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Effects of gelatin addition on the microstructure of freeze-cast porous hydroxyapatite ceramics

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Abstract

Porous hydroxyapatite (HAP) ceramics was prepared by freeze casting and gelatin was used to adjust the pore morphology and microstructure of the porous HAP ceramics. With the gelatin concentration increase, the viscosity of HAP slurry was increased, and the linear shrinkage ratio of the specimen sintered at 1300 °C was also increased. The gelatin addition had great effects on the pore size and pore morphology of the porous HAP ceramics. The experimental results showed that the pore morphology of HAP ceramics was changed from a two-dimensional flat pore to a three-dimensional reticulated pore after gelatin addition.

Keywords: Freeze casting; Hydroxyapatite; Gelatin; Microstructure

1. Introduction

Freeze casting has attracted more and more attention due to it is an environment friendly and cost effective technique [1,2]. Meanwhile, freeze casting can be used to prepare complex ceramics with different pore morphologies and it is also an effective way to avoid drying stress and shrinkage [3]. Freeze casting has been used to prepare many ceramic materials, such as, alumina [4], hydroxyapatite [3,5], tricalcium phosphate [6], Ni-YSZ [7], yttria-stabilised zirconia [8], titanium dioxide [9], silicon nitride [10] and so on.

Porous hydroxyapatite (HAP), a promising material in biomedical application, has been used as bone scaffolds and drug carriers [11,12]. Many works have focused on the microstructure design and pore morphology adjustment of porous ceramics [2,8,13–15]. In this work, freeze casting was employed to prepare porous HAP ceramics, and the gelatin was selected to modify the microstructure of HAP ceramics. The influences of gelatin addition on the viscosity of slurry, porosity, pore morphology of HAP ceramics were investigated.

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2. Experimental procedure

2.1. HAP powder preparation

HAP powder was prepared in our laboratory using a precipitation method. According to the Ca/P molar ratio of 1.67, $(NH_4)_2HPO_4$ solution and $Ca(OH)_2$ solution were mixed and ammonia was added to maintain the pH at 10.0. The mixed solution was then stirred for 2 h to get a precipitate, which was filtered and dried. Finally, the precipitate was calcined at 900 °C for 1.5 h. The resulting HAP powder has a nominal particle size of 0.60 μm and a surface area of 10.40 m^2/g.

2.2. Freeze casting and sintering

For the HAP slurry preparation, ammonium polyacrylate (Lopon 885, BK Giulini, Siegburg, Germany) was used as a dispersant, and distilled water was used as solvent. Firstly, HAP powder, distilled water and 1.5 wt% (based on HAP) dispersant was ball milled with zirconia balls for 24 h, the slurries were then heated up to 40 °C in a water bath. 20 wt% gelatin solution (Sinopharm Chemical Reagent Co. Ltd., Shanghai, China) was added in the HAP slurries. The slurry was then mixed via a machine stirrer in a closed vessel in a water bath of 40 °C for 45 min.

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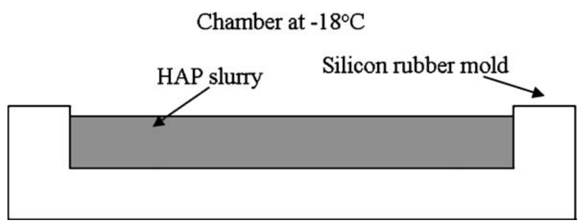

Fig. 1. Schematic of freezing process.

In the experiment, the casting mold was made of silicon rubber, the top of mold was open. The resultant HAP slurries were poured into the columnar mold with a length of 39.5 mm, a width of 8.5 mm, a height of 5.5 mm and a wall thickness of 5.5 mm, respectively. Finally, the mould was frozen in a chamber, where the temperature is −18 °C (Fig. 1). After the slurries completely solidified, the specimens were placed into a lyophilizer to dry (Shanghai Zhongke Biomedicine High-tech Develop Co. Ltd., China). The dried specimens were then moved into a furnace to remove the organic additive at 600 °C for 3 h. Finally, the specimens were sintered at 1300 °C for 1 h in air.

The viscosity of slurry was measured using a coaxial flat rheometry (SR-5 Rheometric Scientific Instrument Company, America). Microstructure and morphology of the HAP specimens were observed by scanning electron microscopy (SEM, JSM-6700F, JEOL, Akishima, Japan). Apparent porosities the HAP specimens were determined by the Archimedes method in distilled water.

