Materials Science and Engineering C 33 (2013) 3802–3810

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Enhanced sintering ability of biphasic calcium phosphate by polymers used for bone scaffold fabrication

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ARTICLE INFO

Article history:
Received 13 June 2012
Received in revised form 7 April 2013
Accepted 7 May 2013
Available online 14 May 2013

Keywords:
Bone scaffolds
Biphasic calcium phosphate (BCP)
Polymers
Selective laser sintering

ABSTRACT

Biphasic calcium phosphate (BCP), which is composed of hydroxyapatite [HAP, $Ca_{10}(PO_4)_6(OH)_2$] and β-tricalcium phosphate [β-TCP, β-$Ca_3(PO_4)_2$], is usually difficult to densify into a solid state with selective laser sintering (SLS) due to the short sintering time. In this study, the sintering ability of BCP ceramics was significantly improved by adding a small amount of polymers, by which a liquid phase was introduced during the sintering process. The effects of the polymer content, laser power and HAP/β-TCP ratios on the microstructure, chemical composition and mechanical properties of the BCP scaffolds were investigated. The results showed that the BCP scaffolds became increasingly more compact with the increase of the poly(L-lactic acid) (PLLA) content (0–1 wt.%) and laser power (6–10 W). The fracture toughness and micro-hardness of the sintered scaffolds were also improved. Moreover, PLLA could be gradually decomposed in the late sintering stages and eliminated from the final BCP scaffolds if the PLLA content was below a certain value (approximately 1 wt.% in this case). The added PLLA could not be completely eliminated when its content was further increased to 1.5 wt.% or higher because an unexpected carbon phase was detected in the sintered scaffolds. Furthermore, many pores were observed due to the removal of PLLA. Micro-cracks and micro-pores occurred when the laser power was too high (12 W). These defects resulted in a deterioration of the mechanical properties. The hardness and fracture toughness reached maximum values of 490.3 ± 10 HV and 1.72 ± 0.10 MPa $m^{1/2}$, respectively, with a PLLA content of approximately 1 wt.% and laser power of approximately 10 W. Poly(L-lactic-co-glycolic acid) (PLGA) showed similar effects on the sintering process of BCP ceramics. Rectangular, porous BCP scaffolds were fabricated based on the optimum values of the polymer content and laser power. This work may provide an experimental basis for improving the mechanical properties of BCP bone scaffolds fabricated with SLS.

1. Introduction

Hydroxyapatite [HAP, $Ca_{10}(PO_4)_6(OH)_2$] and β-tricalcium phosphate [β-TCP, β-$Ca_3(PO_4)_2$] have been widely used as scaffold materials for bone tissue engineering (TE) due to their close chemical similarity with the inorganic component of bone and tooth minerals [1–4]. It is known that HAP possesses good bioactivity and can form strong bonds with human bone. However, this material has a low biodegradability [5]. In contrast, β-TCP can be gradually degraded and absorbed after implantation, which is a benefit for the ingrowth of new bone tissue. However, the fast degradation rate of β-TCP limits its application in TE [6]. To obtain both excellent bioactivity and proper biodegradability, biphasic calcium phosphate (BCP) ceramics, which are composed of a mixture of HAP and β-TCP, are considered to be a better alternative material for bone repair or regeneration than only HAP or β-TCP [7–10].

In addition to compositional requirements, bone tissue engineering scaffolds should also have a porous structure and complex shape [11–14]. Conventional methods for the preparation of bone scaffolds include a variety of techniques, such as hot isostatic pressing, microwave sintering, electrospinning and so on. Nevertheless, these methods have limitations in their application due to the inadequate control over the porous structure and the requirement of a specific mold for individual geometries [15]. In the family of rapid prototyping techniques, selective laser sintering (SLS) allows for a high degree of geometric complexity and individual customization. SLS has been widely used to fabricate porous bone scaffolds with predetermined interconnected networks [16–18]. To date, many studies have concentrated on the fabrication of polymer–ceramic composite scaffolds in which polymers with a content of 30–90 wt.% are used as the matrix material. The commonly used polymers include poly(L-lactic acid) (PLLA) [19], poly(L-lactic-co-glycolic acid) (PLGA), polyvinyl alcohol (PVA) [20], poly-caprolactone (PCL) [21], poly (hydroxybutyrate-co-hydroxyvalerate) (PHBV) [22], etc.

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http://dx.doi.org/10.1016/j.msec.2013.05.017

However, it has been documented that these polymers have disadvantages with respect to hydrophilicity, cell adhesion and the possibility of aseptic inflammation [23,24]. Studies on complete ceramic scaffolds prepared using SLS have scarcely been reported. It is known that in solid state sintering, the densification process is commonly realized by diffusive mass transfer mechanisms, including volume diffusion, surface diffusion and grain-boundary diffusion [25]. In ceramics, there is a low diffusion coefficient due to the strong interatomic forces of ionic bonds or covalent bonds [26,27]. These factors make it difficult for BCP ceramics to densify merely by solid state sintering due to the short sintering time in SLS. In contrast, viscous flow is the main mass transfer mechanism in liquid state sintering [28], which has an enhanced rate of mass transfer compared with diffusion mechanisms [29]. Therefore, liquid state sintering is an effective method for such hard-sintering materials [30].

In this study, a small amount of polymer was added to the BCP powder, which introduced a transient liquid phase to improve the sintering properties. The polymer was decomposed and eliminated from the final sintered BCP bone scaffolds. The morphologies and microstructures of the BCP were characterized using scanning electron microscopy (SEM). The chemical composition evolution was determined by Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy. The sintering behavior of BCP with a small amount of polymers added was also investigated.

