispersant are shown in Fig. 11. At 1.5 mass% dispersant, α-TCP particles are homogeneously dispersed in the HAp matrix without large pores (Fig. 11(b)), while inhomogeneous microstructures containing numerous pores are seen at the other dispersant concentrations (Fig. 11(a), (c) and (d)). Therefore, optimisation of the colloidal process is

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Fig. 7. XRD profiles of upper (a) and lower parts (b) of HAp-40 mass% α-TCP composites obtained by slip casting.

Fig. 8. XRD profiles of upper (a) and lower parts (b) of HAp-40 mass% α-TCP composites obtained by pressure filtration at 4 MPa.

Fig. 9. Change in green density of HAp-20 mass% α-TCP composites with quantity of dispersant.

Fig. 10. Change in the relative density of HAp, α-TCP, HAp-20 mass% α-TCP and HAp-40 mass% α-TCP specimens sintered for 2 h with various quantities of dispersant. α-TCP compact was sintered at 1773 K and the other at 1473 K.
indispensable for producing homogeneous HAp/α-TCP composites.

4. Conclusions

The colloidal process for the preparation of HAp/α-TCP composites was investigated, and the following conclusions were reached.

1. The rheological behaviour of HAp/α-TCP slurries depends on the quantity of polymer dispersant. Addition of the optimum quantity of dispersant enhances the uniform dispersion in the colloidal state. The optimum quantity for the colloidal process is proportional to the mass fraction of α-TCP.

2. Higher pH results in enhancement of the stability of colloidal state of the mixed slurries due to the increase in the absolute value of zeta potential of HAp and α-TCP.

3. In the dehydration process of the slurries, pressure filtration was effective in suppressing the gravity segregation of α-TCP, and resulted in production of homogeneous HAp/α-TCP composites.

4. Optimisation of the colloidal process induces the uniform microstructure of HAp/α-TCP composites. The relative density of HAp/α-TCP composites shows maximum at the most suitable quantity of dispersant.

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