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Gel-casting of β-TCP using epoxy resin as a gelling agent

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Abstract

A water-soluble epoxy resin combined with a polyamine hardener is applied for gel-casting of β-tricalcium phosphate (TCP) ceramics. The influence of dispersant and the solids loading on the rheological behavior of β-TCP slurries are investigated. When the concentration of the slurries increases from 40 vol.% to 55 vol.%, the compressive strength of the dried pieces increases in the range from 36.4 ± 2.1 MPa to 65.8 ± 2.3 MPa, and flexural strength increases from 30.4 ± 1.4 MPa to 36.4 ± 1.7 MPa. The mechanical properties of the sintered pieces are satisfying, with compressive strength, flexural strength, elasticity modulus and the fracture toughness 319 ± 18 MPa, 97.4 ± 6.0 MPa, 90 ± 2 GPa and 1.00 ± 0.07 MPa $m^{1/2}$, respectively. The structures of green body and sintered ceramics are homogeneous, and large defects are not observed.

Keywords: Gel-casting; Suspension; Mechanical properties; Calcium phosphate; TCP

1. Introduction

Beta-tricalcium phosphate $Ca_3(PO_4)_2$ (β-TCP) ceramics has been widely used for the replacement of the bone tissue.[1–3] β-TCP has such similar composition with natural bone and high performance of biocompatibility that it can be easily bonded to bone.[4,5] Moreover, its high dissolution rate in the human biological environment advanced bone growth during the progressive degradation. When it is used as surgical implants, the mechanical strength of β-TCP ceramics is important.[6–8] On the other hand, the surgical implants usually should have complex shapes.

In our previous work,[9] gel-casting process was applied to make complex shaped β-TCP with enhanced mechanical properties. Gel-casting is a novel near-net shaping process for ceramics materials, which was first developed by Janney and co-workers.[10–13] It has been utilized in the forming of many sorts of ceramics in the last decade.[14–19] In this process, polymerization is a free radical reaction that is inhibited by oxygen, resulting in the surface exfoliation phenomenon of green bodies.[13,20] Generally, an N_2-filled chamber is used to avoid the interference of oxygen. However, a technical process under nitrogen is complicated, and hence increases the cost of production.

Recently, a new epoxy resin and hardener system was developed for gel-casting of alumina.[21,22] The advantage of this method is that it can be carried out in an air atmosphere. It suggests a novel field to develop the gel-casting system. In this work, β-TCP ceramics are prepared using epoxy resin as a gelling agent. The effects of the dispersant and the solids loading on the rheological behavior of β-TCP slurries are investigated. The mechanical properties of green and sintered β-TCP sample are also studied.

2. Experimental procedure

2.1. Materials

The β-TCP powder obtained by precipitation from calcium nitrate solution and diammonium hydrogen phosphate solution, with an average particle size of 0.46 μm and a specific surface area of $4.74\ m^2\ g^{-1}$, is used as the raw materials.[9] Polyacrylic acid ammonium salt (Lopon885, 45 wt.% in water, MW = 4000–5000, BK Giulini), is selected as the dispersant. A water-soluble epoxy compound sorbitol polyglycidyl ether (SPGE) (EX614-B, Negase Chemtex, Japan), whose epoxy equivalent weight is 173 g/epoxy equivalent, and a polyamine

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Table 1
EH&S summary for SPGE and IDPA

Monomers	Oral LD_{50} for rats (mg/kg)	Vapor pressure at 20 °C (mmHg)	Inhalation protection	Flash point (°C)	Skin contact
SPGE	5100	<0.5	Ventilation	>160	Irritant
IDPA	810	0.04	Adequate ventilation	118	Irritant, corrosive

hardener 3,3′-iminodipropylamine (IDPA) (Fluka chemika, Switzerland) are employed to consolidate the slurries. The safety data of SPGE and IDPA are described in Table 1.

2.2. β-TCP slurries preparation and characterization

The slurries are prepared by ball milling, in a first stage, an aqueous premix solution with 13 wt.% of sorbitol polyglycidyl ether is prepared. Then powder is progressively added to make solids content between 40 vol.% and 55 vol.% with different amount of dispersant. The formulation of 55 vol.% slurry is given in Table 2. Rheological measurements are performed on a coaxial flat rheometry (SR-5 Rheomeric scientific instrument company, America). Measurements are performed in the shear rate range of 0.1–1000 s^{-1} at 20 °C. Viscosity data are recorded at a constant shear rate of 100 s^{-1}.

