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Ceramics International 38 (2012) 2991–2996

CERAMICS INTERNATIONAL

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Fabrication and properties of porous β-tricalcium phosphate ceramics prepared using a double slip-casting method using slips with different viscosities

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Received 24 July 2011; received in revised form 27 November 2011; accepted 28 November 2011
Available online 19 December 2011

Abstract

A new method to enhance the flexural strength of porous β-tricalcium phosphate (β-TCP) scaffolds was developed. This new method provides better control over the microstructures of the scaffolds and enhances the scaffolds' mechanical properties. Using this technique, we were able to produce scaffolds with mechanical and structural properties that cannot be attained by either the polymer sponge or slip-casting methods alone or by simply combining the polymer sponge and slip-casting methods. The prepared scaffolds had an open, uniform, interconnected porous structure with a bimodal pore size of 100.0–300.0 μm. The flexural strength of the bimodal porous β-TCP scaffold sintered at 1200 °C was 56.2 MPa and had porosity of 61.4 vol%. The scaffolds obtained provide good mechanical support while maintaining bioactivity, and hence, these bioscaffolds hold promise for applications in hard-tissue engineering.

Keywords: β-TCP; Porous scaffolds; Double slip-casting; Viscosity; Flexural strength

1. Introduction

Bioactive materials are known to form strong bonds to bone and soft tissue through the formation of a crystalline β-tricalcium phosphate (β-TCP) layer on their surfaces upon contact with body fluid. Third-generation biomaterials have been developed with a focus on tissue regeneration to promote specific cellular responses at a molecular level with minimally invasive surgery [1,2].

Porous calcium phosphate biomaterials are very important materials in bone tissue engineering. It is of great interest to obtain pore diameters of greater than 100 microns [3–5] and a number of pore interconnections to allow in the shortest possible time the bioresorption of the scaffold and subsequent new bone formation. The bioresorption of the scaffold should be in timely accordance to the new bone formation. Thus, the scaffolds should be resorbed or degraded only shortly after the complete formation of new bone throughout the defect. For this purpose, it is necessary to design highly porous scaffolds that include the necessary macroporosity to ensure bone oxygenation and angiogenesis [10]. Therefore, designed porous scaffolds should contain a network of interconnected pores in which more than 60% of pores have a size ranging from 150 to 400 μm and, at least 20% of the pores should be smaller than 20 μm. Pores with sizes <1 μm are appropriate for interacting with proteins and are mainly responsible for bioactivity. However, pores with sizes between 1 and 20 μm are important in cellular development, the type of cells attracted, and the orientation and directionality of cellular ingrowth. Moreover, pores with sizes between 100 and 1000 μm play an important role in cellular and bone ingrowth because pores of this size are necessary for blood flow distribution and have a predominant function in the mechanical strength of the substrate [6]. Consequently, the porosity of three-dimensional scaffolds is a very important factor due to the great influence of the porosity on the final behavior of the implant [5].

Various methods to impart porosity to a ceramic body are known, and most are based on the admixing of a foreign

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0272-8842/$36.00
doi:10.1016/j.ceramint.2011.11.078

combustible organic material that is burnt out during firing [7–9]. The gel-casting [10,11], freeze casting [12], and replica methods [13,14] have also attracted intense attention due to their potential for precise pore structure control. The coating of polymer foams with a ceramic slip is the most widespread processing approach for producing an open pore structure. These techniques enable materials to be fabricated with precise control over the micro- and macropore structure and the desired geometry, but the mechanical strength of the scaffolds was usually low due to the high porosity, large macropore size and interconnected structures. The limitation of the scaffold strengths is one of the major challenges in the scaffold fabrication field. Similarly, the poor mechanical properties of β-TCP scaffolds have severely hindered their clinical applications [15–17]. For many years, a number of studies have been focused on the improving of mechanical strength of β-TCP bioceramics [15–21].

Replication of polymer foams was one of the first techniques developed for producing cellular ceramics with controlled macroporosity and a desired geometry [22,23]. The macropores are size controllable and maintain high interconnectivity and high porosity. Therefore, it is desirable to combine this method with the double slip-casting method that produces nanopores, resulting in macroporous bioscaffolds with an optimum pore structure, overall porosity and improved mechanical strength. In order to attain micropores, a foaming agent was added. In this article, we report the success of this method, leading to a new technique that integrates the double slip-casting technique with the polymer sponge and foaming agent replication method; the result is a superior nanomacroporous β-TCP scaffold for bone tissue engineering. We studied the structural, mechanical, and chemical properties of the scaffolds prepared under various processing conditions. Slip preparation was also an important aim of this investigation.

