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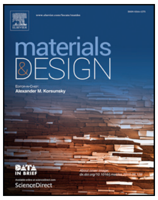

Ti scaffolds with tailored porosities and mechanical properties using porous polymer templates

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ABSTRACT

This study proposes a simple, useful approach to produce three-dimensionally macrochanneled titanium (Ti) scaffolds with tailored porosities and mechanical properties using porous polylactic acid (PLA) templates that can be prepared by conventional solid freeform fabrication (SFF) technique. Specifically, methylcellulose (MC) polymer was used as a binder since it could effectively bind coarse Ti particles and remain chemically stable inert in organic solvents used to dissolve PLA polymer. A Ti slurry-filled PLA was immersed in chloroform to remove the PLA template, followed by sintering at 1300 °C for 3 h in a vacuum. The use of a relatively small amount of a MC binder and removal of the PLA template in solvent enabled the construction of straight Ti frameworks and macrochannels in a 3-D periodic pattern without severe impurity contamination. This tightly controlled porous structure enabled the achievement of high compressive strengths without a catastrophic failure, while the compressive strength increased from ~72 MPa to 121 MPa with a decrease in overall porosity from ~75 vol% to ~67 vol%. In addition, the porous Ti scaffolds showed good biocompatibility, which was assessed by *in vitro* cell tests in terms of attachment, proliferation, and differentiation of MC3T3-E1 cells.

1. Introduction

Titanium (Ti) and its alloys are one of the most widely used metals in biomedical applications, for example, as dental and orthopedic implants, on account of their excellent mechanical properties (*e.g.*, high strength and toughness) with high corrosion resistance and good biocompatibility *in vitro* and *in vivo* [1,2]. In addition, when formulated into porous structures, these materials can provide favorable 3-D spaces and biocompatible surfaces for bone cell attachment, proliferation, and differentiation, as well as new bone formation [3,4]. Furthermore, porous Ti scaffolds can have much higher mechanical strengths with a ductile fracture than bioceramics and polymers, thus allowing them to be used for load-bearing applications.

Thu far, a variety of manufacturing techniques have been developed to produce porous Ti scaffolds, including the sintering of metal powders [5], space holder method [6], replication of a polymeric sponge [7], freeze casting [8,9,10,11], and solid freeform fabrication (SFF) techniques [12]. Basically, preferred manufacturing techniques should have the ability to construct three-dimensionally interconnected pores in a controlled manner, particularly in order to provide excellent biomechanical functions *in vivo*. In addition, the contamination of Ti metal with impurities (*e.g.*, oxygen, carbon, and hydrogen) should be minimized during both the manufacturing stage and post- treatment at elevated temperatures. Otherwise, the porous Ti scaffolds produced will become brittle, which may cause catastrophic failure during service.

Among these manufacturing techniques, SFF techniques have recently gained increasing interest on account of their great ability to create tightly controlled open porous structures, thus providing significantly improved mechanical properties with excellent bone regeneration *in vivo* [3,13,14,15]. Basically, SFF techniques can create successive layers of metal powder-based feedstocks according to predetermined 3D designs using their unique consolidation mechanism. For example, selective laser sintering (SLS) [16], selective laser melting (SLM) [17], and direct metal laser sintering [18] using lasers, as well as electron beam melting (EBM) using electron beams [19] can selectively sinter or melt thin layers of metal powders. However, these techniques require complex, expensive equipment, and the manufacturing processes should be carried out in a tightly controlled inert environment to avoid oxygen contamination. On the other hand, powder-based 3D printing techniques can create green objects by selectively spreading organic binders onto metal powder beds [20,21]. In addition, slurry/paste-based SFF techniques, including 3-D fiber deposition (3DF) [22] and direct ink writing (DIW) [23], can solidify green filaments comprised of metal powders and organic binders. These approaches can produce

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porous scaffolds in a cost-effective way but are limited to relatively simple external shapes. In addition, special care should be taken to completely remove polymer binders at high temperatures in a tightly controlled inert environment without contaminating the Ti metal. Another promising approach is to utilize porous polymer scaffolds as a template that can be prepared by conventional SFF techniques, in which powder-based slurries are cast into polymer templates, followed by heat-treatment at high temperatures [24]. However, there are concerns over the removal of polymer templates and polymer binders without deteriorating the intrinsic properties of Ti metal.

We herein propose a useful way of producing three-dimensionally macrochanneled Ti scaffolds with high mechanical strength, ductile fracture, and good biocompatibility by using porous polylactic acid (PLA) templates that can be prepared by fused deposition modeling (FDM), as shown in Fig. 1 (A)–(D). In particular, methylcellulose (MC) polymer is used as a binder to prepare aqueous Ti slurries, since it can possess strong adhesive properties that can effectively bind coarse Ti particles [22,25] and remain chemically stable in organic solvents (*e.g.*, chloroform, tetrahydrofuran, and dioxane) used for dissolving PLA [26]. As a consequence, a PLA template can be completely removed in chloroform without destroying the 3-D porous structure of a Ti/MC green body. This approach - the use of a small amount of MC binder and removal of a polymer template in solvent - can mitigate impurity contamination often caused during heat-treatment at high temperatures. Three types of porous Ti scaffolds with tailored porosities were produced and their physical, chemical, mechanical, and biological properties were investigated to demonstrate their potential as bone scaffolds. The porous structure (*i.e.*, overall porosity and pore sizes), microstructure, crystalline phases, and chemical compositions of porous Ti scaffolds were characterized using several analysis tools. The mechanical properties and fracture behavior of porous Ti scaffolds were examined by compressive strength tests. The *in vitro* biocompatibility was also examined by *in vitro* cell tests using a pre-osteoblast cell line.

