Rapid preparation and performance of degradable ceramic scaffolds based on stereolithography

Suocheng Songa, Zongqiang Gaoa, Haiman Xuq, Chonggao Baoa, Bingheng Lua, Baochao Zhengb, Wencai Dongb and Haiqiang Mac

*Collaborative Innovation Center of High-end Manufacturing Equipment, Xi’an Jiaotong University, Xi’an, China; †The Second Affiliated Hospital of Xi’an Jiaotong University, Xi’an Jiaotong University, Xi’an, China; ‡Northwestern Polytechnical University, Xi’an, China; ©State Key Laboratory for Mechanical Behavior of Materials, Xi’an Jiaotong University, Xi’an, China; †Institute of Advanced Wear & Corrosion Resistant and Functional Materials, Jinan University, Guangzhou, China

ABSTRACT
A simple and systematic research and development process were explained for ceramic additive manufacturing to obtain degradable ceramic scaffolds. First, the degradation rate of calcium silicate/β-tricalcium phosphate ceramics was controlled by adjusting component ratios. After soaking in the simulated body fluid, many cluster-like and silkworm pupa-like apatite deposits were formed on the surface of the prepared ceramic through the dissolution-precipitation process. Meanwhile, the deposition process was summarized. Then, according to the light-curing principle of the ceramic paste, the ceramic paste suitable for stereolithography was studied and prepared by considering three aspects: viscosity, solid content, and single-layer curing depth. Finally, ceramic scaffolds with a uniform structure were prepared by stereolithography, debinding, and sintering in sequence. Compared with the ceramics prepared by pressure forming, the open porosity increased by 8.1%, and the bulk density and flexural strength decreased by 3.83% and 16.11%, respectively.

CONTACT Suocheng Song suocheng0105@126.com Collaborative Innovation Center of High-end Manufacturing Equipment, Xi’an Jiaotong University, 99 Yanxiang Road, Xi’an, Shanxi Province 710054, P. R. China

1. Introduction
Massive bone defects caused by the removal of bone tumors, infections, trauma, etc., are prevalent in clinical practice [1–6]. The autogenous bone source is limited in such patients, and the surgical procedure easily leads to secondary damage [7,8]. Furthermore, the implantation of allogeneic bone inevitably results in immune responses and disease transmission [9–13]. Artificial bone is hardly used to repair massive bone defects in recent decades because of flexural strength and shape restrictions. The loss of healthy anatomic landmarks in damaged bone leads to a series of complications, such as crimpation, malformation of rotation, and delayed union. These complications often cause lifelong harm to patients and their families, increasing the social burden significantly. Considering this background, degradable scaffolds are good auxiliary tools to promote the recovery of broken bones [14–16]. The individual and degradable marrow cavity scaffold was explored by using additive manufacturing (AM) technologies in this work, trying to solve the problems mentioned above. Moreover, because no mold is required, the cost of a single scaffold is not high. Figure 1 shows the idea of the marrow cavity scaffold. The marrow cavity scaffold prepared by the AM technology based on CT data plays the role of support and positioning, and the broken bone (see the colored parts in Figure 1) is attached to the scaffold surface to ensure rapid healing. It is necessary to systematically study the material properties and manufacturing process of the scaffolds.

The manufacturing process of ceramic scaffolds consists of forming and sintering, which decisively influence their structure and performance. Various manufacturing methods are available, including pressure forming, slip casting, and AM. Compared with the other two methods, AM technologies, which overcome the shortcomings of traditional production methods, have evident advantages in the non-mold and rapid manufacturing process [17–20]. AM technologies are new approaches to prepare individual, complex structural components with high precision and reliability. Table 1 presents the characteristics of various AM technologies [21–30]. Stereolithography (SLA) with the highest solid content and precision is an excellent technique to rapidly manufacture ceramics with complex structural components. The main factor affecting ceramic SLA is the characteristics of the ceramic paste itself. The homogeneity, viscosity, solid content, and single-layer curing depth (SLCD) of the ceramic paste directly affect the final outcomes [21,26–28,30]. In general, it is easy to finally achieve higher mechanical properties and lower sintering shrinkage by improving the solid content of the ceramic paste. In practice,
scaffolds based on SLA. First of all, a systematic study was undertaken on the effect of the β-TCP-to-α-CS ratio on the degradability, physical properties, and flexural strength. The deposition process of apatite on the surface of the α-CS/β-TCP ceramic in the SBF is summarized. Secondly, according to the Beer-Lambert law, a light-cured ceramic paste was prepared with good uniformity, appropriate fluidity, and high solid content. Finally, ceramic scaffolds with the uniform structure were prepared by SLA, debinding, and sintering in sequence.