2. Experimental procedure

2.1. Materials and methods

β-Tricalcium phosphate (β-TCP) powders were synthesized as follows. Distilled water in the 90 wt% was added into the mixture of calcium hydrogen phosphate di-hydrate (Wako Pure Chemical Industries, Ltd.) and calcium carbonate (Wako Pure Chemical Industries, Ltd.) at the molar ratio of 2:1. The slurry was mechanically agitated at 50 rpm for 24 h at room temperature. The reacted slurry was dried and calcined in air at 720 °C for 8 h to produce fine β-TCP powders. The powder was composed of clusters of submicron crystallites, and the particle sizes were in approximately 0.41 μm (for β-TCP1) and 0.86 μm (for β-TCP2).

The procedure for synthesizing bimodal porous β-TCP ceramics is shown in Fig. 1. The mixture was obtained by adding a solution of 1.5 wt% deflocculant (Seluna D-305 from Chukyo Oils and Fats Co., Ltd.) to β-TCP1 powder with a solid content of 58.5 wt%. The solution was then diluted 10 times with water to make slurry-1. Slurry-1 was mechanically agitated using zirconia balls in a zirconia pot mill at 50 rpm for 2.0 h at room temperature. The slurry was added 0.5 wt% of foaming agent (Emma-RU D-3-D of Kao Corp.) to make a slip-1. The specimen was obtained by dipping a polyurethane block (medium pore size type supplied by Ube Industries Inc.) into slip-1, after which it was dried under vacuum for 5 min to yield dried specimen-1. Slip-2 was obtained by adding β-TCP2 powder with a solid content 62.5 wt% to a solution of 1.5 wt% deflocculant (Seluna D-305 from Chukyo Oils and Fats Co., Ltd.); this mixture was diluted 10 times with water to make slurry-2. The procedure for producing slip-2 was the same as that for slip-1. Dried specimen-1 was dipped into slip-2, and then the sample was dried under vacuum for 5 min. The dried

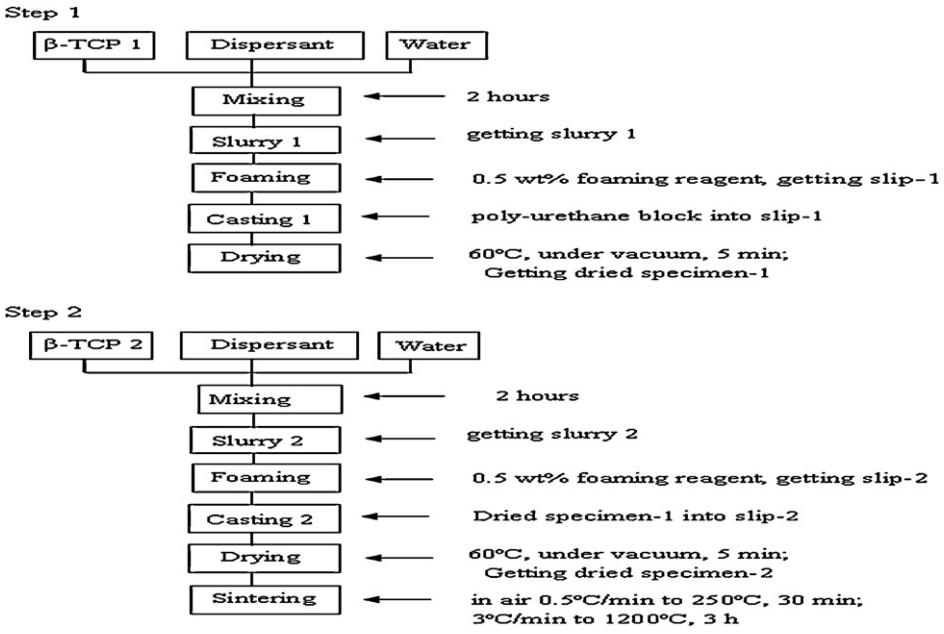

Fig. 1. Synthetic procedure for bimodal porous β-TCP ceramics.

specimen-2 samples were heated at a rate of 0.5 °C/min to 250 °C and then incubated at 250 °C for 30 min to decompose the deflocculant and the polyurethane template. These samples were subsequently heated again at a rate of 3 °C/min to 1200 °C, incubated for 3 h at 1200 °C, and cooled down to room temperature at a rate of 3 °C/min to yield the final samples. All of the slurries were aqueous, and deionized (DI) water was used in all experiments.

