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Preparation of the reticulated hydroxyapatite ceramics using carbon-coated polymeric sponge with elongated pores as a novel template

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Abstract

This paper proposes a novel, simple way to improve the compressive strength of reticulated porous hydroxyapatite (HA) ceramics using carbon-coated polymeric sponges with elongated pores as a novel template. This template allowed samples to have two interconnected pore networks with a preferential orientation, in which an addition pore network was newly formed by removing the carbon-coated polymeric struts, while preserving the pre-existing pore network. The compressive strength of the sample was as high as 2.9 ± 0.3 MPa with a porosity of 76% when tested parallel to the direction of pore elongation. In addition, the *in vitro* cell test using a pre-osteoblast cell line revealed the samples to have good biocompatibility.

Keywords: A. Suspensions; B. Porosity; C. Mechanical properties; D. Apatite; E. Biomedical applications

1. Introduction

Porous calcium phosphate (CaP) ceramics have great potential for applications in bone tissue engineering on account of their excellent biocompatibility [1]. Thus far, considerable effort has been made to develop new manufacturing methods for producing porous CaP ceramics with advanced functions [2–6]. Among these methods, the sponge replication method can achieve high porosity and good interconnections between the pores [2,7–9], which is quite beneficial to bone ingrowth and the vascularization of newly formed tissue [10]. In addition, this method can produce functionally graded materials (FGM) with a porosity gradient by tailoring the pore structure of the starting polymeric foams, which would enhance their mechanical properties [11–14].

This study examined the utility of carbon-coated polymeric sponges with elongated pores as a novel template for improving the mechanical properties of reticulated porous hydroxyapatite (HA) ceramics by creating two interconnected pore networks with a preferential orientation. The schematics showing the unit cells of a HA-coated template and reticulated porous HA ceramics with the elongated pores after sintering are illustrated in Fig. 1(A) and (B), respectively. To accomplish this, the as-received polymeric sponges were stretched to 50% elongation at 200 °C for 2 h. The elongated polymeric sponges were then coated in sequence with the carbon and HA slurries (Fig. 1(A)). The prepared samples were heat-treated at 800 °C for 3 h to remove the template and at 1250 °C for 3 h to sinter the HA walls. This approach allowed the reticulated porous HA ceramics to have a highly elongated porous structure, wherein an additional pore network was newly formed by removing the carbon-coated polymeric struts, while preserving the pre-existing pore network, resulting in the formation of two interconnected pore networks (Fig. 1(B)). The compressive strength of the samples was measured and compared with those of the samples prepared using either a conventional polymeric sponge or carbon coated sponge without elongation. In addition, the preliminary osteoblastic activity of the sample was also evaluated using *in vitro* tests to assess its biocompatibility.

2. Experimental procedure

Reticulated porous hydroxyapatite (HA) ceramics with high compressive strength were produced using carbon-coated

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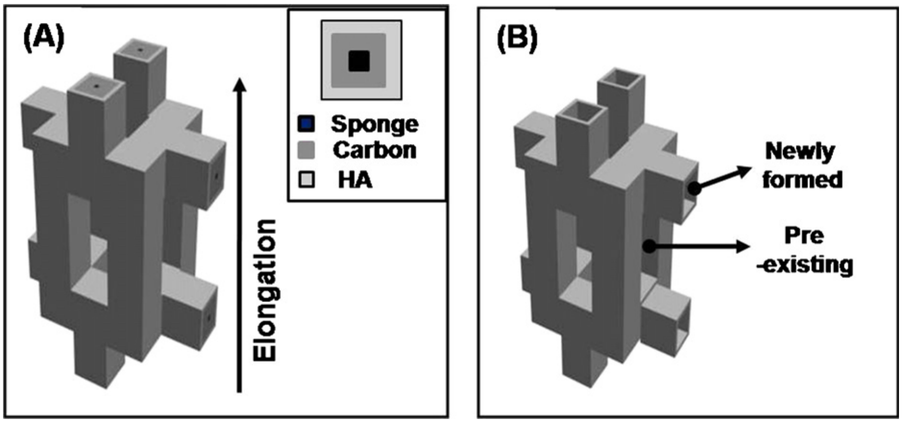