2.3. Gel-casting and sintering

The obtained slurries are degassed before casting into moulds (50-mm length, 6-mm width and 7-mm height). Then the moulds are put in water bath at 45 °C for 45 min in order to gel the system and have a strong green pieces. The gelled pieces are carefully dried to avoid cracking. They are kept firstly for 15 h at 95% relative humidity (RH), 40 °C, then at 90% RH, 60 °C for 9 h, and then 8 h in air. Finally, they are dried at 100 °C for 8 h.

TG/DTA are determined by thermogravimetric analysis (TG/DTA, STA 449C, Netzsch Instruments, Germany). The green blocks are heated to 600 °C at a heating rate of 1.0 °C/min to burn out the polymers and other volatiles, followed by the pressureless sintering at 1100 °C for 5 h for densification purpose. The sintering temperature is carefully controlled below 1125 °C to avoid transformation from β to α phase.[23]

The density and distribution of pore size of green pieces are determined using Hg intrusion porosimetry with a Micromeritics Pore Sizer 9320. Three-point bending test is performed on the Instron 5566 universal testing machine using specimens with dimensions of 3 mm in thickness, 4 mm in width and 36 mm in length at a crosshead speed of 0.5 mm/min. The compressive strength of the green and sintered pieces was measured in Instron 5500R universal testing machine, at a crosshead speed 2.0 mm/min. The sample for compressive test is cut in the size of 5 mm × 5 mm × 10 mm. The indentation test is performed in a microhardness tester (IF, AkashIII, Japan), with a Vickers indenter, applying a load of 2.0 kg for 10 s. Interference lenses are used in the optic microscope to determine clearly the indentation. The fracture toughness (K_{IC}) of the samples is determined using the indentation technique by measuring the crack length and using known equations. At least five measurements are prepared for each test. The microstructure of the pieces is observed on the fractured surface and polished surface in scanning electron microscopy (SEM) (model EPMA-8705Q, HII, Shimadzu, Japan). The average grain size at different sintering temperatures is calculated using the linear intercept method. At least 50 grains are measured to get the average value.

Table 2
Components of 55 vol.% β-TCP slurry using water-soluble epoxy ether for gel-casting

Components	Function	Content (wt.%)
SPGE	Monomer	2.74
IDPA	Hardener	0.85
Deionized water	Solvent	18.28
β-TCP	Ceramics powder	77.51 (55 vol.%)
Lopon885	Dispersant	0.62

3. Results and discussions

3.1. β-TCP slurries preparation and characterization

3.1.1. Effect of dispersant content

Selecting a proper dispersant with suitable quantities for the powder is essential to obtained well-dispersed slurries. The strong influence of dispersant concentration can be easily deduced from Fig. 1, which shows the viscosity of 50 vol.% β-TCP slurry at 100 s^{-1}. When the amount of dispersant is lower than the saturation limit of dispersant adsorption on the β-TCP particles, the suspension is unstable and had higher viscosity.[24] The minimum viscosity is obtained when dosage of dispersant is 0.75 wt.% based on β-TCP powder. Since the pH of the present slurry is about 9.5, the dispersant (PAA-NH_4) might dissociate

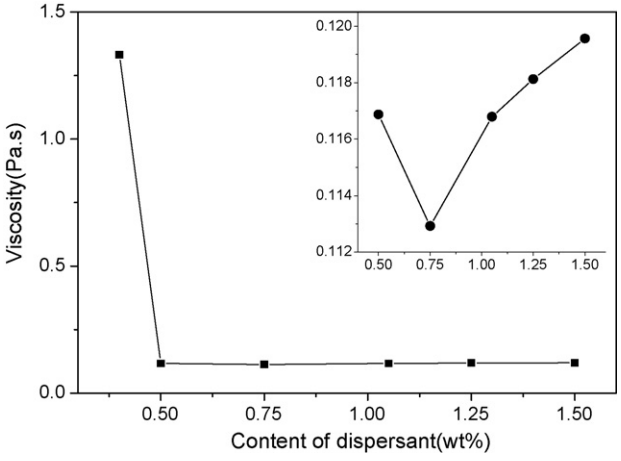


Fig. 1. Influence of dispersant content on the viscosity of β-TCP slurries versus shear rate (50 vol.%).

