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Production of porous calcium phosphate (CaP) ceramics with highly elongated pores using carbon-coated polymeric templates

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Abstract

This study reports a new way of enhancing the compressive strength of porous calcium phosphate (CaP) ceramics by creating highly elongated pores. These elongated pores were produced by casting a CaP/camphene slurry into stretched polymeric sponges with a thick carbon coating layer used as a template. The sample produced after sintering at 1250 °C for 3 h showed a highly elongated porous structure with a porosity of 38 ± 1.2 vol%, where elongated pores with a size of 512 ± 96 μm were formed as a replica of the template. In addition, CaP walls with a thickness of 841 ± 239 μm were fully densified without any noticeable defects due to the high CaP content of 40 vol% in the CaP/camphene slurry. The compressive strength of the sample was as high as 21 ± 4.9 MPa when tested parallel to the direction of pore elongation, which is much higher than that (12 ± 2.4 MPa) of the sample tested normal to the direction of pore elongation. The sample also showed good biocompatibility, as assessed by the *in vitro* cell test using a pre-osteoblast cell line.

Keywords: Suspensions; Porosity; Mechanical properties; Apatite; Biomedical applications

1. Introduction

Porous calcium phosphate (CaP) ceramics have great potential for applications in bone tissue engineering, because of their excellent biocompatibility and 3-dimensionally interconnected pores that can stimulate the attachment, proliferation, and differentiation of cells when implanted [1,2]. However, these materials often have relatively poor mechanical properties, which would limit their wider applications as bone substitutes [2,3]. Therefore, considerable effort has been made to improve the compressive strength of porous materials without sacrificing the high porosity by controlling their pore structure, for example, using solid freeform fabrications (SFFs) [4,5] and unidirectional freeze casting [6–10].

The polymeric sponge replication method is one of the most useful techniques for producing porous materials, particularly, with high porosity and good interconnections between the pores [11,12]. Furthermore, the mechanical properties of these materials can be improved further, for example, by tailoring the pore structure of the starting polymeric sponges [13–16] and by filling the hollow struts with a ceramic slurry using a vacuum infiltration process [17].

More recently, our group demonstrated the utility of stretched polymeric sponges as a novel template, which can create highly elongated pores, leading to a considerable increase in compressive strength [18]. However, the porous materials produced by this technique, even when using modified polymeric sponges, still have limited mechanical properties because of their high porosity.

Therefore, this study proposes a simple way of improving the compressive strength of porous CaP ceramics by creating highly elongated pores. To accomplish this, a CaP/camphene slurry was cast into stretched polymeric sponges with a very thick carbon coating layer used as a template, which is unlike the conventional polymeric sponge replication method. This simple approach allows porous CaP ceramics to have a highly elongated porous structure with a relatively low porosity, while

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preserving the good interconnections between the pores. The pore structure and densification of CaP walls were characterized by scanning electron microscopy (SEM). The crystalline structure was evaluated by X-ray diffraction (XRD). The compressive strengths of the porous CaP ceramics were measured either parallel or normal to the direction of pore elongation. The preliminary osteoblastic activity of the samples was also evaluated using *in vitro* tests to assess their biocompatibility.

2. Experimental procedure

Fig. 1 shows a schematic diagram of the experimental procedure used to produce porous calcium phosphate (CaP) ceramics with highly elongated pores by casting a CaP/camphene slurry into carbon-coated polymeric templates, followed by heat-treatment at 800 °C for 3 h to remove the template and at 1250 °C for 3 h to sinter the CaP walls. The as-received polyurethane sponges (15 pores per in., Jeil Urethane Co., Korea) were stretched to 50% elongation at 200 °C for 2 h, as described elsewhere [18], and then coated with a carbon slurry that had been prepared by dispersing commercial carbon black powder (Cabot Black Pearls BP-120; Cabot Corp., Boston, MA) in ethanol containing triethyl phosphate (TEP; $(C_2H_5)_3PO_4$, Aldrich, USA) as a dispersant, and polyvinylbutyral (PVB; Aldrich, USA) as a binder [19]. The carbon coated sponges were dried in an oven at 60 °C for 30 min. The coating/drying step was repeated several times until the sample had a sufficient carbon coating layer, which would result in the formation of large pores suitable for bone ingrowth.