2. Experimental procedures

2.1. Materials

The raw materials mainly included β-TCP (purity 98.4%, D50 = 3 and 10 μm, density 3.07 g/cm³, Msea international institute for materials genome), α-CS (purity 98.7%, D50 = 3 and 10 μm, density 2.90 g/cm³, Msea International institute for materials genome), Tripropylene glycol diacylate (TPGDA) and ethoxylated trimethylolpropane triacrylate (TMP3EOTA) (photosensitive resin, analytically pure, Shanghai Guangyi Chemical Co., Ltd.), γ-(2,3-epoxypropoxy) propytrimethoxysilane (KH560, dispersant, analytically pure, Shanghai Aladdin Co., Ltd.), KOS110 (dispersant, analytically pure, Sinopharm Chemical Reagent Co., Ltd.), Ammonium polyacrylate (dispersant, analytically pure, Tianmen Hengchang Chemical Co., Ltd.), 2,2-Dimethoxy-2-phenylbenzene (photoinitiator,
analytically pure, Sinopharm Chemical Reagent Co., Ltd.). Tris-HCl buffer solution (1 mol/L, pH 8.0, Qingdao Jishikang Biological Technology Co., Ltd.) and simulated body fluid (SBF, pH = 7.4–7.5, Shanghai Enzyme Link Biotechnology Co., Ltd.) were used to evaluate the solubility of the immersed sample and the precipitates on the surface, respectively. Both solutions were replaced every 24 hours.

### 2.2. Preparation principle of the ceramic paste

The process of photosensitive resin absorption of UV light follows the Beer-Lambert law. The law shows the relationship between SLCD \((C_d)\), resin sensitivity \((D_p)\), light energy \((E)\), and critical energy \((E_c)\) [44]:

\[
C_d = D_p \ln \left( \frac{E}{E_c} \right)
\]  

(1)

According to the Beer-Lambert law, the SLCD of the ceramic paste can also be qualitatively analyzed. According to Griffith, various factors influence the ceramic paste sensitivity \((D_p)\), as shown in formula 3 [45]:

\[
D_p = \frac{2 d_c}{3 \omega V_c} \left( \frac{n_r}{n_t - n_r} \right)^2 = \frac{d_c}{V_c}
\]  

(2)

where \(n_r\) is the refractive index of photosensitive resin, \(n_t\) is the refractive index of ceramic particles, \(d_c\) is the particle size of ceramic particles, \(\omega\) is the scattering efficiency value, and \(V_c\) is the volume fraction of ceramic particles. When the difference in refractive index between ceramic particles and photosensitive resin is high, \(D_p\) mainly depends on \(n_r\). When the difference is slight, \(D_p\) depends on the ceramic particle size and ceramic’s solid content. Figure 3 shows the scattering efficiency of UV light passing through the ceramic paste.

### 2.3. Sample preparation and stereolithography

When studying the properties of \(\alpha\)-CS/\(\beta\)-TCP ceramics, the traditional pressure forming method was used. The forming pressure was 200 MPa. Both the heating rate and cooling rate were 5°C/min. The sintering temperature was 1100°C, with a holding time of 3 h. The preparation process of the ceramic paste was divided into three stages. First, the two powders were wet-mixed in a planetary ball mill at 200 rpm for 4 h. Then after drying, the mixed powders and resin additives were mixed using a homogenizer (ZYMC-200 V, Shenzhen Zhongyi Technology Co., Ltd.) at 1200 rpm for 30 s. Finally, the mixed paste was mixed again at 1500 rpm for 30 s. The ceramic three-dimensional (3D) printer (C900) from 3DCeram Sinto company was used in this experiment. The laser spot diameter was 30 μm. The printing power was 128 mW, with a scanning speed of 2500 mm/s and a layer thickness of 50 μm.

**Figure 3.** Scattering efficiency of UV light passing through the ceramic paste.

### 2.4. Characterization technique

The microstructure of the samples was observed under a scanning electron microscope (JEOl JSM-IT500LA). An x-ray diffractometer (XRD, Bruker D8 Advance) was used to detect the phase composition. The density and open porosity were measured using the Archimedes principle. The flexural strength was obtained using a three-point test at a falling speed of 0.5 mm/min using a universal testing machine. All the samples used for the flexural strength test were cut into parallelepips measuring 4 × 3 × 25 mm. The ceramic paste viscosity was measured using a rheometer (Anton Paar MCR 302) with a shear rate of 20/s.

