Improving the properties of porous hydroxyapatite ceramics by fabricating methods

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Hydroxyapatite (HA) ceramic is a widely used material for bone graft substitutes primarily because of its close composition to human bone and its high biocompatibility with surrounding living tissues [1–5]. In recent years, attention has been particularly focused on the fabrication of porous bioceramics, for the porous network allows the tissue to infiltrate, which further enhances the implant-tissue attachment [6–10]. Up to now, porous HA bioceramics have been applied in filling bone defects, eye ball prosthesis, dental implants, and so on [11–13], which has developed into an important division of the biomedical field. However, as indicated by Hulbert *et al.* [14], macropores of at least 100 μm are needed to host the cellular and extracellular components of bone and blood vessels, and those greater than 200 μm are expected to be effective on osteoconduction. At the same time, researchers [15, 16] found that the rate of cell ingrowth connects with pore size. Therefore, porous HA ceramic with controlled pore characteristics is an important research subject.

Many methods [10, 13, 17–21] have been developed to fabricate porous HA ceramics, where a mixture of HA powder with polymeric powders is the most widely used method. Voids of identical geometry with the starting polymer particles are formed during the process of burning-out the polymeric particles and maintained within the fired HA solid. Such feature makes it easy to control the pore size, shape and porosity in porous HA ceramics. Some researchers [10, 13, 21–23] have studied the influence of pore size and porosity on the mechanical properties and implant property of porous HA ceramics. However, the influence of different fabrication processes on mechanical properties and porosity development of porous HA ceramics needs further deepening.

In the present study, porous HA ceramics with controlled pore size containing polymethyl methacrylate (PMMA) as a pore-forming agent were prepared by dry pressing and slip casting processes, respectively. The pore characteristics and mechanical properties of the porous HA ceramics were compared and discussed. The influence of PMMA particle size and volume fraction on the properties of porous HA ceramics was also investigated.

PMMA powder with different particle size ($D = 1.19$ g/cm^3, Coral Chemistry Factory of Shanghai, China) was used as pore-forming agent. The morphology of the powders is spherical, which is expected to benefit the control of the pore characteristics of HA ceramics. Weight loss analysis (TGA) of the PMMA powder was performed in air with a heating rate of 10 °C/min in order to determine the thermal decomposition range.

HA powder with size less than 0.1 μm (Ca/P=1.69, D=3.16 g/cm^3, Sichuan University, China) was used as starting powder. Polyacrylic acid (PAA) (30 wt%, Nanjing University of Chemical Technology, China) with molecular weight less than 15,000 was used as dispersant. Polyvinyl alcohol (PVA) (Jinshan Petrochemical Works, China) with a 280,000 molecular weight was used as binder.

In the dry pressing route, HA powders and PMMA spheres containing PVA and PAA were ball milled in distilled water for 6 h. The milled slurry was dried with agitation to avoid inhomogeneity in air. The dried lumps were crushed and uniaxially pressed with a steel die at 30 MPa to produce green pellets with a dimension of 45 × 8 × 5 mm^3. Then the green bodies were cold isostatically pressed at 100 MPa for 2 min. After burning out the organic additives at 550 °C with a heating rate of 0.5 °C/min, the samples were continuously sintered to 1200 °C for 2 h with a heating rate of 5 °C/min.

In the slip casting process, 20 vol% HA powders containing 1.0 wt% PAA were ball-milled mixed in distilled water at pH = 11.5 for 12 h. Then PMMA particles and 2.0 wt% PVA were added into the suspension. After milling for another 12 h, the above suspensions, free of foam, were slipped into a plaster mold with casting area of 50 × 50 mm^2. After being demolded, the green bodies were dried at 100 °C and sintered in the same way as the samples prepared by dry pressing.

Fractured surfaces were observed by model EPMA-8705Q scanning electron microscopy (SEM). Macropore size distribution was analyzed from SEM images by LeicaQwin software for image analysis. The porosity of samples was measured by Archimede's method. The microporosity was analyzed using Poresizer 9320 Mercury porosimetry. The flexural strength of porous HA ceramics was performed on an Instron 1195 machine with a span length of 30 mm and a crosshead speed 0.5 mm/min.