In a separate process, a CaP/camphene slurry with a CaP content of 40 vol% was prepared by mixing commercial CaP powders (NT-BCP, Oss-Gen Co., Korea) and camphene ($C_{10}H_{16}$, Alfa Aesar/Avocado Organics, Ward Hill, MA, USA) with the assistance of 4 wt% of an oligomeric polyester dispersant (Hypermer KD-4, UniQema, Everburg, Belgium) using ball-milling at 60 °C for 24 h. The resulting CaP/camphene slurry was then cast into the templates with dimensions of ∼15 mm × 15 mm × 15 mm, followed by freeze-drying to remove the solid camphene. The green samples were then heat-treated at 800 °C for 3 h to remove the template and at 1250 °C for 3 h to sinter the CaP walls.

The pore structure of the porous CaP ceramics and microstructure of the sintered CaP walls were characterized by scanning electron microscopy (FE-SEM, JSM-6701F, JEOL Techniques, Tokyo, Japan). Micro-computed tomography (μ-CT) (Skyscan 1173, Skyscan, Kontich, Belgium) was also used to examine the 3-dimensional pore structure. The porosity was calculated from their dimensions and weight and the pore size was analyzed from SEM images of the samples. The crystalline phases of the sample were characterized by X-ray diffraction (XRD, M18XHF-SRA, MacScience Co., Yokohama, Japan).

The compressive strengths of the samples, ∼11 mm × 11 mm × 10 mm in size, which had been prepared by slightly grinding their top and bottom surface, were examined using a universal testing machine (OTU-05D, Oriental TM Corp., Korea) at a crosshead speed of 5 mm/min. To evaluate the effect of the creation of highly elongated pores on the compressive strength of the porous CaP ceramics, the samples were loaded either parallel or normal to the direction of pore elongation. The stress and strain responses of the samples were monitored during the compressive strength tests. Five samples were tested to obtain the average value and standard deviation.

In vitro cell tests of the samples were carried out using a pre-osteoblast cell line (MC3T3-E1; ATCC, CRL-2593, USA). The cells were plated at a density of 5×10^4 cells/mL and cultured in a humidified incubator in an atmosphere containing 5% CO_2 at 37 °C. Minimum essential medium (α-MEM: Welgene Co., Ltd., Seoul, Korea) supplemented with 10% fetal bovine serum (FBS, Life Technologies, Inc., USA) and 1% penicillin–streptomycin was used as the culturing medium. Cell attachment was observed by SEM after culturing for 1 and 3 days.

3. Results and discussion

Porous CaP ceramics with highly elongated pores could be produced successfully by casting a CaP/camphene slurry into stretched polymeric sponges with a very thick carbon coating layer as a template. The 3-dimensional pore structure of the sample was first characterized by micro-computed tomography

Fig. 1. A schematic diagram showing the experimental procedure used to produce porous CaP ceramics with highly elongated pores using a stretched polymeric sponge with a very thick carbon coating layer as a template.

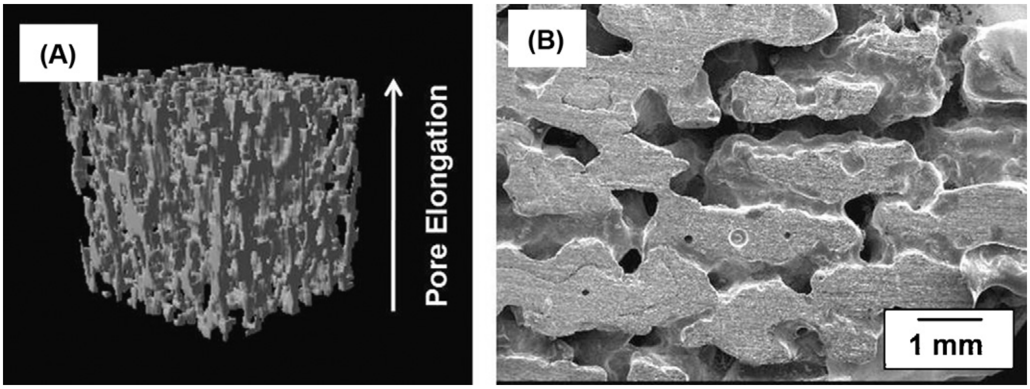

Fig. 2. (A) Typical reconstructed 3-dimensional μ-CT image of the sample and (B) SEM image showing the pore structure developed parallel to the direction of pore elongation.

(μ-CT), as shown in Fig. 2(A). An anisotropic pore structure was observed, where highly elongated pores were formed uniformly throughout the sample after removing the carbon-coated template by heat-treatment at 800 °C for 3 h. The construction of the elongated pores was examined more closely by scanning electron microscopy (SEM), as shown in Fig. 2(B). The samples showed highly elongated pores with a thickness of 512 ± 196 μm, surrounded by CaP walls with a thickness of 841 ± 239 μm. The overall porosity of the sample, which was calculated by measuring its mass and dimensions, was 38 ± 1.2 vol%. It should be noted that the overall porosity and pore size can be controlled further simply by adjusting the thickness of the carbon coating layer on the polymeric struts.

