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Short communication

Macroporous alumina scaffolds consisting of highly microporous hollow filaments using three-dimensional ceramic/camphene-based co-extrusion

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ABSTRACT

This study proposes a novel type of macroporous ceramic scaffolds, which are comprised of hollow tubular filaments with a highly microporous structure, using 3-dimensional ceramic/camphene-based co-extrusion (3D-CoEx). The use of an initial feedrod, comprised of a camphene core and an alumina/camphene shell, enabled the construction of hollow tubular frameworks and micropores through the removal of the camphene phase. The produced scaffolds showed 3-dimensionally interconnected macropores with dimensions of ~250–300 μm × 400–550 μm, which were surrounded by hollow alumina filaments (~500 μm in diameter) featuring a number of micropores (several tens of microns in size). This unique macro/micro-porous structure could achieve a combination of both the reasonably high compressive strength of ~5.4 MPa and very high porosity of 86 vol%. In addition, the final mechanical properties and overall porosity of the porous alumina scaffolds could be fine-tuned by adjusting initial alumina content in the alumina/camphene.

1. Introduction

For the last few decades, the use of porous bioceramic scaffolds with open porous structures has been extensively investigated for the repair of diseased or damaged bone tissues [1]. Fundamentally, porous ceramic scaffolds should have both high mechanical strength to withstand loads applied to defect sites and high porosity to provide large surface areas for fast new bone formation. However, higher porosity generally causes a severe reduction in mechanical properties [2], which remains as one of the major obstacles for the production of porous ceramic scaffolds with advanced functions.

Recently, ceramic-based solid freeform fabrication (SFF) techniques have demonstrated great potential to endow porous ceramic scaffolds with significantly improved mechanical properties combined with excellent bone regeneration abilities in vivo [3–7]. This great ability lies in the fact that SFF techniques can construct tightly controlled porous structures (e.g., 3D periodic pores with perfect pore interconnectivity) through the selective consolidation of ceramic-based layers according to predetermined computer aided design (CAD) files [8–10]. Thus far, a variety of SFF techniques using their unique ceramic-based feedstocks and consolidation mechanisms have been explored, including direct-ink-write assembly [3,11,12], 3D deposition/robocasting [6,7,13], extrusion freeforming [14,15,16], freeze-form extrusion fabrication [4,17], 3D printing [18,19], and stereolithography/digital light processing [20,21]. However, most of these techniques can achieve only relatively low porosities (e.g., <70 vol%) because of their limited ability to create thin ceramic frameworks, thus usually excluding maximizing the bone regeneration ability of porous ceramic scaffolds. In addition, little attention has been given to the construction of microporous ceramic filaments [22], which can mimic the hierarchical porous architecture of natural bone [23].

We herein propose a novel type of porous ceramic scaffolds, comprised of hollow tubular filaments with a highly microporous structure (Fig. 1(A),(B)), using 3-dimensional ceramic/camphene-based co-extrusion (3D-CoEx) [22]. In particular, a hollow lattice structure was adopted as a framework for macroporous ceramic scaffolds, since it can provide high specific strength [24,25]. As a consequence, the unique macro/micro-porous structure coupled

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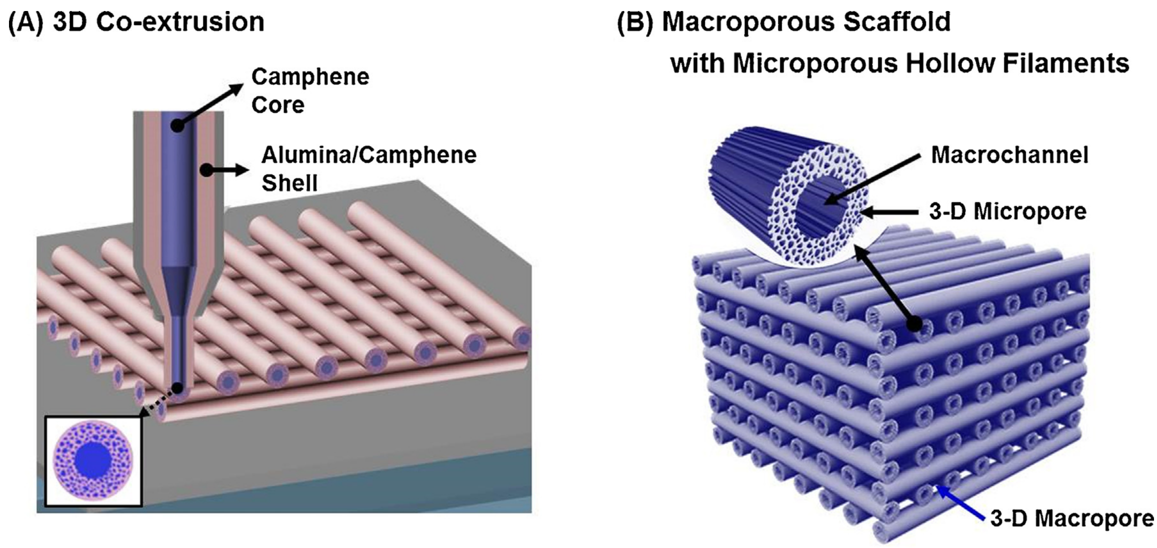