### 3. Results and discussion

#### 3.1. Material properties

The properties of the composite depend on its composition. Therefore, the physical, mechanical, and degradation properties of \(\alpha\)-CS/\(\beta\)-TCP ceramics have been investigated by adjusting the content of the two components.
3.1.1. Factors affecting physical and mechanical properties

Six kinds of material proportions were prepared, as shown in Table 2. The theoretical densities of β-TCP and α-CS were 3.07 g/cm³ and 2.90 g/cm³, respectively. In general, the bulk density of α-CS/β-TCP ceramics should slowly decrease with an increase in α-CS content. Figure 4(a) shows that the bulk densities, open porosities, and flexural strength of α-CS/β-TCP ceramics vary with an increase in α-CS content. In practice, the bulk densities and flexural strength decreased significantly with an increase in α-CS content. The rapid increase in open porosity is the main reason for this trend. Figure 4(b) shows the pore size distribution of the samples by the SEM image analysis. The maximum pore size increased with an increase in α-CS content. Most pores in all the samples measured ≤1 μm. To further explore the reason, the fracture morphologies of four samples are shown in Figure 5. Figure 5(a) shows that sample CS0 has a high density and the main fracture form is transgranular. Figure 5(b) shows

Table 2. Material composition and nomenclature of six kinds of samples.

| Designation | Raw material ratio |
|-------------|--------------------|
| CS0         | α-CS: 0 wt%, β-TCP: 100 wt% |
| CS20        | α-CS: 20 wt%, β-TCP: 80 wt% |
| CS40        | α-CS: 40 wt%, β-TCP: 60 wt% |
| CS60        | α-CS: 60 wt%, β-TCP: 40 wt% |
| CS80        | α-CS: 80 wt%, β-TCP: 20 wt% |
| CS100       | α-CS: 100 wt%, β-TCP: 0 wt% |

Figure 4. Various properties of α-CS/β-TCP ceramics: (a) bulk densities, open porosities, and flexural strength of α-CS/β-TCP ceramics vary with an increase in α-CS content; (b) pore size distribution.

Figure 5. Fracture morphologies of four samples: (a) CS0, (b) CS20, (c) CS40, and (d) CS100.
that the porosity of sample CS20 is significantly increased. According to the original powder morphology and energy spectrum analysis, the long strip particles are α-CS. With the further increase in α-CS content, the density of sample CS40 drops rapidly (see Figure 5(c)). Figure 5(d) shows that α-CS has poor sinterability at 1100°C. The morphological changes in Figure 5 explain the trend in Figure 4 adequately.

3.1.2. In vitro degradation test

Figure 6 shows the degradation rate of six samples in Tris-HCl buffer over time. According to the results, the degradation rate of the samples increased significantly with an increase in α-CS content. At present, the degradation process of ceramics is generally considered to consist of buffer erosion and hydrolysis reaction [39–41]. The pores in the samples facilitated the infiltration of the buffer, and the hydrolysis reaction then occurred. The surface and the sintering necks between the particles in contact with the buffer began to dissolve gradually. The hydrolysis reaction formula of β-TCP is as follows:

\[
2Ca_3(PO_4)_2 + 6H_2O = 6Ca^{2+} + PO_4^{3−} + H_2PO_4^{-} \\
+ 2HPO_4^{2−} + H_2PO_4 + 6OH^{-}
\]

(3)

The bulk densities of the samples decreased significantly with a further increase in α-CS content. The higher the porosity, the larger the contact area between the samples and the buffer. This was the main reason why the degradation rate increased with an increase in α-CS content. Therefore, the degradation rate of α-CS/β-TCP ceramics can be controlled by adjusting the α-CS content.

According to the results presented in Figure 4 and Figure 5, the α-CS/β-TCP ceramic with the appropriate material ratio could be selected in practical application. In order to reduce the research workload, the following experiment takes the sample CS40 as an example because the content of the two components is close.

The surface morphology and the change in the composition of sample CS40 were observed before and after soaking in the SBF for 30 days. Figure 7(a) shows the surface morphology of sample CS40 before soaking. Similar to the fracture morphology, the surface has some holes and a long strip of α-CS particles. After 30 days of soaking in the SBF, the surface of sample CS40 became dense, and granular sediments were formed (see Figure 7(b)). Figure 7(c) is an enlarged view of Figure 7(b). The granular sediments formed on the surface are composed of many clusters and silkworm pupa-like particles. Figure 7(d) is an enlarged view of the red rectangular area in Figure 7(c). The clusters are composed of a large number of small crystal grains. Interestingly, some dense silkworm pupa-like particles have formed on the clusters. Figure 7(e) shows the XRD pattern and atomic percentage of the sample CS40 surface before and after soaking in the SBF. After 30 days of soaking, there was a decrease in the intensity of the diffraction peaks of α-CS and β-TCP. The molar ratio of Ca to P was also closer to the stoichiometric molar ratio of Ca to P in HAp (1.67). Thus, the morphology of the granular sediments in Figure 7 is consistent with the morphology of HAp in previous studies [39,46,47].