3. Results and discussion

3.1. The viscosity of the HAP slurry

Gelatin can be dissolved in water at temperature above 35 °C and forms a gel network at room temperature. In order to avoid forming gel of the added gelatin, the HAP ceramic slurry must be kept at temperature above 35 °C in a water bath. Fig. 2 shows the viscosities of HAP slurries at 40 °C with solids loading of 50 wt%. The viscosities of HAP slurries increase with the increment of gelatin concentration. Without gelatin addition,

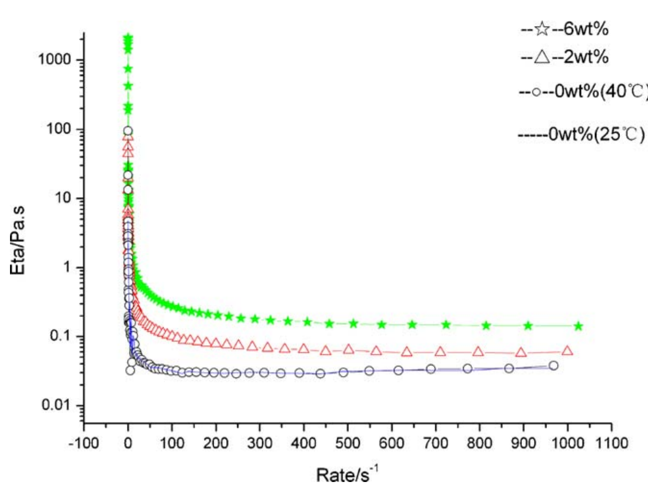

Fig. 2. The viscosities of HAP slurries at 40 °C with of 50 wt% HAP and gelatin concentration of 0 wt%, 2 wt% and 6 wt%.

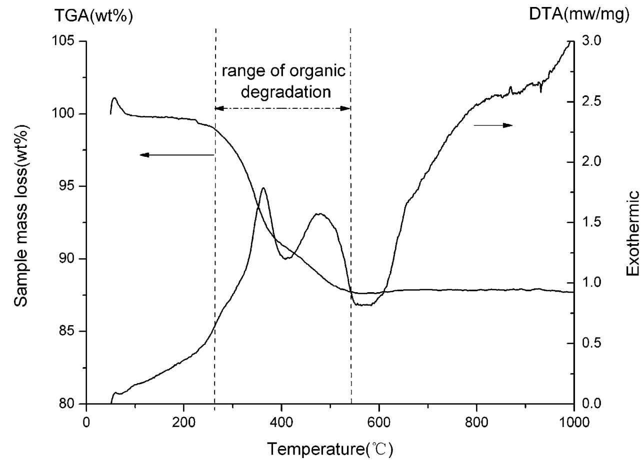

Fig. 3. TGA and DTA analyses of the green body, the heating rate was 10 °C/min in air. The green specimen has an initial solids loading of 30 wt% and 6 wt% gelatin.

the viscosities of 50 wt% HAP slurries measured at 25 °C and 40 °C are almost the same. The viscosities of all slurries are decrease with the shear rate increase and arrive a stable value when the shear rate is at 100 S^{-1}, the shear thinning properties of HAP slurries are suitable to freeze casting.

3.2. TGA–DTA analysis of the HAP green body

The weight change of green specimen was characterized by TGA and DTA analyses, the result is shown in Fig. 3. The weight loss happened at the temperature from 250 °C to 550 °C and all the organic additives can be completely removed near to 600 °C. Considering this factor, all the green bodies were heated to 600 °C at a heating rate of 2 °C/min and hold the 600 °C for 3 h to ensure all organic additives can be completely removed.

3.3. Influence of gelatin addition on the microstructure of HAP ceramics

Fig. 4 shows the SEM micrographs of HAP ceramics. The pore morphologies of HAP ceramics are obvious different. Fig. 4(a) shows that HAP ceramics without gelatin addition are composed of lamellar pores and ceramic walls. During the freezing process, ice crystals grew and expelled ceramic particles, resulting in the lamellar pores. HAP particles were rejected by the growing ice crystals and were piled up to form ceramic walls between the growing lamellar ice crystals. However, a small fraction of HAP particles were entrapped within the dendritic ice crystals, resulting in the particles bridge among the ceramic walls. With gelatin addition, the microstructure of HAP ceramics was changed remarkably. When 2 wt% gelatin was added to the 50 wt% HAP slurry, the pore morphology of HAP ceramics shown in Fig. 4(b) was changed from the lamellar pore to the homogeneous spherical pores. While the gelatin concentration increased to 6 wt%, the pore morphology of HAP ceramics shown in Fig. 4(c) became to the reticulated pore. During the freezing process, the gelatin solution was slowly gelatinized and the phase separation