In general, materials produced by the freeze casting of ceramic/camphene slurries often have pores that are formed by camphene dendrites grown during freezing of the slurry, when the ceramic content in the slurry is lower than a critical value [20]. Therefore, a high CaP content of 40 vol% was used to avoid the formation of pores in the CaP walls. The CaP walls were densified quite well after sintering at 1250 °C for 3 h, as shown in Fig. 3(A). In addition, the free surface of the CaP wall that was initially in contact with the carbon coating layer showed a smooth and dense surface, suggesting complete removal of the carbon coating layer without deteriorating the CaP walls.

One of the most striking features of the stretched polymeric sponges with a carbon coating layer as a template is the easy removal of the template by simple heat-treatment. In other words, conventional polymeric templates or molds that are generally prepared using solid freeform fabrications (SFFs) experience considerable volume expansion during heat-treatment, which would require a troublesome binder removal process to avoid the formation of defects [4]. On the other hand, the carbon-coated template can be removed by thermal oxidation with negligible volume change, which results in good shape tolerance of the porous CaP ceramics.

The crystalline structure of the sample after sintering at 1250 °C for 3 h was characterized by XRD, as shown in Fig. 4. The sample showed peaks corresponding to those of hydroxyapatite (HA) (JCPDS file No. 9-432) and β-tricalcium phosphate (β-TCP) (JCPDS file No. 9-169). This suggests that the sample produced is a type of biphasic calcium phosphate (BCP), consisting of HA and TCP phases. No secondary phases were observed, suggesting that the carbon-coated template could be removed successful by heat-treatment without altering the CaP walls. The biphasic calcium phosphate (BCP) without any secondary phases obtained in this study would be expected to have superior biocompatibility and osteoconductivity compared to pure HA and TCP phases [18,21,22].

Compressive strength tests of the samples loaded either parallel or normal to the direction of pore elongation were carried out to evaluate the effect of pore elongation on the

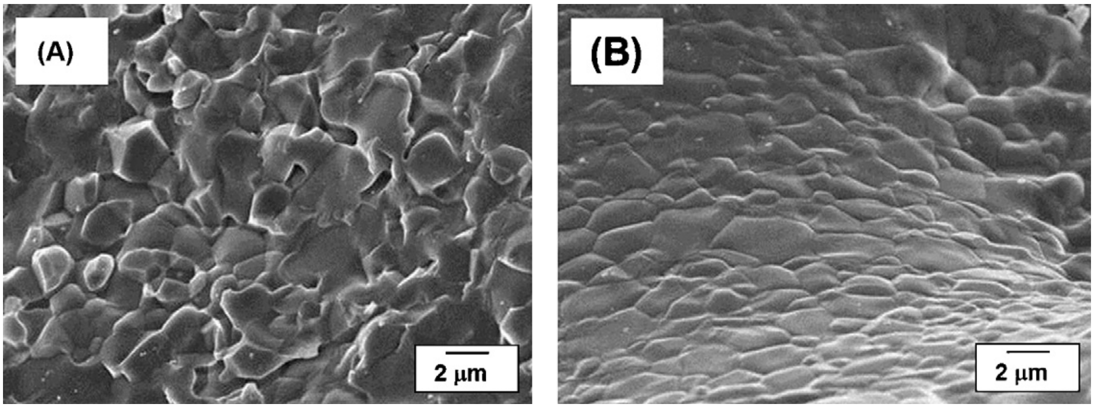

Fig. 3. SEM images of the samples showing the microstructures of (A) the fracture surface and (B) the free surface of the CaP walls.

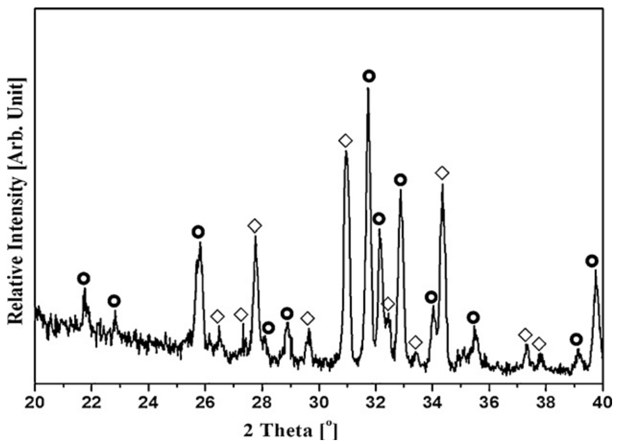

Fig. 4. Typical XRD pattern of the sample after sintering at 1250 °C for 3 h (○: HA, ◇: TCP).