Figure 8 summarizes the previous research results [41,43,47–50] concerning the deposition process of apatite on the surface of the α-CS/β-TCP ceramic in the SBF. After the ceramic was immersed in SBF, the Ca\(^{2+}\) ions on the surface were exchanged with the H\(^+\) ions in the SBF, increasing the concentration of OH\(^−\) in the SBF. Meanwhile, many negatively charged siloxy groups were generated on the ceramic surface, which could adsorb Ca\(^{2+}\) ions in the SBF to the ceramic surface. In addition, Ca\(^{2+}\) and PO\(_4^{3−}\) ions recombined. In addition, the ceramic gradually released calcium and phosphorus, increasing the supersaturation of calcium and phosphorus in the SBF. In this way, apatite gradually deposited, nucleated, and grew on the ceramic surface. Finally, an apatite layer covered the entire ceramic surface. It can be seen from the previous research [46,48,51] that α-CS gradually converted to the amorphous silica. Then the amorphous silica was partially dissolved in the SBF, and there were silicate ions on the ceramic surface.

3.2. Preparation of the α-CS/β-TCP ceramic paste

TPGDA is a kind of monomer with two functional groups and TMP3EOTA has three functional groups. Compared with TMP3EOTA, TPGDA has lower shrinkage rate and activity during the light-curing process. TPGDA and TMP3EOTA were selected as the UV monomers and their mass ratio was 4:1 to reduce shrinkage.
and deformation in this experiment. The introduction of TMP3EOTA could properly improve the UV curing activity of the mixed resin. Furthermore, the combination of two kinds of resins could effectively avoid the crack defects during the debinding process for their different thermal decomposing temperature.

3.2.1. Influencing factors of the ceramic paste viscosity

Dispersant is a kind of surfactant material and changes the surface energy of ceramic particles. The addition of appropriate dispersant can ensure that the ceramic particles are uniformly distributed in the ceramic paste, reducing the ceramic paste viscosity. Three types of dispersants (KH560, KOS110 and Ammonium Polyacrylate) were selected and each of their additive amounts was 3.5 wt.% of the ceramic paste. The mass ration of α-CS to β-TCP was 4:6 and both their particle sizes were 3 μm.

Figure 9 shows the effect of different dispersants on the ceramic paste viscosity with different solid content. When the solid content was low, there was little difference in viscosity. As the solid content increased by 55 vol.%, the dispersion effect of KH560 was significantly better than the other two. The viscosities of the three ceramic pastes were also visually represented in the three photos in the right part of Figure 9. The viscosities of the ceramic pastes can be qualitatively compared by the length of the gravity drop of the ceramic paste in 10 s. Thus, KH560 was chosen as the appropriate dispersant. The effect of the additive amount of KH560 on the

Figure 7. Surface morphology and changes in the composition of sample CS40 before and after soaking in the SBF for 30 days: (a) before soaking, (b) after soaking, (c) and (d) two forms of deposited apatite; (e) XRD and energy spectrum analysis results.
ceramic paste viscosity was also researched. The additive amounts of KH560 in the ceramic paste were 3.0 wt.%, 3.5 wt.%, 4 wt.% and 4.5 wt.%, respectively. Figure 10 shows the ceramic paste viscosity varies with an increase in KH560 content. When the additive amount of KH560 varied from 3 wt.% to 4 wt.%, the viscosity-reducing rate gradually slowed down. As the additive amount increased continuously, the ceramic paste viscosity increased slightly. KH560 is a kind of silane coupling agent and can connect ceramic particles with photosensitive resin (see Figure 10). Therefore, the appropriate additive amount of KH560 was 4.0 wt.%.

The powder material has a huge specific surface area, which greatly increases the ceramic paste viscosity. In order to explore the effect of particle size on the ceramic paste viscosity, α-CS and β-TCP with the particle size of 10 μm were selected. Figure 11 shows the ceramic paste viscosities vary with the ceramic particle sizes and solid contents. The trend in Figure 11 is similar to that in Figure 9. The viscosity of the ceramic paste containing larger particles is significantly less under the same solid content. The smaller the ceramic particle size, the larger the specific surface area. The larger specific surface area leads to an increase in the contact area between the resin and the ceramic particles,
thereby increasing the internal friction and viscosity. However, it is noteworthy that small ceramic particles usually lead to higher sintered density and mechanical properties. Therefore, the ceramic paste with the particle size of 3 μm was selected in this experiment to obtain higher mechanical properties and precision.