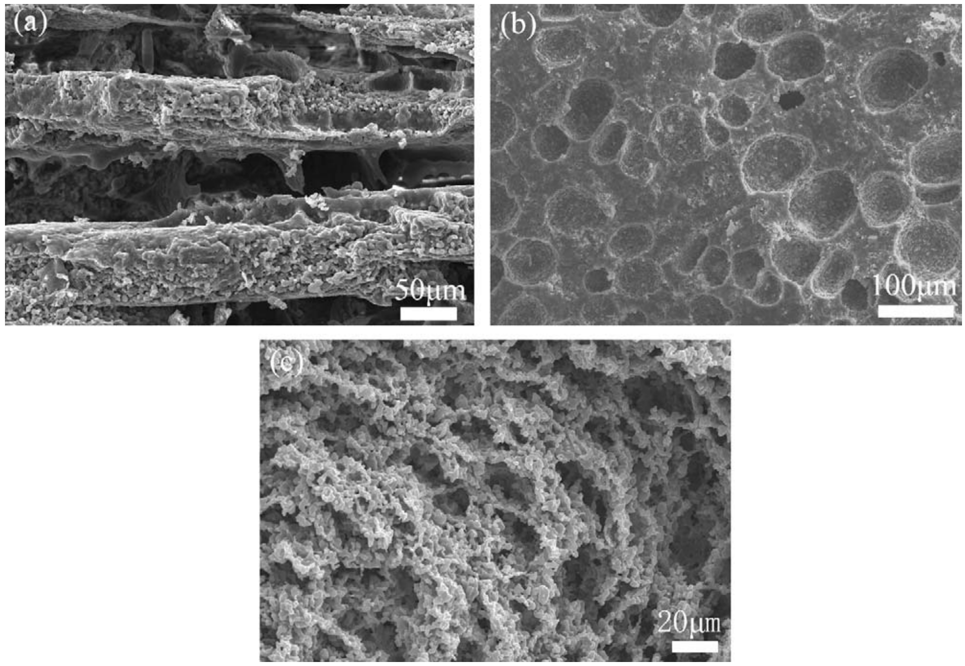

Fig. 4. SEM micrographs of HAP ceramics with solids loading of 50 wt% and different gelatin concentrations of 0 wt% (a), 2 wt% (b) and 6 wt% (c).

happened with temperature further decrease. Finally, the HAP green body was consist of gelatin contained ceramic particles and ice crystals phases. After the ice crystals sublimation, the HAP ceramic green body with special pore structure can be obtained. The gelatin addition can modify not only the pore size but also the pore morphology. The SEM micrographs of HAP ceramics showed that gelatin can hinder the ice crystal growth, resulting in the microstructure of HAP ceramics gradually changed from two-dimensional lamellar structure to three-dimensional reticulated pore.

In the experiment, the freeze-cast HAP specimen was easily to collapse without the gelatin addition. However, after 2 wt% gelatin addition, the mechanical strength of porous HAP can be significantly improved. The reason is that the gelled gelatin formed a network, which binded the ceramic particles together and prevent from their collapse in the green body. The gelatin also modified the microstructures which enhanced the bending strength of HAP ceramics after sintering.

3.4. Influence of gelatin addition on the porosity and shrinkage of HAP ceramics

Table 1 lists the porosity of HAP ceramics with different gelatin concentrations. The apparent porosity is close to the total porosity. Therefore, it is reasonable to suggest that the pores in HAP ceramics are open and interconnected. The final shrinkage ratio and porosity of HAP ceramics are associated with two factors: the expansion during freezing and the shrinkage during sintering. With 2 wt% gelatin addition, the open porosity of HAP ceramics decrease from 44.37% to 40.66% and the linear shrinkage ratio of the specimen increases from 21.40% to 25.05%. The phenomena can be explained that gelatin addition is helpful to prevent from ice abnormally growing and get the uniform microstructure of green body, resulting in the small porosity and large linear shrinkage ratio. With gelatin further increase to 6 wt%, the open porosity of HAP ceramics increases to 45.76% and linear shrinkage ratio also increases to 27.08%. The reason is that gelatin is also an organic additive, more gelatin addition resulted in the increase of the porosity and linear shrinkage of HAP ceramics. Therefore, 6 wt% gelatin addition HAP ceramics has 45.76% open porosity and 27.08% linear shrinkage ratio.

The most important factor is that gelatin addition modified the freeze processing of HAP slurry and the ice crystals abnormally growth was also hindered, the all SEM micrographs clearly show the microstructure evolvement of porous HAP ceramics.

Table 1
Apparent porosity, total porosity and shrinkage of porous HAP with solids loading of 50 wt% and varied gelatin concentrations.

Gelatin concentration (wt%)	Apparent porosity (%)	Total porosity (%)	Linear shrinkage ratio (%)
0	44.37	46.19	21.40
2	40.66	42.23	25.05
6	45.76	46.65	27.08

4. Conclusions

Microstructure-controllable HAP ceramics have been successfully fabricated by freeze casting. With gelatin addition, the large and noninterconnected lamellar pores were changed into small and interconnected cellular pores. Gelatin addition has greatly effect on not only the pore size and pore morphology of the HAP ceramics but also the viscosity of slurry, the porosity and shrinkage of HAP ceramics.

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