2.2. Measurements

The average particle diameter of the slurries was measured using a SA-CP3 instrument (Shimadzu Co.). The average particle specific surface area of dried slurries was measured using the BET method (Shimadzu, Flow Sorb II 2300). The rheological properties of the slips were characterized using a digital viscometer (DV-II+ of Brook field). The crystal phases of the synthesized powder and that of the sintered body were examined using a MAC Science MXP^3 X-ray CuKα diffractometer at 40 kV and 20 mA. The densities of the β-TCP porous bodies were obtained by the water immersion method based on the Archimedean principle. The pore size distribution was measured using mercury intrusion porosimetry (AutoPore IV 9500, Shimadzu Co.). Scanning electron microscopy (SEM) and EDX analyses of the powders and sintered body were performed using a Hitachi S-3000 SEM coupled with a Horiba EMAX-2200 X-ray analyzer. The bending strength of the porous β-TCP-sintered body was measured by a three-point bending method (SHIMADTU autograph AG-500A) in which the supporting parts were set 40 mm apart from one another with a crosshead speed of 0.5 mm/min.

3. Results and discussion

3.1. Powder and slip characterization

The particle sizes and the specific surface areas of the two slurries are listed in Table 1. β-TCP1 and β-TCP2 have bimodal particle size distributions, centered at approximately 0.3 and 0.9 μm and at approximately 0.4 and 1.5 μm, respectively.

Fig. 2 shows the effect of the dispersant concentration on the viscosity of the suspensions at various loadings of β-TCP powder. The viscosity can be seen to approach a minimum for the dispersant concentration. The behavior has been explained elsewhere [24,8].

The slips prepared in this work displayed a shear thinning or pseudoplastic behavior. This behavior was characterized by a decrease in the viscosity at increasing shear rates and is typically found in dispersions of β-TCP suspensions containing

Table 1
Particle size and specific surface area of β-TCP 1 and β-TCP 2.

Powders	Powder particle size (μm)	Specific surface area (m^2/g)
β-TCP 1	0.34	36.24
β-TCP 2	0.75	16.67

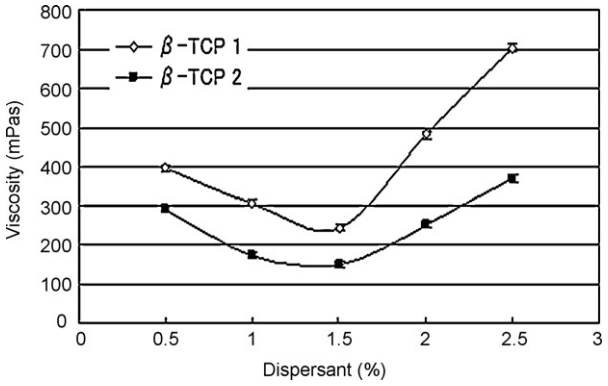

Fig. 2. Viscosity measured at a shear rate of 10.2 s^{-1}, plotted as function of dispersant concentration for β-TCP suspension containing 58.5 and 62.5% β-TCP, respectively.

a high percentage of solids. In the fabrication of ceramic foams, a slight pseudoplasticity favors the generation of the foam because lower viscosities are obtained under shearing and static conditions. This property significantly improves the foam's stability because the viscosity increase delays the collapse of the fluid films around the bubbles. The particle size and the powder concentration greatly influence the rheological behavior of a slip [25]. To obtain a β-TCP slip with a reasonably low viscosity for solid loading, β-TCP 1 and β-TCP 2 powder concentrations of 58.5 and 62.5 wt% were selected, with 1.5 wt% dispersant for both. The viscosity of the slips containing 58.5 or 62.5 wt% β-TCP powders showed similar behaviors for all deflocculant concentrations tested.

The rheology of the slips displayed in Fig. 3(a) appears to be typical of pseudoplastic fluids. This behavior was confirmed by plotting the shear stress against the shear rate (Fig. 3(b)). The shear stress of a slip prepared with the β-TCP1 powder, which has a larger specific surface area than that of the β-TCP2 powder, was larger than that of a slip prepared with the β-TCP2 powder. Similarly, the viscosity of a slip prepared with the β-TCP1 powder was larger than that of a slip prepared with the β-TCP2 powder.