### Table 3. The SLCD of the ceramic paste under different exposure intensities.

| Addition of photoinitiator /wt % | Exposure intensity/ mJ·cm⁻² | SLCD / μm |
|---------------------------------|-----------------------------|-----------|
| 0.3                             | 35.5                        | 18        |
|                                 | 49.9                        | 50        |
|                                 | 68.0                        | 85        |
|                                 | 89.1                        | 116       |
|                                 | 106.7                       | 147       |
|                                 | 35.5                        | 46        |
|                                 | 49.9                        | 79        |
| 0.6                             | 68.0                        | 105       |
|                                 | 89.1                        | 140       |
|                                 | 106.7                       | 168       |
|                                 | 35.5                        | 21        |
|                                 | 49.9                        | 72        |
| 0.9                             | 68.0                        | 100       |
|                                 | 89.1                        | 127       |
|                                 | 106.7                       | 150       |

3.2.2. Effect of the photoinitiator on the SLCD

Under UV light, the photoinitiator generates free radicals or cations, thereby initiating the polymerization reaction. The additive amount of the photoinitiator has a great impact on the curing efficiency and SLCD. The solid content of the ceramic paste was 55vol.% and the additive amounts of the photoinitiator were 0.3 wt.%, 0.6 wt.% and 0.9 wt.%, respectively. Table 3 presents the SLCD of the ceramic paste under different exposure intensities. The SLCD first increased and then decreased with an increase in the additive amount of the photoinitiator. The optimal additive amount of the photoinitiator was 0.6 wt.%. According to the Beer-Lambert law, taking the lnE as the X-axis, the SLCD as the Y-axis, the software OriginPro was used to fit the data points in Table 3 (see Figure 12). However, the results in Figure 12 and Table 3 were contradictory. The main reason for this might be that when the photoinitiator was added too much, the light-curing speed of the ceramic paste surface was too fast. The cured layer on the surface prevented the UV light from continuing to penetrate the ceramic paste.

![Figure 11. The ceramic paste viscosities vary with the ceramic particle sizes and solid contents.](image1)

![Figure 12. Data fitting results in Table 3 using OriginPro.](image2)

![Figure 13. The TG-DSC curve of sample CS40 based on stereolithography.](image3)

![Figure 14. The debinding and sintering curve and linear shrinkage rates in three directions after debinding and sintering.](image4)
3.3. Stereolithography, debinding and sintering

According to Table 3, the 3D printing layer thickness was set to 50 μm. For the green body after UV curing, subsequent debinding and sintering were the final and most important preparation processes. Many physical and chemical phenomena occurred during the debinding and sintering processes, such as melting, evaporation, and thermal decomposition. As the temperature rose, those resins in the green body became liquid and gaseous and were then discharged from the holes in the green body. If the thermal decomposition rate was too fast, the green body was easy to crack.

The decomposition temperatures of TPGDA and TMP3EOTA were different. The resins in the green body were discharged as the temperature rose (see Figure 13). Figure 14 shows the debinding and sintering curve and the linear shrinkage rates in three directions after debinding and sintering. The linear shrinkage rates in the X-axis, Y-axis and Z-axis were 7.26%, 7.69% and 12.06%, respectively. The linear shrinkage rate in the Z-axis was significantly greater than that in the X-axis and Y-axis, which was determined by the characteristics of layer by layer accumulation during the light-curing process. This might be due to the blocking of UV light by the ceramic particles in the Z-axis direction, thereby hindering the resin curing.

Figure 15(a) presents the prepared samples with complex structure and Figure 15(b) shows the corresponding microstructure. The bulk density, open porosity and flexural strength of the sample based on SLA were 2.01 g/cm³, 34.7% and 27.97 MPa, respectively. Compared with the samples prepared by pressure forming, the open porosity increased by 8.1%, and the bulk density and flexural strength decreased by 3.83% and 16.11%, respectively.

4. Conclusions

The physical and mechanical properties of the α-CS/β-TCP ceramic were investigated through traditional technology. The degradation rate of the α-CS/β-TCP ceramic could be effectively controlled by adjusting the component ratios. After soaking in the simulated body fluid, many apatite deposits formed on the α-CS/β-TCP ceramic surface. On this basis, the development process of the α-CS/β-TCP ceramic was comprehensively studied based on stereolithography. After stereolithography, debinding, and sintering, complex structural samples with highly uniform microstructure were prepared. This research provides a specific theoretical basis for the preparation of ceramic materials based on stereolithography.

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Disclosure statement

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