TGA (thermogrametric analysis) curve of PMMA particles is presented in Fig. 1. It can be seen that PMMA particles mostly decompose from 220 to 400 °C in air basically by an oxidation process, resulting in a

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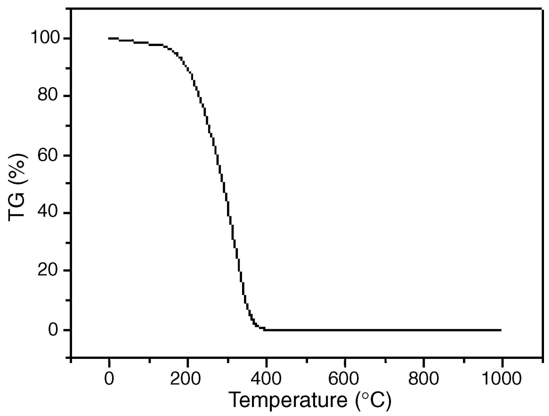

Figure 1 TG curve of PMMA in air at heating rate of 10 °C/min.

TABLE I Properties of porous HA ceramics as a function of PMMA (sintered at 1200 °C, holding 2 h)

		Flexural strength (MPa)		Total porosity (%)	
Content of PMMA (vol.%)	Particle size of PMMA /μm	Dry pressing process	Slip casting process	Dry pressing process	Slip casting process
36	120–50	1.4	8.0	51.5	51.1
30	260–50	–	2.8	–	49.9
	120–150	4.0	9.1	48.2	50.6
	50–75	12.8	12.4	33.5	50.0

dramatic loss in weight. A stable weight is attained at about 400 °C, which indicates that the PMMA particles have been completely decomposed at about 400 °C. In order to let PMMA decompose completely and decrease the cracks in HA ceramics, the heating rate of the green HA body should be very slow at sintering temperature below 400 °C.

Fig. 2 shows the macroscopic structure of dry pressed and slip cast samples. The samples made by two kinds of processes show a nearly homogeneous macropore distribution, and the macropore size increases with added PMMA particle size. However, the macropore size in both kinds of samples is smaller than the size of added PMMA particles, which is caused by the shrinkage of the samples during sintering. It can also observed that, when the particle size of added PMMA is the same, there is no significant difference in the macropores size of samples made by both methods, which is confirmed by the data tested by LeicaQwin software image analysis (see Fig. 3). With PMMA particle size of 120–150 μm, the average macropore sizes of the dry pressed and slip cast samples were 97 and 96 μm, respectively.