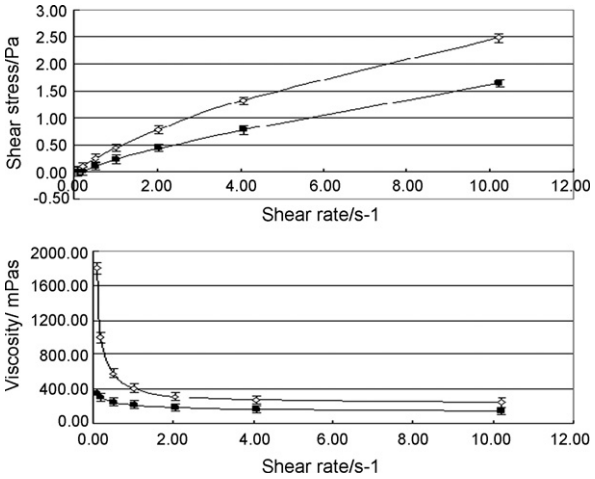

Fig. 3. Flow behavior of suspensions containing β-TCP1 58.5% and β-TCP2 62.5%. Plots of (a) viscosity and (b) shear stress against shear rate are shown.

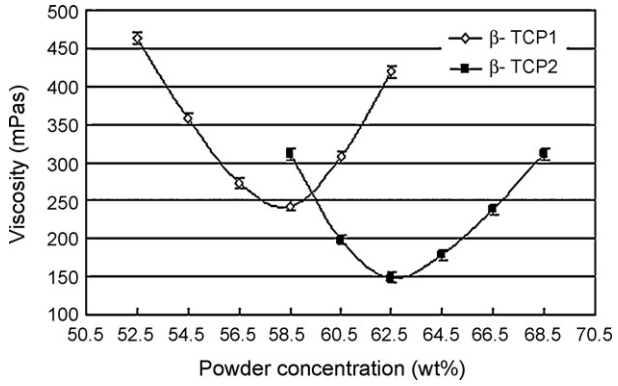

Fig. 4. The viscosity for β-TCP slurries containing 1.5 wt% of deflocculant with 0.5 wt% of foaming reagent as a function of β-TCP powder concentration.

Slip casting is a common shaping/forming process, and many studies focused on identifying a method suitable for forming a high density HAp body have been reported [26,27]. To improve the density of the β-TCP sinter, suspensions with a high β-TCP concentration have been prepared using a deflocculant. The nature of the surface of β-TCP particles influences the rheological behavior of the slurries. An increase in the viscosity occurs above a certain specific surface area over the range of 10–15 m^2/g [27]. Therefore, suspensions with high β-TCP concentrations were obtained using a β-TCP powder with a relatively low specific surface area [27]. Here, fine β-TCP powders with high specific surface areas were applied; thus, the solid loading at the minimum viscosity was relatively low. The results are shown in Fig. 4.

The slip rheology is important because the process involves casting. In common with other casting operations, very fluid systems are required to enable easy filling of high-complexity shapes. The high-viscosity characteristics of slip systems at low shear rates are thus a critical factor for the production of complex-shaped foamed bodies.

Therefore, first we dipped a poly-urethane block into the slip-1 forming single slip-casting, then the dried specimen was dipped into the slip-2 forming double slip-casting. The large viscosity slip-1 is to raise the adhesion power of slip-1. The low viscosity slip-2 is used is to repair the defect of slip-1 forming specimen, and strengthen the connection between the pores wall. Therefore, the density of the bridge between the pores is higher after slip-2 casting.

The specimens obtained by double dipping slip-casting 0.5 wt% polyurethane foam into slip-1 or slip-2 was dried under vacuum. The specimen was heated at 1200 °C for 3 hours. The purpose of the heat-treatment process is to drive off the volatiles and the urethane foam to form a porous network. XRD analysis showed that β-TCP produced only peaks that corresponded to β-TCP. This was a further evidence that the material in this study was single-phase β-TCP that did not decompose to secondary phases on sintering/heating.

3.2. Porous body properties

3.2.1. Porous body characterization

Fig. 5 shows the scaffolds of the bimodal porous bodies prepared by the double slip-casting method. These figures show that the scaffolds have an open, interconnected, uniform porous macrostructure (Fig. 5(a) and (b)) and microstructure (Fig. 5(c)). In this study, bimodal-type β-TCP porous materials with both macropores of 200 μm or more and micropores of 1.0 μm in size were successfully fabricated. Attained macropores was depended polymer sponge, the micropores was depended foaming agent.