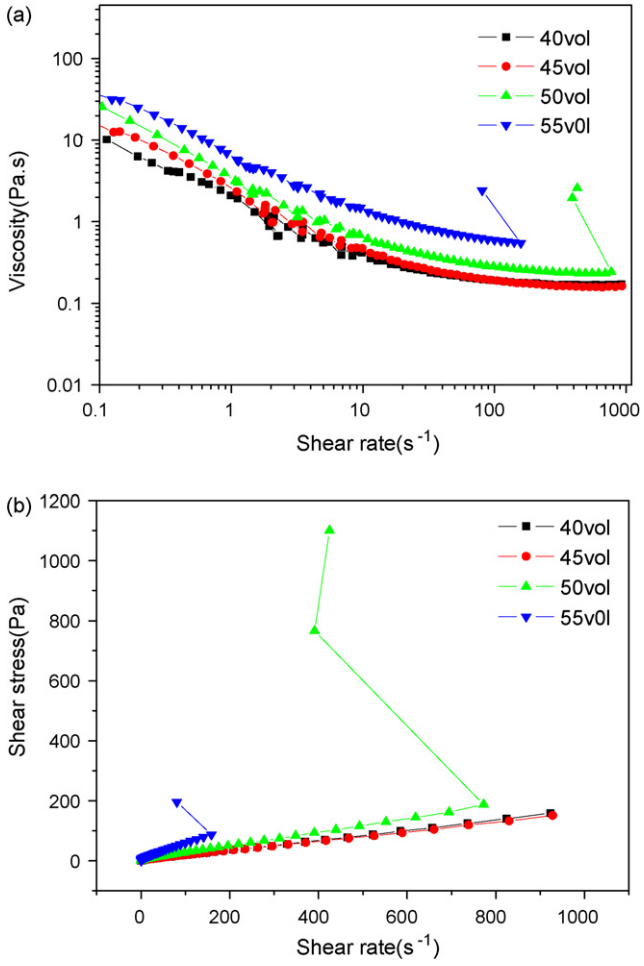


Fig. 2. Properties of β-TCP suspensions with different solids content.

into ionized PAA and NH_4^+. The negative charged PAA may be adsorbed on the particle surface and thus provide the electrostatic effect to stabilize the slurry, thereby resulting in a decrease in the viscosity of the slurry.[25]

3.1.2. Effect of solids loading

In gel-casting, the green density of the cast part has close correlation with the solids loading of the slurry. Consequently, it is important to prepare slurries with high solids content. On the other hand, low viscosity is beneficial for both mixing and casting in slurry processing.[10,12] It is, therefore, important to maintain slurry fluidity while optimum solids content. The rheological curves of slurries containing different amount of solids content are shown in Fig. 2. In general, the β-TCP suspensions are shear thinning and, with the increase of the solids loading the viscosity increased. Fig. 2a shows that the viscosity is also strongly dependent on the solids content, and the viscosity at shear rate 100 s^{-1} increases from 0.18 Pa s (40 vol.%) to 0.59 Pa s (55 vol.%). At low solids content, β-TCP suspensions are quasi-Newtonian. As the solids concentration increase, the slurries gradually become dilatant. Nevertheless, Fig. 2a shows that the viscosity of a 55 vol.% slurry is only 0.59 Pa s of shear rate at 100 s^{-1}, which are suitable for gel-casting.