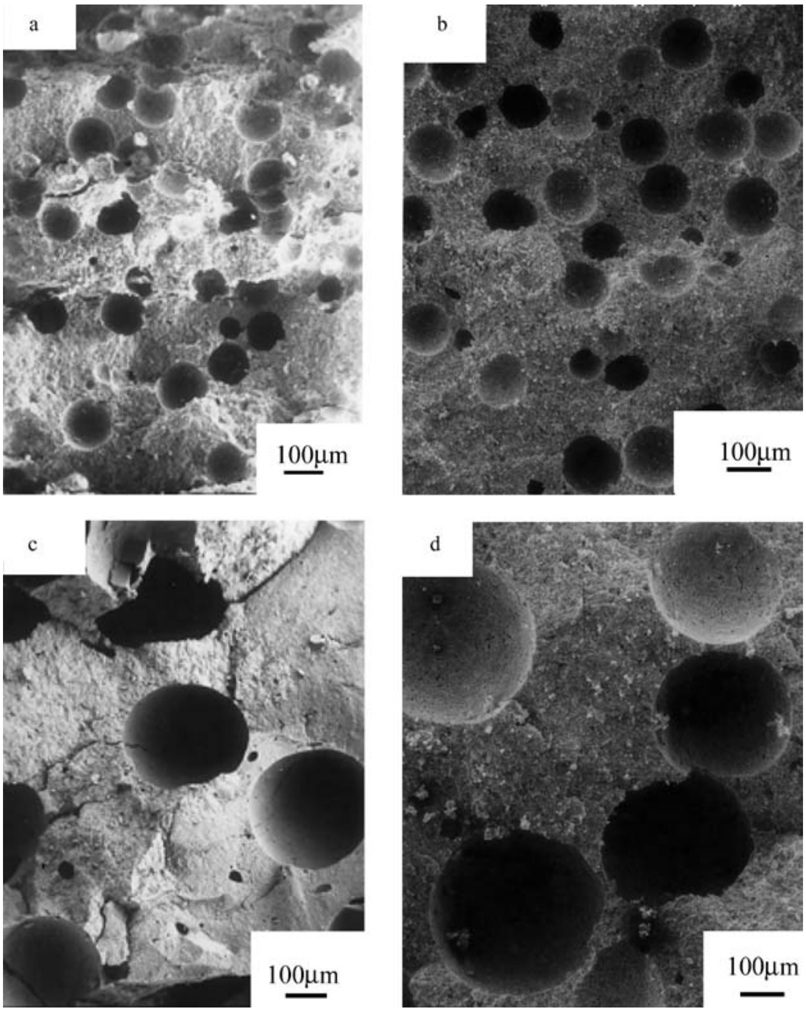

Figure 2 SEM photographs of porous HA ceramics with macroscopic examination [(a, c) prepared by dry pressing; (b, d) prepared by slip casting]: (a) added 30 vol%, 120–150 μm PMMA particles, (b) added 30 vol%, 120–150 μm PMMA particles, (c) added 23 vol%, 260–350 μm PMMA particles, (d) added 30 vol%, 260–350 μm PMMA particles.

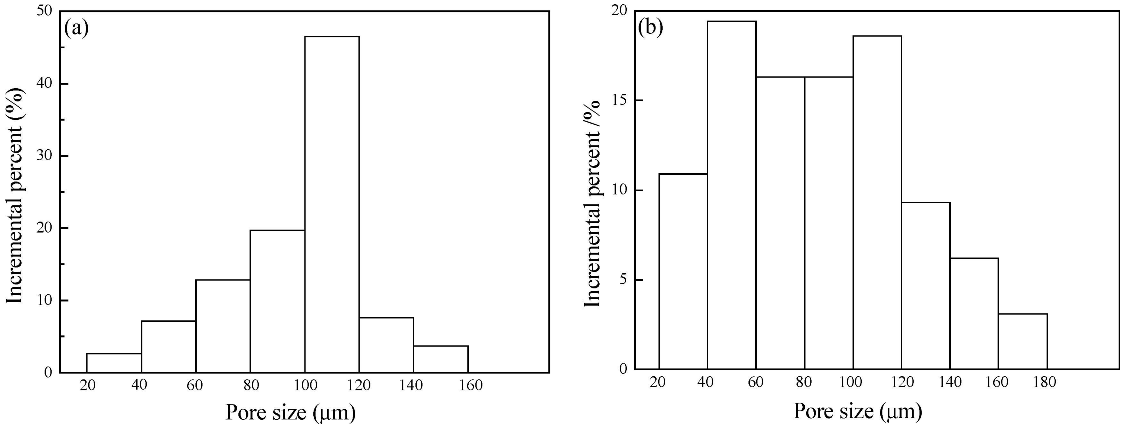

Figure 3 Macropore size distributions of porous HA ceramics (PMMA particle size: 120–150 μm):(a) prepared by dry pressing, (b) prepared by slip casting.

At the same time, many microcracks exhibit in the dry pressed samples, which are caused by two factors. One is the large mismatch of thermal expansion coefficient between HA powders and PMMA particles, the other is the difficulty of gas release due to the application of pressure. But this does not occur in slip cast bodies due to the absence of substantial pressure stress. Microcracks contribute to reduction of the mechanical properties of the samples. So dry pressed porous HA ceramics have lower strength than those made by slip casting technique, which is proved by the data of bending strength (see Table I).

Fig. 3 shows the macropore size distribution of porous HA ceramics prepared by dry pressing and slip casting processes, respectively. The macropore size of the porous HA ceramics fabricated by slip cast process exhibits a broader distribution than those made by dry pressing process, which is caused by increasing content of organic substance, existing of residual air bubbles in the suspension and absence of pressure stress.

The microscopic examinations of porous HA ceramics fabricated by dry pressed and slip cast processes are shown in Fig. 4. There are many micropores in both samples, which are considered to be result of sintering effect. Dry pressed porous HA ceramics have bigger micropores size and less micropores than that of the slip casting porous HA ceramics, which is in good agreement with the data tested by Mercury porosimetry (see Fig. 5).

Fig. 5 shows that the micropores size distribution of porous HA ceramics made by two process, respectively. The micropore size of the dry pressed porous HA ceramics exhibits two-peak distribution, one sharp peak is at about 0.3–0.6 μm, the other weak peak is at 1–6 μm. That of slip cast samples exhibits single-peak distribution of 0.6 – 2 μm. Therefore, slip casting method is beneficial to the micropores distribution and internnection.