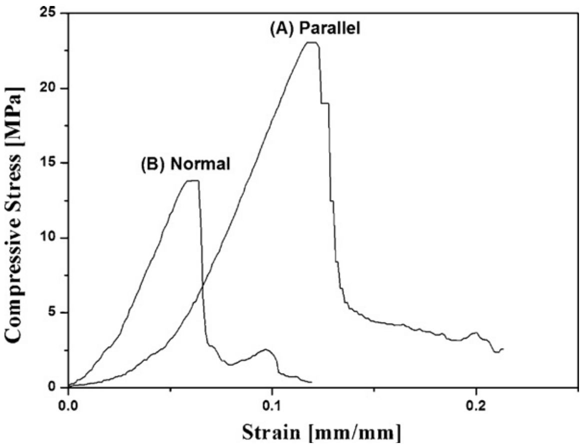

Fig. 5. Typical compressive stress versus strain responses of the samples tested parallel and normal to the direction of pore elongation.

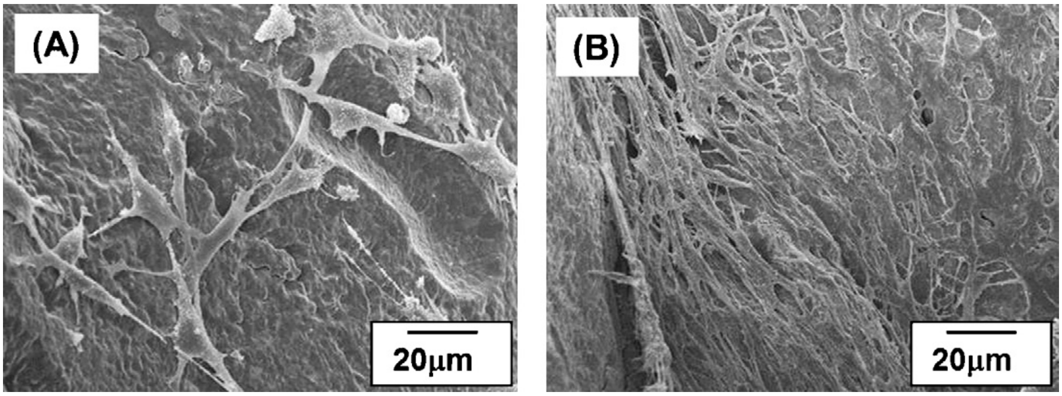

Fig. 6. Typical SEM images of the cells cultured for (A) 1 day and (B) 3 days on the surface of the CaP walls.

mechanical properties of the porous CaP ceramics. Fig. 5(A) shows the typical stress versus strain responses of the samples. Both samples exhibited brittle fracture behavior associated with catastrophic failure of the CaP walls [23]. However, the compressive strength (21 ± 4.9 MPa) of the sample tested parallel to the direction of pore elongation was much higher than that (12 ± 2.4 MPa) of the sample tested normal to the direction of pore elongation. This suggests that the compressive strength of the porous CaP scaffolds can be improved significantly by creating highly elongated pores, which can be achieved using stretched polymeric sponges with a carbon coating layer as a template.

The preliminary osteoblastic activity of the samples was also evaluated by *in vitro* tests using a pre-osteoblast cell line after culturing for 1 and 3 days, as shown in Fig. 6(A) and (B), respectively. The cells appeared to grow and spread actively on the sample surface after culturing for 1 day (Fig. 6(A)). Furthermore, the surface was covered almost completely with the cells after culturing for 3 days (Fig. 6(B)). This highlight the potential of these porous HA scaffolds as a bone scaffold with outstanding biocompatibility.

4. Conclusions

Porous CaP scaffolds with highly elongated pores were produced by casting a CaP/camphene slurry with a high CaP content of 40 vol% into stretched polymeric sponges with a carbon coating layer as a template. This simple process allowed the creation of highly elongated pores with a size of 512 ± 96 μm, surrounded by dense CaP walls with a thickness of 841 ± 239 μm. The sample showed a high compressive strength of 21 ± 4.9 MPa with a porosity of 38 ± 1.2 vol% when compressed parallel to the direction of pore elongation. This compressive strength was much higher than the sample (12 ± 2.4 MPa) compressed normal to the direction of pore elongation. Furthermore, the cells grew and spread actively on the surface of the sample, suggesting good biocompatibility.

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