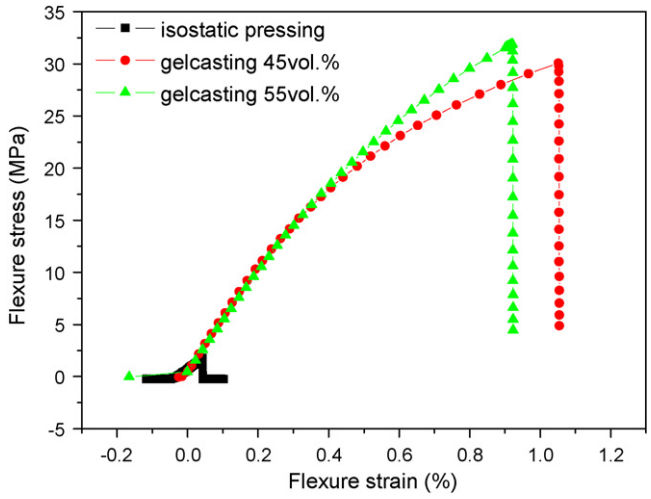


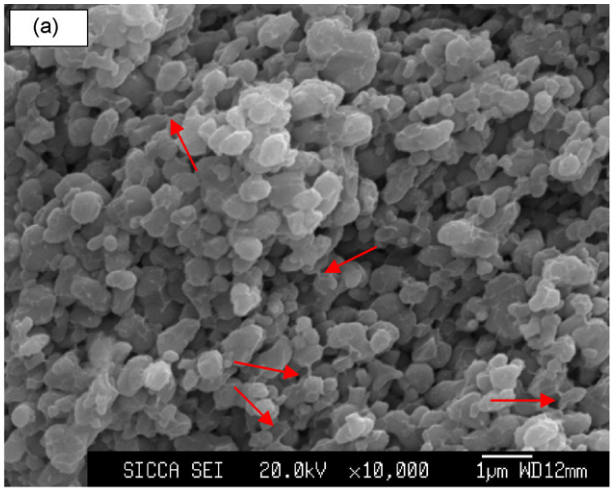
Fig. 3. Flexure stress versus flexure strain of green pieces prepared by different methods. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

3.2. Characterization of green pieces

After casting, solidification and drying, well-shaped green bodies are obtained. Neither contraction nor cracking is observed. The pieces show enough strength for handling. The density and mechanical properties of the green pieces with different solids loading are showed in Table 3. Because of high solids content in the slurries, high relative densities in the green pieces are obtained. It increases from 45.5 ± 2.6% to 59.9 ± 0.2% as solids loading increases from 40 vol.% to 55 vol.%. A beneficial result of the gel-casting process is the high strength of the dried green blocks.[26] The compressive strength of dried pieces is range from 36.4 ± 2.1 MPa to 65.8 ± 2.3 MPa, and flexural strength from 30.4 ± 1.4 MPa to 36.4 ± 1.7 MPa as solids concentration ascending. Moreover, green pieces prepared by gel-casting method show plastic deformation when they were fracture, in contrast to the green pieces prepared by isostatic pressing method show brittle deformation when they were fracture. The type of fracture is proved by flexure stress versus flexure strain curves in Fig. 3. The green pieces produced in gel-

Table 3
Density and mechanical properties of β-TCP green pieces

Solids loading (vol.%)	Relative density (%TD)	Compressive strength (MPa)	Flexural strength (MPa)
40	45.5 ± 2.6	36.4 ± 2.1	30.4 ± 1.4
45	49.1 ± 0.2	42.6 ± 2.3	33.7 ± 2.1
50	55.1 ± 0.1	54.5 ± 5.1	35.2 ± 1.7
55	59.9 ± 0.2	65.8 ± 2.3	36.4 ± 1.7



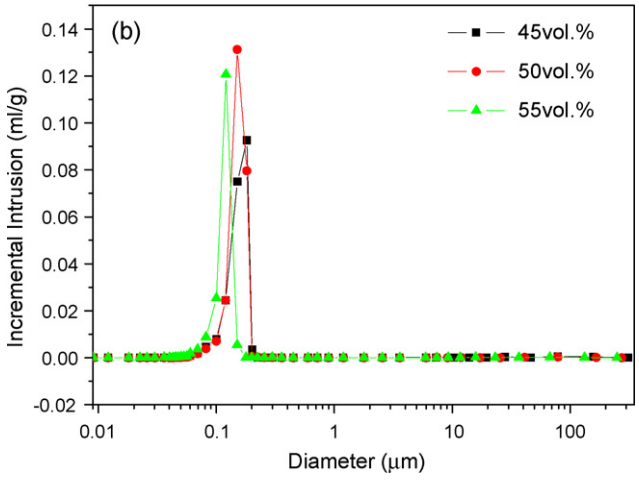


Fig. 4. (a) Micrograph of the fractured surface of green sample and (b) pore size distribution of β-TCP dried sample with different solids content. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

casting have longer flexure strain and higher flexure stress than those produced in isostatic pressing, indicating the existence of polymer and homogeneous packing. The green mechanical properties are significantly improved with respect to those obtained by conventional forming procedures, such as injection molding, slip casting and some gel-casting procedures,[26,27] so that the parts can be easily handled and machined in the green state. The high strength comes from the cross-linking gel network and the homogenous packing of particles. This is confirmed in the fracture surface of green sample prepared by gel-casting method (Fig. 4a). As shown by red arrows, the dried gels adhere to β-TCP particles and bind them together. There are pores with different sizes in the green bodies. As shown in Fig. 4b, the pore diameter distribution of β-TCP green samples with different solids content, obtained by Hg intrusion porosimetry, is a monomodal distribution type. The maximum distribution of pore size in green pieces decreases with the ascending of solids content of the slurries. Also, green pieces with lower solids content have bigger pore size than those with higher solids content.