The properties of porous HA ceramics are illustrated in Table. I. At a given PMMA volume, the porosity of dry pressed porous HA ceramics decreases as the PMMA particle size decreases, which may be caused by the decrease of microcracks and increase of closed macropores. However, the porosity of slip casting porous HA ceramics has no obvious change with the PMMA particle size. At the same time, the mechanical properties of both kinds of porous HA ceramics increase sharply as the PMMA particle size decreases. That is to say, macropore size has great influences on the mechanical properties of porous HA ceramics. It can also be noticed that, with the same PMMA added, the slip cast porous HA ceramics show a higher strength than the dry pressed HA ceramics, which is caused by

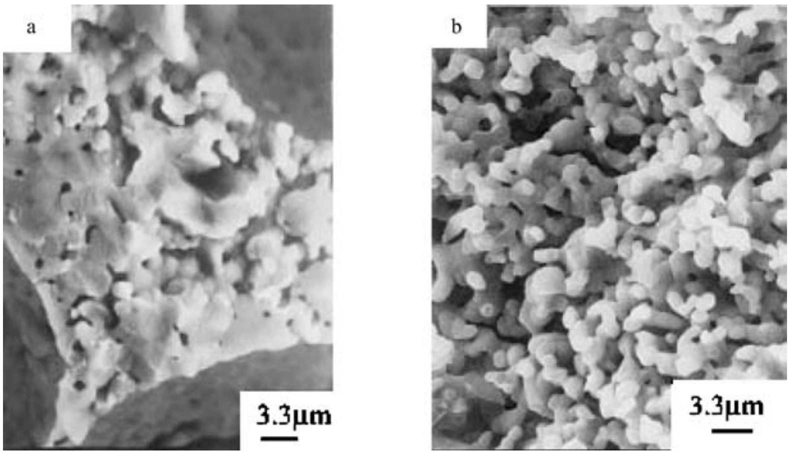

Figure 4 SEM Photographs of porous HA ceramics with microscopic examination (PMMA particle size: 120–150 μm):(a) prepared by dry pressing (b) prepared by slip casting.

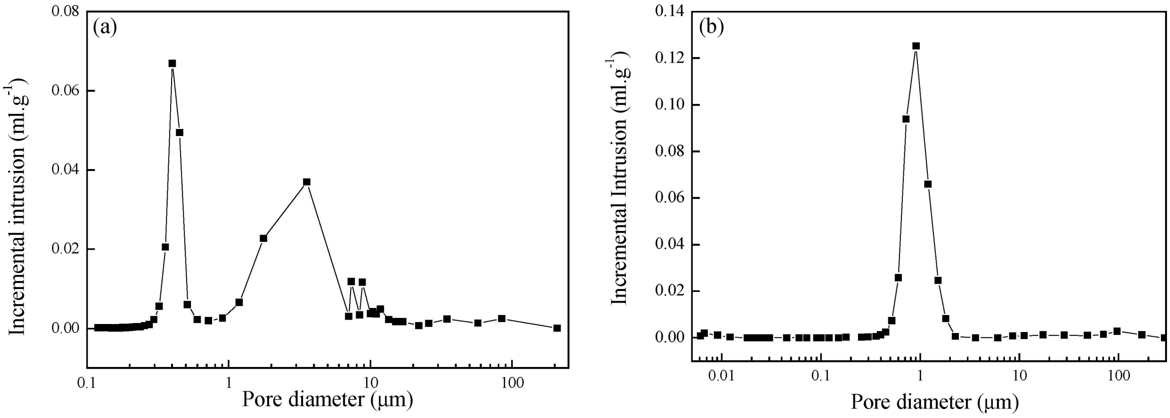

Figure 5 Micropore size distributions of porous HA ceramics (PMMA particle size: 120–150 μm):(a) prepared by dry pressing, (b) prepared by slip casting.

the occurrence of microcracks in the dry pressed porous HA ceramics.

In conclusion, the porous HA ceramics were fabricated by dry pressing and slip casting processes. The ceramics prepared by both kinds of processes show a nearly homogeneous macropore distribution, and the macropore size is determined by the size of added PMMA particles. The strength of two kinds of ceramics is influenced by added PMMA particle size and volume. In contrast to the dry pressing samples, the slip cast samples have a broader macropore size distribution and a narrower micropore size distribution. At the same time, the slip cast samples have higher strength than the dry pressed samples due to absence of microcracks. Based on the above results, slip casting method can improve the properties of the porous HA ceramics greatly.

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