Fig. 1. Schematics showing the unit cells of (A) the HA-coated template and (C) the reticulated porous HA ceramics with the elongated pores after sintering.

polymeric sponges with elongated pores as a novel template, as shown in Fig. 1. To accomplish this, the as-received polyurethane sponges (15 pores per inch, Jeil Urethane Co., Korea) with dimensions of approximately 7 mm × 35 mm × 17 mm were first stretched to 50% elongation and kept in an oven at 200 °C for 2 h to create the elongated pores [15]. The prepared polymeric sponges were then coated with a carbon slurry that had been produced 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 [16]. 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 thickness of the carbon coating layer, which would result in the formation of large pores that are suitable for bone ingrowth. Subsequently, 3 layers of the carbon-coated sponges were stacked and coated again with the carbon slurry to produce larger samples. In a separate process, a hydroxyapatite (HA) slurry was also prepared by dispersing commercial HA powder ($Ca_{10}(PO_4)_6(OH)_2$; Alfa Aesar Co., Milwaukee, WI, USA), which had been calcined at 900 °C for 3 h, in ethanol containing TEP and PVB. The templates were then coated with the HA slurry and then dried in an oven at 60 °C for 30 min. The coating/drying step was repeated several times to increase the thickness of the HA coating layer. For comparison, samples with similar porosity were also produced using either an as-received sponge or carbon coated sponge without elongation as a template. The HA coated templates were heated slowly to 800 °C at a heating rate of 150 °C/h and maintained at this temperature for 5 h to burn out the template and binders in the HA slurry. This was followed by sintering at 1250 °C for 3 h to densify the HA struts.

The pore structures and microstructures of the sintered HA walls of the fabricated samples were examined by scanning electron microscopy (FE-SEM, JSM-6701F, JEOL Techniques, Tokyo, Japan). The porosity was calculated from their dimensions and weight. The pore size was also analyzed from the SEM images of the samples. In addition, the porous structure of the sample was examined using a micro-computed tomography scanner (Skyscan 1173, Skyscan, Kontich, Belgium). The crystalline phases of the samples were characterized by X-ray diffraction (XRD, M18XHF-SRA, MacScience Co., Yokohama, Japan).

The compressive strengths of the samples, ~12 mm × 21 mm × 11 mm in size, were examined using a universal testing machine (Model 5565, Instron Corp., Danvers, MA) at a crosshead speed of 5 mm/min. The samples were compressed either parallel or normal to the direction of pore elongation. For comparison, samples produced using either the as-received polymeric sponge and carbon coated sponge without elongation as a template were also tested. The stress and strain responses of the samples were monitored during the compressive strength tests. Five samples were tested to obtain the average values and standard deviation.

In vitro cell tests of the samples were performed 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. The cell attachment was observed by SEM after culturing for 1 day.

3. Results and discussion

A carbon coated polymeric sponge with elongated pores was used as a novel template to improve the compressive strength of the reticulated porous HA ceramics. The prepared template had a highly anisotropic pore structure, in which elongated pores were formed thoroughly parallel to the direction of pore elongation, as shown in Fig. 2(A). In addition, the surface of the polymeric strut was coated uniformly with the carbon layer, as shown in Fig. 2(B). The carbon coating layer rounded the severely curved triangular polymeric strut, which would eliminate crack-like defects at the apices of the internal voids that are often formed in reticulated porous materials [16,17]. The carbon coated strut was as thick as >1 mm. The measured porosity of the sample was approximately 77 ± 0.8 vol%.