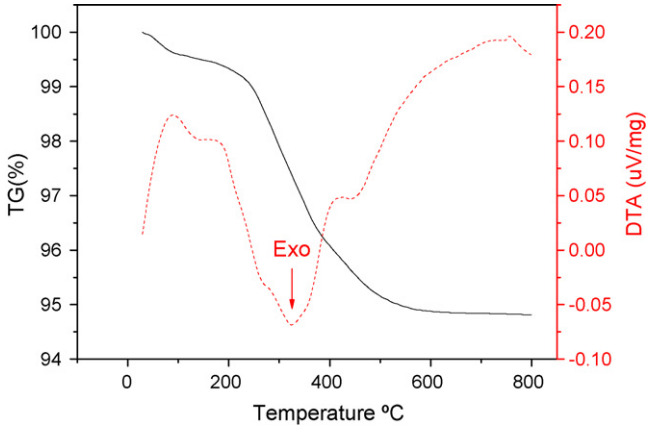


Fig. 5. TG/DTA curves of β-TCP piece with 50 vol.% solids content in air.

Fig. 5 is the TG-DTA pattern of β-TCP green pieces with 50 vol.% solids content. The total mass loss in the heat-treated process is only about 4.5 wt.% according to the low organic content in green pieces. Organic content in green pieces include the monomer, hardener and dispersant as shown in Table 2. The first endothermic peak at 95 °C indicates the removal physically adsorbed water. The dominating weight loss occurred between 200 °C and 550 °C, corresponding to an exothermic peak at about 320 °C. This wide burn out range allows an easy binder burn out process. In present work, a heating rate of 1.0 °C/min is applied successfully to remove the binders without cracks.

3.3. Characterization of sintered pieces

The relative density and shrinkage of sintered pieces versus the solids content in slurries are shown in Fig. 6. The relative density of sintered pieces increased with the ascending of the solids content, raises from 0.765 at 40 vol.% to 0.974 at 55 vol.%. Meanwhile, the shrinkage of the sintered bodies increases from about 14.0% to 16.1%. Higher solids content in slurries lead to higher green density and final density in sintered bodies. With 55 vol.% solids content in slurries, the green samples can be easily densified at 1100 °C for 5 h sintering.

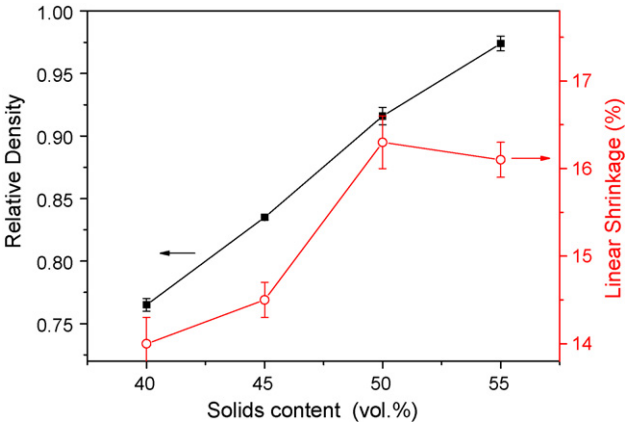


Fig. 6. Effects of solids content in slurries on shrinkage and relative density of sintered bodies.

Table 4
Mechanical properties of β-TCP sintered pieces in comparison with reported sintered β-TCP pieces and cortical bone

Properties	β-TCP ceramics from gel-casting	β-TCP ceramics reported[6,8]	Cortical bone[3]
Compressive strength (MPa)	319 ± 18	460–687	100–230
Flexural strength (MPa)	97.4 ± 6.0	140–154	50–150
Elasticity modulus (GPa)	90 ± 2	33–90	7–30
Fracture toughness (MPa $m^{1/2}$)	1.00 ± 0.07	–	2–12