2. Experimental procedure

2.1. Porous PLA template preparation

Porous PLA templates were produced by a FDM system (3DISON; ROKIT, Geumcheon-gu, Seoul, Korea) using PLA filaments at 215 °C. The PLA filaments were extruded through a nozzle with a diameter of 0.4 mm and deposited in accordance with predetermined designs. To control the overall porosity of the porous Ti scaffolds, three types of porous PLA templates with different porous structures were produced by adjusting the dimensions of the macrochannels (*i.e.* distances between the PLA frameworks), while the dimensions of the PLA frameworks were kept constant (Table 1).

2.2. Ti/MC slurry preparation

Commercially available Ti powder (325 mesh; Alfa Aesar/Avocado Organics, Ward Hill, MA, US) was used as the starting material. As the liquid medium, an aqueous MC solution with a concentration of 2.5 wt% was prepared by dissolving methylcellulous polymer (MC; Sigma Aldrich, St. Louis, MO, US) in water. Subsequently, an aqueous Ti slurry was prepared by mechanically mixing Ti powder and the MC solution with the assistance of an oligomeric polyester dispersant (Hypermer KD-6; UniQema, Everburg, Belgium) using a high shear mixer. The amount of the Ti powder in the slurry was ~64 wt%.

2.3. Ti slurry casting, PLA template removal, and heat-treatment

The prepared Ti slurries were cast into the porous PLA templates and centrifuged to ensure complete infiltration into the macrochannels. The Ti slurry-filled PLA templates were then dried at 70 °C for 24 h in an oven to remove water used as a solvent for Ti slurries and then immersed in chloroform (Sigma Aldrich, St. Louis, MO, US) for 24 h to remove the PLA templates. The chloroform was refreshed several times

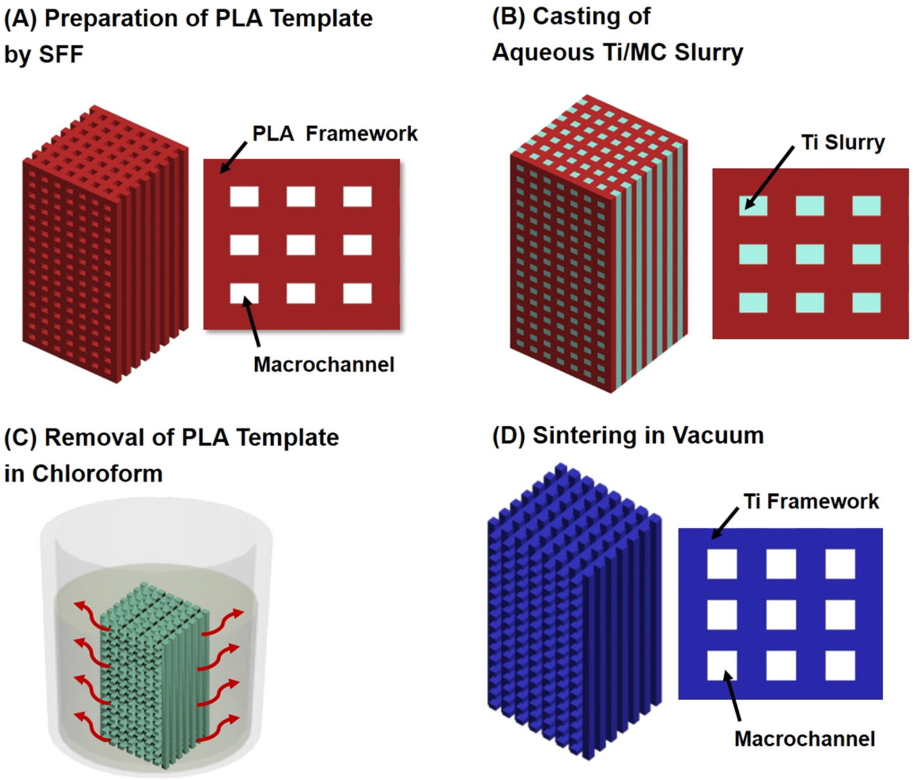

Fig. 1. Schematic diagrams showing all of the procedures for the production of three-dimensionally macrochanneled Ti scaffolds using porous polymer templates: (A) the preparation of a PLA template using solid freeform fabrication, (B) the casting of a Ti/MC slurry, (C) removal of the PLA template in solvent, and (D) heat-treatment in a vacuum.