Fig. 3(A) shows a typical reconstructed 3-dimensional μ-CT image of the sample produced using the carbon-coated

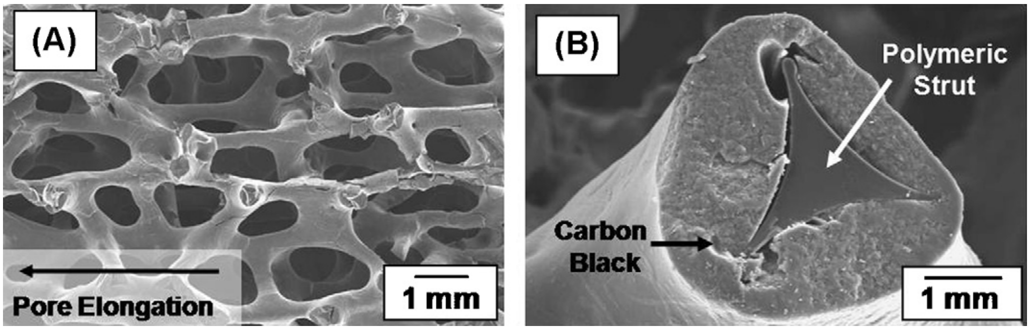

Fig. 2. SEM images of the carbon coated polymeric sponge showing (A) the elongated pores and (B) the carbon coating layer on the polymeric strut.

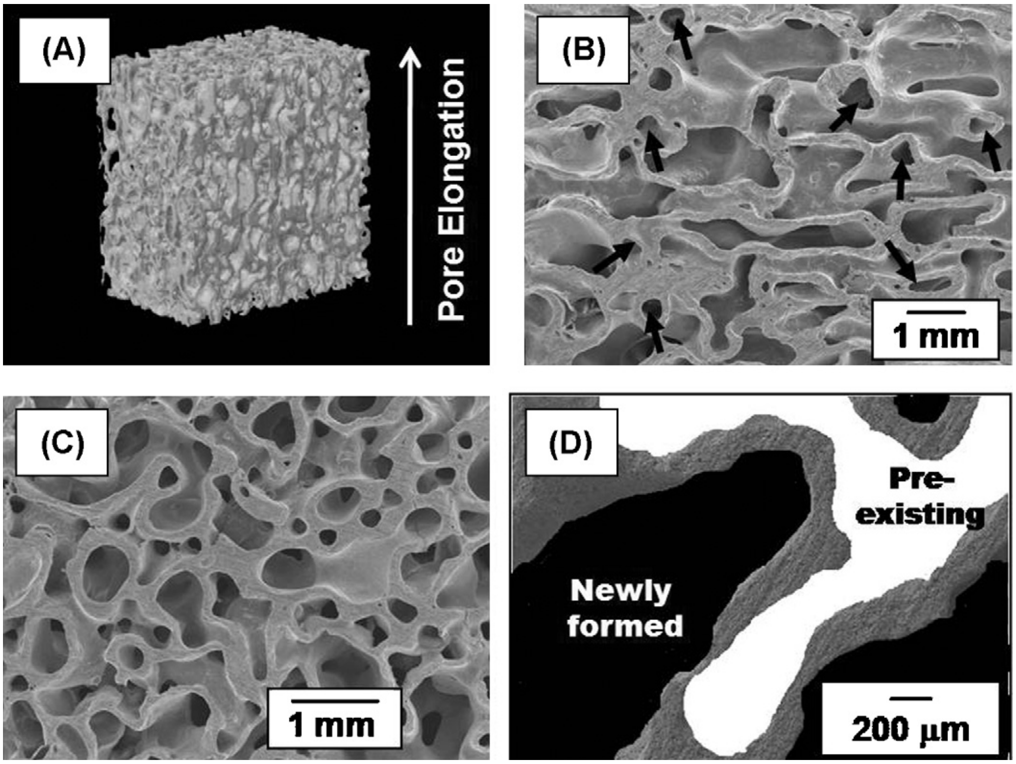

Fig. 3. Typical 3-dimensional reconstructed (-CT image of reticulated porous HA ceramics with the elongated pores (A), SEM images of the sample showing the pore structures developed parallel (B) and normal (C) to the direction of pore elongation, and a digitally colored image of the sample (D).