2. Materials and methods

2.1. Materials

The HAP powder consisted of long needle-like particles of width 20 nm and length 150 nm, which were supplied by the Nanjing Emperor Nano Material Co., Ltd. The powder was prepared using the sol–gel method with a Ca/P ratio of 1.65 ± 0.1 and a composition of $Ca_{10}(PO_4)_6(OH)_2 \geq 99.5\%$, heavy metal ≤ 8 ppm and As ≤ 1 ppm. β-TCP powder (99%) was purchased from the Kun Shan Chinese Technology New Materials Co. Ltd. The powder was subjected to thermal treatment after co-precipitation with $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$. The resulting powder had a Ca/P radio of 1.50 ± 0.03 and an average particle size of approximately 200 nm. The PLLA powder (99%) was obtained from the Jinan Daigang Biomaterial Co., Ltd. It was prepared through the ring-opening polymerization of lactide catalyzed by stannous octoate. The parameters of the resulting PLLA were as follows: average Mw of 10 kDa, viscosity of 0.51–1.0 dl g^{-1}, glass transition temperature of 60–65 °C and melting temperature of 175–185 °C. PLGA (Medisorbs, LA:GA = 50:50) powder was obtained from the Shanghai Linc-Bio Science Co., Ltd, China. The PLGA particles were colorless with an inherent viscosity of 0.15–0.8 dl g^{-1}, average Mw of 5–100 kDa, glass transition temperature of 49–60 °C and melting temperature of 170–220 °C.

It has been reported that BCP scaffolds with HAP/β-TCP (50/50 w/w) possess good biocompatibility and osteoconduction [31], while BCP with a ratio of 20/80 w/w has been proven to stimulate the osteogenic differentiation of human mesenchymal stem cells and induce bone regeneration at the fastest rate in vivo [32,33]. The BCP (HAP/β-TCP 20/80, 50/50 w/w) powders combined with 0, 0.5, 1, 1.5 and 2 wt.% polymers for the sintering experiments were obtained by physical blending [34,35]. The powders were ground and milled with a mortar and pestle for 30 min and were thoroughly mixed.

2.2. Preparation

The mixed BCP/polymer powders were processed using a homemade SLS system [36,37] for bone scaffolds. A CO_2 laser (model Firestar® t-Series 100 W, Synrad Co., USA) was used in the SLS system with a laser beam diameter of 3 mm, rated voltage of 30 V and rated current of 75 A. The powder particles were found to remain discrete; therefore, the scaffolds could not take shape at a laser power below 6 W. However, the scaffolds tended to curl up at a laser power above 12 W. Thus, the proper range of laser power was determined as 6–12 W. To determine the optimal laser power for BCP, the experiments were performed under the following sintering parameters: laser power of 6, 8, 10 and 12 W; scan speed of 100 mm/min; layer thickness of 0.2 mm; and laser spot diameter of 2 mm.

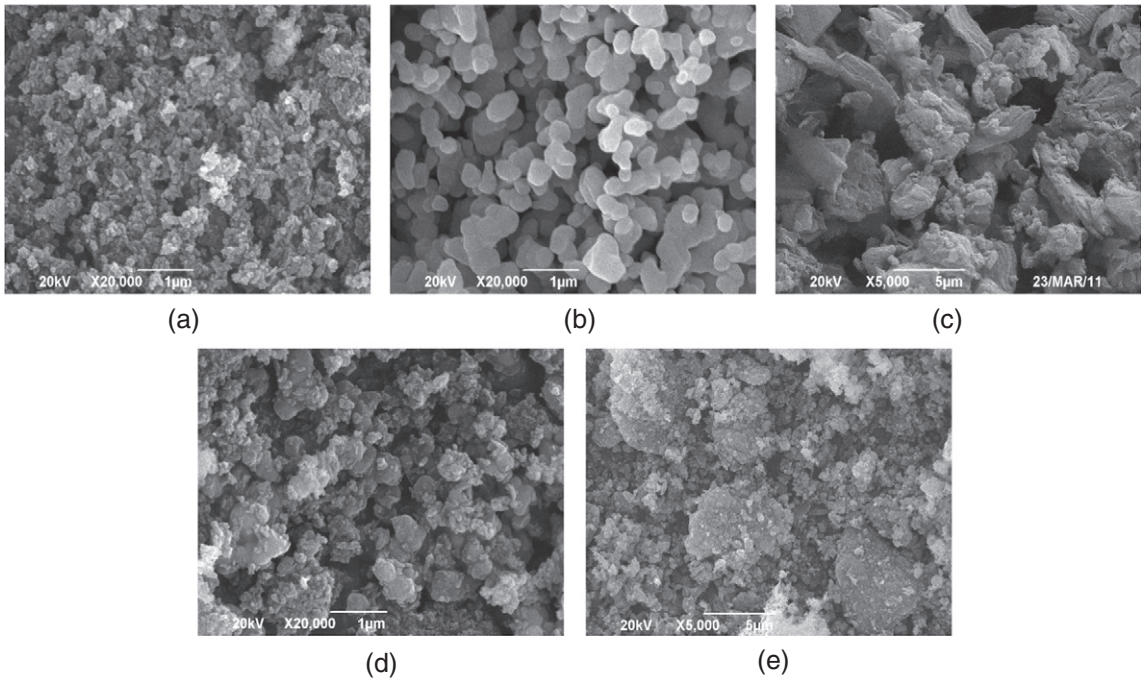

Fig. 1. Micrographs of the raw materials for the sintering experiments. a: HAP, b: β-TCP, c: PLLA, d: BCP, and e: BCP combined with 1 wt.% PLLA.