The mechanical properties of the sintered samples are satisfying, with compressive strength, flexural strength, elasticity modulus and fracture toughness 319 ± 18 MPa, 97.4 ± 6.0 MPa, 90 ± 2 GPa and 1.00 ± 0.07 MPa $m^{1/2}$, respectively. The mechanical properties of these pieces are within the range of reported data for cortical bone,[3,28] but still lower than reported work (Table 4).[6,8] It is difficult to obtain compact β-TCP ceramics by colloidal process, so the mechanical properties reported are usually come from the hot isostatic pressing. In those methods the relative density of sintered ceramics was usually higher than 99.7% TD. However, those methods are costly and difficult to prepare pieces with complex shapes. Polished surface and fracture micrographs of pieces after sintering are shown in Fig. 7. A typical structure of ceramic materials with high density is observed in Fig. 7a. The crystalline size is between 1.0 μm and 5.0 μm. The average grain size is 2.59 ± 0.62 μm determined by the linear intercept method. The sample is mostly inter-crystalline failure type in the fracture micrograph (Fig. 7b).

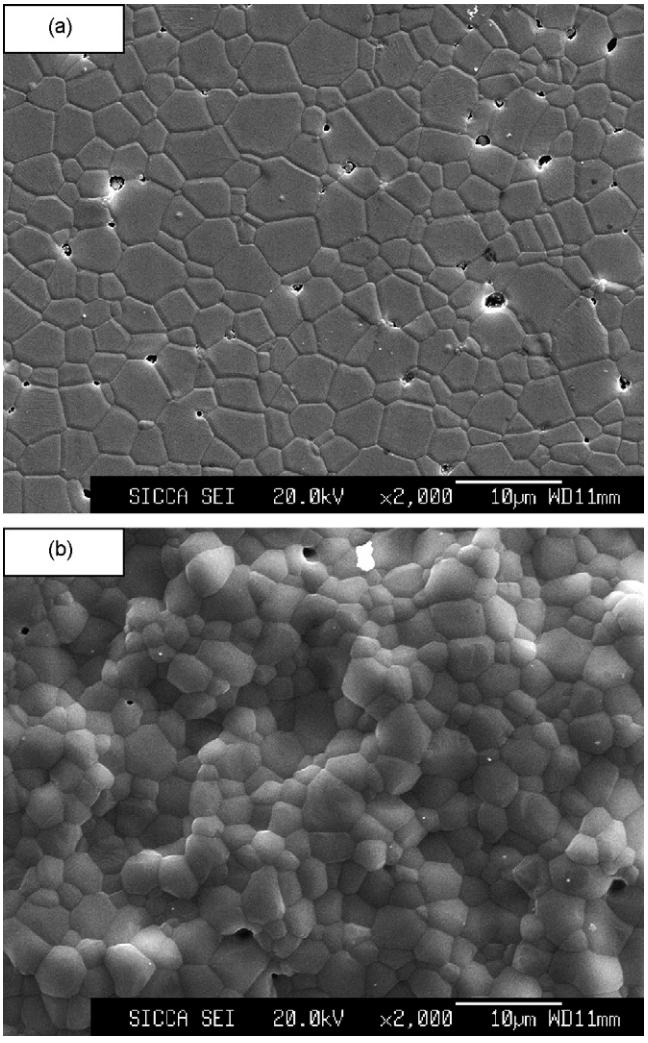


Fig. 7. Microstructure of polished surface (a) and fracture (b) of β-TCP pieces.

4. Conclusions

In this work, a water-soluble epoxy resin combined with a polyamine hardener is applied for gel-casting of β-TCP. It is confirmed that the concentration of dispersant and solids content strongly influence the rheological behavior of the β-TCP suspensions. The optimum concentration of dispersant is 0.75 wt.%. The β-TCP suspensions are fluid at high solids content. After casting, solidification and drying, the green pieces have high density with high strength for further machining. The compressive strength of dried pieces is in range from 36.4 ± 2.1 MPa to 65.8 ± 2.3 MPa, and flexural strength from 30.4 ± 1.4 MPa to 36.4 ± 1.7 MPa as solids concentration range from 40 vol.% to 55 vol.%. The mechanical properties of the sintered pieces are satisfying, with compressive strength, flexural strength, elasticity modulus and the fracture toughness 319 ± 18 MPa, 97.4 ± 6.0 MPa, 90 ± 2 GPa and 1.00 ± 0.07 MPa $m^{1/2}$, respectively. The structures of green body and sintered ceramics are homogeneous, and large defects are not observed. Results show that the combination of epoxy resin and polyamine hardener is effective for gel-casting of TCP ceramics.

Acknowledgements

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