Fig. 1. Schematic diagrams of 3-dimensional ceramic/camphene-based co-extrusion (3D-CoEx) for the production of macroporous ceramics consisting of highly microporous hollow filaments: (A) 3D-CoEx process using an initial feedrod consisting of a camphene core and ceramic/camphene shell and (B) macroporous ceramic scaffolds consisting of highly microporous hollow filaments.

with a tubular geometry obtainable using 3D-CoEx would allow for the simultaneous attainment of both high porosities and high mechanical properties. To accomplish this, an initial feedrod comprised of a camphene core and an alumina/camphene shell was used (Fig. 1(A)), so that subsequently removing both the camphene core and the camphene dendrites in the alumina/camphene shell simultaneously forms not only a hollow tubular structure but also a number of micropores. Alumina was used as a model ceramic on account of its advantageous mechanical properties and reasonable biocompatibility [1]. The porosity and mechanical properties of the porous alumina scaffolds were tailored by controlling the alumina content in alumina/camphene slurries (15 vol%, 20 vol%, and 25 vol%).

2. Experimental

Commercially available alumina powder (Kojundo Chemical Lab Co., Ltd., Japan) with a mean particle size of 0.3 μm was used as the ceramic component. Camphene ($C_{10}H_{16}$, Sigma–Aldrich, St. Louis, MO, US) with a purity of 95% was used directly used as-received without further purification.

Alumina/camphene slurries with various alumina contents (15 vol%, 20 vol%, and 25 vol% in relation to the camphene) were prepared by a warm ball-milling process at 60 °C. The appropriate amount of alumina powder was added to molten camphene at 60 °C with the assistance of 3 wt% of an oligomeric polyester dispersant (Hypermer KD-4, UniQema, Everburg, Belgium) and then ball-milled for 24 h. To form the initial feedrod for co-extrusion, the resulting alumina/camphene slurries were cast in molds with a diameter of 20 mm containing a camphene core with a diameter of 10 mm and then kept at room-temperature for 30 min for complete solidification.

The prepared feedrods were extruded through a reduction die with a diameter of 1 mm at a constant speed of 1 mm/min and then deposited layer-by-layer at a stacking sequence of 0°/90° using a computer-controlled moving machine (Jimotor Co., Seoul, Korea). The green bodies comprised of 3-D alumina/camphene filaments were then heat-treated in an oven at 43 °C for 2 h to induce continual growth of the camphene dendrites formed in the alumina/camphene filaments [26], while a load of ~2 kPa was applied to enhance the bonding between the alumina/camphene filaments. Finally, the green samples were freeze-dried to remove the camphene dendrites and sintered at 1600 °C for 3 h to densify the alumina frameworks.

The macroporous structures of porous alumina scaffolds produced with various alumina contents (15 vol%, 20 vol%, and 25 vol%) were evaluated by micro-computer tomography (μ-CT, Skyscan 1173 X-ray Micro-tomography System, Skyscan, Kontich, Belgium) at a resolution of 20 μm with a 1.0 mm aluminum filter. The macroporous and microporous structures of the porous scaffolds were characterized by field emission scanning electron microscopy (FE-SEM; JSM-6701F; JEOL Techniques, Tokyo, Japan). The size of the macropores, macrochannels, micropores, and thicknesses of the alumina walls were roughly measured from the FE-SEM images of the samples. The overall porosity of the porous scaffolds was calculated from their weight and dimensions, while the microporous structure of the alumina filaments was characterized by mercury porosimetry (AutoPore IV 9500, Micromeritics Instrument Co., Norcross, GA, US).

Compressive strength tests were used to evaluate and compare the mechanical properties of the porous alumina scaffolds produced with different alumina contents (15 vol%, 20 vol%, and 25 vol%). Specimens with dimensions of 15 × 6 × 12 mm were unidirectionally compressed at a crosshead speed of 1 mm/min using a screw-driven load frame (OTU-05D; Oriental TM Corp., Korea). Five specimens were tested to obtain the mean value and standard deviation.

3. Results and discussion

The 3D-CoEx process enabled the production of macroporous alumina scaffolds comprised of hollow tubular filaments with a highly microporous structure. Regardless of initial alumina contents in alumina/camphene slurries (15 vol%, 20 vol%, and 25 vol%), all of the produced scaffolds showed the 3-D periodic construction of the microporous hollow filaments. Representative μ-CT images of the porous scaffold produced with an initial alumina content of 25 vol% are shown in Fig. 2(A) and (B). Hollow alumina filaments were well constructed in a 3-D periodic pattern, where the macrochannel in the alumina filament was formed by removing the camphene core. This finding suggests that the camphene phase can be effectively used as the fugitive material to create the macrochan-