polymeric sponge with elongated pores. Elongated pores were formed well throughout the sample by resembling the original pore structure of the template. The construction of elongated pores was examined more closely by scanning electron microscopy (SEM), as shown in Fig. 3(B) and (C). The sample preserved a highly elongated porous structure, in which an additional pore network, marked by the arrows in Fig. 3(B), was newly formed by removing carbon-coated polymeric struts, while preserving the original pore network. The size of the original pores and newly formed pores was 599 ± 321 and 991 ± 407 μm, respectively, suggesting that both pores would provide a favorable environment for bone ingrowth [1]. On the other hand, slightly distorted pores were formed normal to the direction of pore elongation (Fig. 3(C)). However, unlike conventional sponge replication, rounded pores were formed by the carbon coating layer, which would improve the mechanical properties of the reticulated HA ceramics. It should be noted that the two pore networks were separated completely by the HA walls, as shown in Fig. 3(D), in which black and white regions represent the pre-existing pores and newly formed additional pores, respectively. This would make it possible to infiltrate polymeric materials into only one pore network, allowing the production of porous polymeric scaffolds with a bioactive CaP coating layer (Fig. 1(B)) [18].

Fig. 4(A) and (B) shows the effect of the carbon coating layer on the densification of the HA walls. The free surface of the HA wall exposed to air showed a relatively smooth surface with a number of grains and some pores (Fig. 4(A)). On the other hand, the surface of the HA wall that was initially in contact with the carbon coating layer showed a relatively rough morphology, which was presumably due to the roughness of the carbon coating layer (Fig. 4(B)).

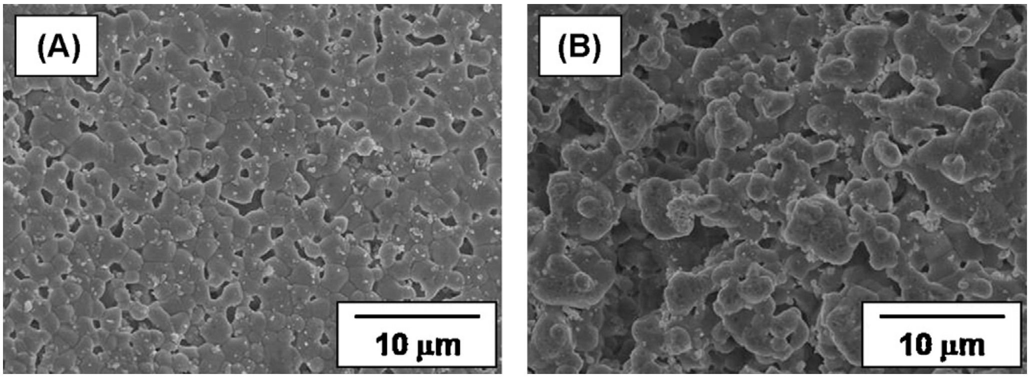

Fig. 4. SEM images of the surface morphology of the HA walls exposed (A) to air and (B) to the carbon coating layer.

The crystalline structure of the sample was examined by XRD, as shown in Fig. 5. The sample showed strong peaks that corresponded well to those of the hydroxyapatite (HA) crystal (JCPDS file No. 9-432). No secondary phases, including crystalline β-tricalcium phosphate (β-TCP), were detected, suggesting that the carbon coating layer could be removed completely without altering the crystalline structure of the reticulated porous HA ceramics.

The compressive strength of the reticulated porous HA ceramics with elongated pores was measured to determine their structural integrity as a bone scaffold. The samples were compressed either parallel or normal to the direction of pore elongation. Basically, both samples prepared exhibited similar fracture behavior, in which the stress increased linearly with an elastic response and then decreased rapidly due to rapid fracture, which is a typical characteristic of brittle ceramics [19]. However, the sample showed a high compressive strength of 2.9 ± 0.3 MPa when compressed parallel to the direction of pore elongation, which was much higher than the 1.4 ± 0.4 MPa for the sample compressed normal to the direction of pore elongation and even those for the samples produced using either an as-received polymeric sponge (0.9 ± 0.4 MPa) or carbon-coated polymeric sponge (1.5 ± 0.4 MPa), as shown in Fig. 6.