3.2.2. Pore structure

Fig. 6 shows the pore size distribution of the bimodal porous β-TCP ceramic scaffolds prepared by heating the foam in a β-TCP slip; the peak height of the distribution curve indicates the number of pores. A vast number of micropores, generally in the size range of 0.1–2.0 μm, and 50.0–300.0 μm macropores were detected using a mercury porosimeter.

The number of pores in a specimen obtained with single slip-casting was greater than that of the samples obtained by double slip-casting followed by heating at 1200 °C, which agreed with the porosity results, as shown in Fig. 5. The pore sizes of those specimens obtained by single slip-casting were larger than those of double slip-cast specimens. For the single slip-cast specimen, the peak intensities in the pore size distribution curve

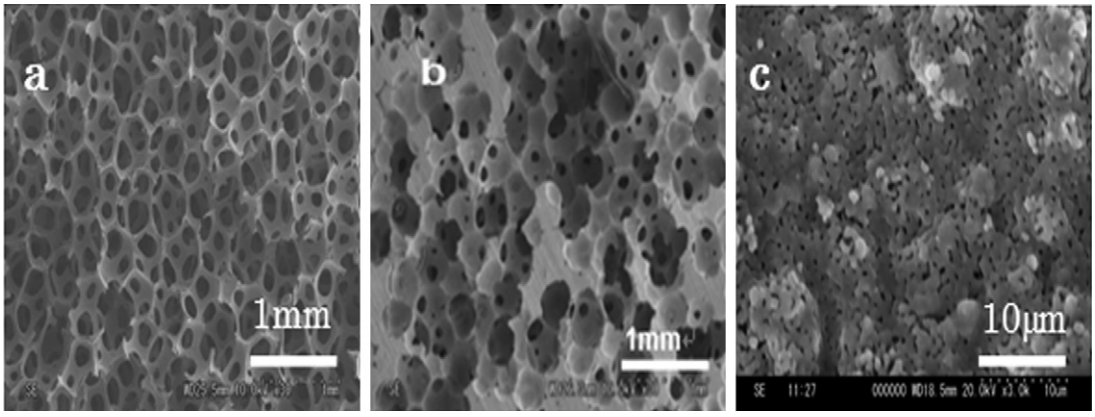

Fig. 5. SEM micrographs of (a) macropores formed by single slip-casting, (b) macropores formed by double slip-casting and (c) microporous β-TCP scaffolds obtained by heating the foam dipped in 58.5 and 62.5 wt% β-TCP slips with 1.0 wt% deflocculant and 0.5 wt% foaming reagent at 1200 °C for 3 h.

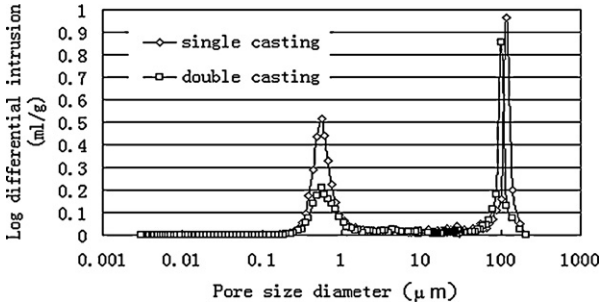

Fig. 6. Pore size distribution of bimodal porous β-TCP ceramic scaffolds prepared by heating the foam dipped in β-TCP slip with 1.0 wt% of deflocculant and 0.5 wt% of foaming reagent at 1200 °C for 3 h; (□) single-slip casting with the slip milled for 2.0 h; (◇), double-slip casting with the slip milled for 2.0 h.

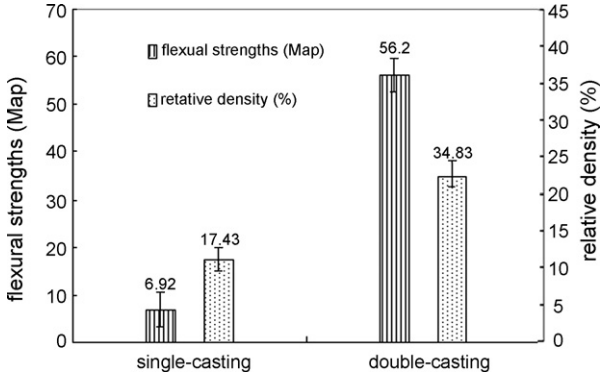

Fig. 7. Relationship between relative density and flexural strength of the β-TCP porous scaffolds prepared by heating the foam dipped in slip-1 and silp-2 at 1200 °C for 3 h.

were higher for micropores than macropores. The total percentage of pores of the single slip-cast specimen was larger than that of the double slip-cast specimen, as shown in Fig. 6.