The improvement in compressive strength of the reticulated porous HA ceramics produced using the carbon-coated polymeric sponge with elongated pores was attributed not only to pore elongation but also to the carbon coating layer. Schematic diagrams demonstrating the mechanical responses of the reticulated porous HA ceramics without and with elongation pores are shown in Fig. 7. When compressed parallel to the direction of pore elongation, the sample can endure the applied load more efficiently because of an increase in the active resisting area of HA walls which are parallel to the loading direction, marked by the black lines [15,20]. In addition, the creation of elongated pores can decrease the wall length (*l*) which is one of the most important parameters determining the fracture of the HA walls, leading to a higher compressive strength [15,21]. The use of a carbon coating layer can also contribute to an increase in compressive strength, because it can eliminate the sharp cracks at the aspics of the triangular voids within the HA walls and increase the resistance

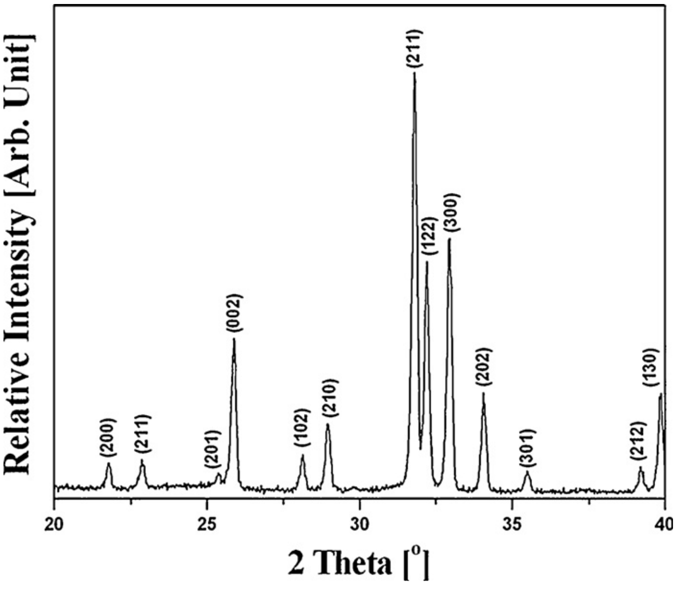

Fig. 5. Typical XRD pattern of the sample after sintering at 1250 °C for 3 h. The peaks of the crystalline HA phase were indexed.

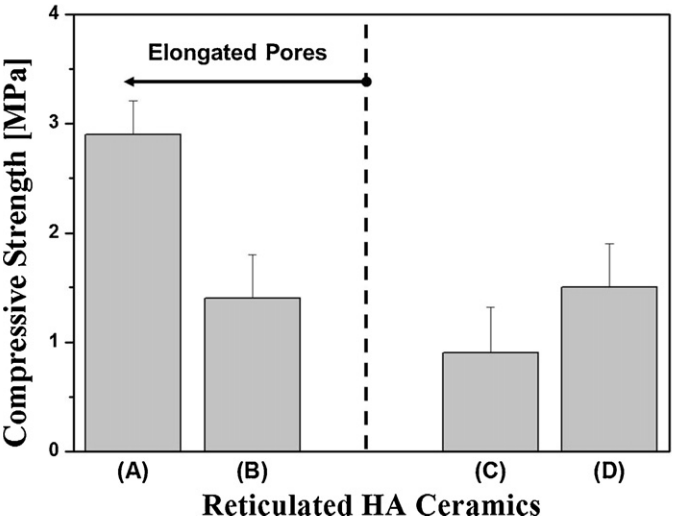

Fig. 6. Compressive strengths of the reticulated porous HA ceramics produced using various polymeric sponges as a template: carbon coated sponge with elongated pores tested parallel (A) and normal (B) to the direction of pore elongation, as-received polymeric sponge (C), and carbon coated sponge (D).

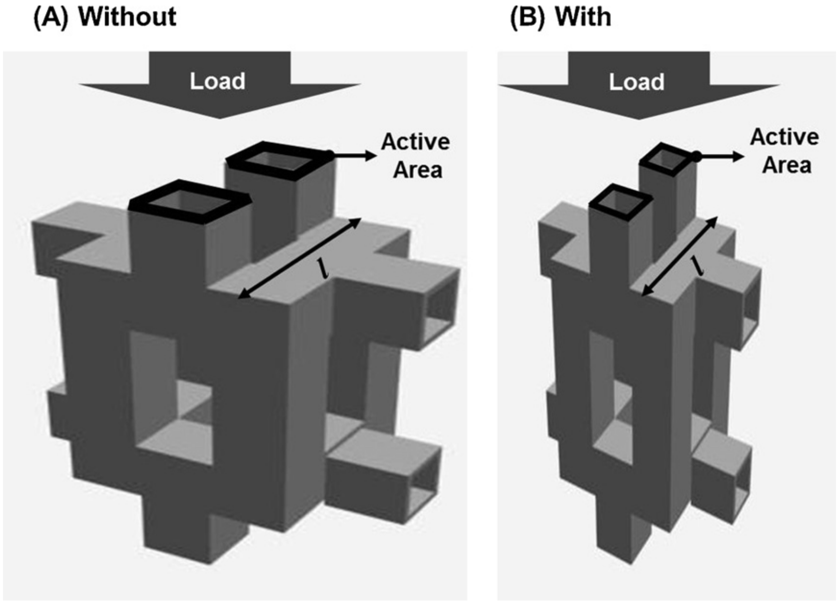

Fig. 7. Schematic diagrams demonstrating the mechanical responses of the reticulated porous HA ceramics without (A) and with (B) elongation pores.

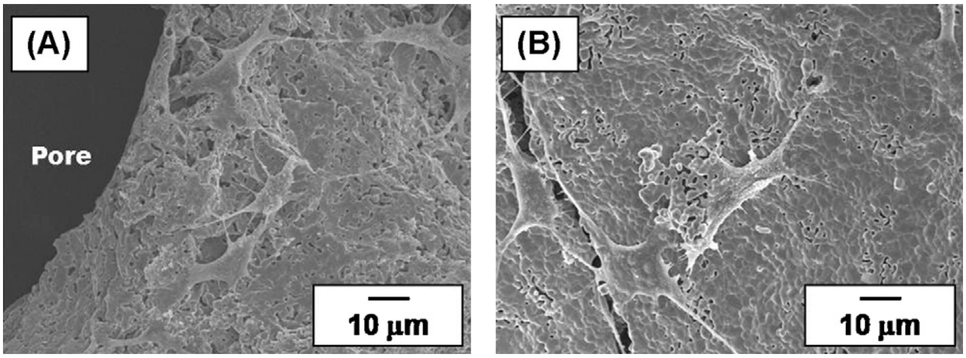

Fig. 8. Typical SEM images of the cells cultured for 1 day on the surface of the HA walls exposed (A) to air and (B) to the carbon coating layer.

to the bending of the HA walls achieved by the creation of the larger voids [16,19,21].

The preliminary osteoblastic activity of the samples was also evaluated by *in vitro* tests using a pre-osteoblast cell line. Fig. 8(A) and (B) shows typical SEM images of the cells cultured for 1 day on the surfaces of the HA walls exposed to air and carbon coating layer, respectively. The cells appeared to grow and spread actively on both surfaces, suggesting the potential of the reticulated porous HA ceramics as a bone scaffold.

4. Conclusions

Reticulated porous HA ceramics containing two interconnected pore networks with a preferred orientation were produced using carbon-coated polymeric sponges with elongated pores as a novel template. An additional pore network was newly formed by removing the carbon-coated polymeric struts, while preserving the original pore network. The size of the original and newly formed pores was 599 ± 321 and 991 ± 407 µm, respectively. The sample showed high compressive strength of 2.9 ± 0.3 MPa at a porosity of 77 vol%, when tested parallel to the direction of pore elongation. This was attributed to the construction of elongated pores formed by stretching the as-received polymeric sponge and the large internal voids within HA walls formed by removing carbon coating layer. In addition, the sample showed good biocompatibility, as assessed by the *in vitro* cell tests.

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