Single slip-casting and double slip-casting formed micropores of the same size, but the macropores were different in size. The number of micropores was greater for single slip-casting than for double slip-casting. The macropores formed by the double slip-casting method were smaller than those formed by the single slip-casting, as confirmed by mercury porosimetry (Fig. 6). The large spherical pores and interconnecting pores were large enough for cells to pass through and proliferate, and the size of the small pores was sufficiently small to allow nutrients to circulate through the scaffold to induce cell growth [28].

3.2.3. Mechanical properties

The flexural strength of the porous β-TCP ceramics was measured using a three-point fixture. The test of rectangular pieces used the β-TCP sintered body prepared from heating the foam dipped in the 58.5 and 62.5 wt% β-TCP slips containing 1.5 wt% deflocculant and 0.5 wt% foaming reagent yielded flexural strengths of 6.92 and 56.2 MPa for the single and double slip-cast specimens, respectively. The porosities of these bimodal porous β-TCP ceramic scaffolds were 72.60 and 61.4%, respectively. The flexural strength obtained for the bimodal porous β-TCP ceramic scaffolds prepared in this study by double slip-casting was seven-times greater than that of the single-cast specimen and three-times greater than that found in a previous study [25]. Because the fracture of brittle materials such as ceramics is primarily a weak-link process, the micropores within the porous β-TCP ceramic are assumed to have no significant influence on the strength relative to the influence of the macropores. Each macropore is essentially a macro-defect in the brittle ceramic material. The bimodal porous β-TCP ceramic scaffolds obtained in study by double slip-casting have strong macropore walls, as shown in Fig. 4(b). Double slip-casting can provide the firm wall support associated with the large macropores. In this study, a polyurethane block and higher viscosity slip-1 were used to make a porous ceramic scaffold. However, the ceramic scaffolds were relatively weak. Lower viscosity slip-2 was used to strengthen and repair the relatively weak links of the ceramic scaffolds. Therefore, the connecting part of the ceramic scaffolds became more robust.

Fig. 7 depicts the bending strength of the porous β-TCP scaffolds as a function of the density. After only single slip-casting, the relative density was lower. However for double slip-casting, the relative density was remarkably large. As expected, the strength remarkably increases with the increase in the density due to the augmentation of the overall solid area, as density increase under load explains this trend.

4. Conclusions

The flexural strength of porous ceramic scaffolds depends on the porous framework. In this study, a new approach combining the double slip-casting and polymer sponge methods to fabricate porous β-TCP scaffolds was developed. This method combines the advantages of both methods. A scaffold with a flexural strength of 56.2 MPa and a porosity of 61.4% was developed. The resultant bimodal porous β-TCP ceramic scaffolds showed very high flexural strength. Scaffolds with a pore size range of 100.0–300.0 μm and an interconnected macroporous structure were fabricated. Because the macroporous structure of the produced scaffold replicates the polymer sponge template, the pore size and shape are controllable, and scaffolds with complex shapes can be fabricated. In addition the viscosity choice is very important. Choosing the large viscosity slip is to raise the adhesion, increase the cementation of slip and polymer sponge template. The low viscosity slip is used is to repair the defect of large viscosity slip forming specimen, and strengthen the connection between the pores wall. Therefore, the density of the bridge between the pores is higher after low viscosity slip casting. Because the scaffolds are formed by in situ polymerization, the aggregation of β-TCP slip at the bottom of the scaffold due to gravitational force can be prevented, leading to a homogenous microstructure. The technique introduced in this study could be applied to the development of other bioceramics such as HAp and biphase of HAp/β-TCP ceramics with enhanced mechanical strength for load-bearing tissue engineering. The flexural strength obtained for the bimodal porous β-TCP scaffolds was greater than that reported in the literature. This study shows that the bimodal

pore structure of the β-TCP scaffolds obtained could be potentially suitable for applications in hard-tissue engineering.

Acknowledgments

The project is sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars; State Education Ministry and China postdoctoral Science Foundation; and a project funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

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