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ScienceDirect

Ceramics International 41 (2015) 14029–14034

CERAMICS INTERNATIONAL

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Preparation and characterization of hydroxyapatite–sodium alginate scaffolds by extrusion freeforming

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Received 12 March 2015; received in revised form 28 June 2015; accepted 3 July 2015

Available online 11 July 2015

Abstract

Extrusion freeforming is a facile approach to produce complex 3D structures with controlled architecture and porosity. In this work, a new slurry system, mainly containing hydroxyapatite (HA) and sodium alginate (SA), has been used to fabricate porous hydroxyapatite scaffolds. After cross-linking in 5% calcium chloride ($CaCl_2$) solution for 24 h, HA–SA composite scaffolds were sintered at 1000–1300 °C for 2 h. The properties of HA–SA composite scaffolds before and after sintering have been investigated. The new slurry system has greatly improved the quality of porous hydroxyapatite scaffolds.

Keywords: A. Sintering; Extrusion freeforming; Hydroxyapatite; Sodium alginate; Porous scaffold

1. Introduction

Interconnected porous scaffolds with tailored mechanical properties are often used as extracellular matrix (ECM) biomimetic structure to guide for cell ingrowth in bone tissue engineering [1]. Extrusion freeforming, a rapid prototyping technique, has been widely studied in constructing bone regeneration scaffolds for its facile process condition and tailored porosity [2–4]. Through careful control of the key parameters (slurry properties, printing and sintering conditions etc.), 3D structures with designed interconnected porosity can be easily constructed [5–7].

However, some flaws such as fused horizontal pores and cracking of the filament during drying period have been mentioned in some cases [8,9]. Many approaches have been studied to improve such drawbacks. For instance, Luo et al. [8] designed a XXYY pattern and their researches indicated that the XXYY pattern, compared to the XY pattern, had significantly reduced the defect of fused horizontal pores. A similar pattern was used in Cho's study [10]. More recently, Colosi et al. [9] developed a novel dispensing system based on two coaxial needles which could deliver sodium alginate and calcium chloride solution simultaneously. The introduction of modified structure could solve the problem of fused horizontal pores to a certain extent. In spite of the improvements mentioned above, the defects of fused horizontal pores and cracking of the filament during drying have not been resolved completely.

In this work, a new slurry system, major components of HA and SA, has been used to fabricate 3D porous HA scaffolds with extrusion freeforming system. There are two main processes: (1) HA–SA scaffolds fabrication, (2) scaffolds sintering at 1000, 1100, 1200, and 1300 °C for 2 h. The structural and physical–chemical properties of HA–SA scaffolds have been investigated comprehensively.

2. Materials and methods

2.1. Materials

Commercially available HA nano powder (needle like particle, 60-nm width and 150-nm length) was purchased from

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http://dx.doi.org/10.1016/j.ceramint.2015.07.016
0272-8842/

Emperor Nano Material, China. Sodium alginate (chemical grade) and calcium chloride anhydrous (analytical grade) were obtained from Tianjin Damao Chemical Reagent Co., China. Ammonia water and some other necessary chemical reagents used in the experiments were supplied by Sinopharm Chemical Reagent Co. Ltd.

2.2. Preparation of HA scaffold via extrusion freeforming system

The preparation of HA–SA scaffolds includes HA–SA composite slurry preparation and scaffolds extrusion deposition. To prepare the HA–SA composite slurry, 1.0 g sodium alginate was fully dissolved in 30 ml distilled water with 0.5 g ammonia water treatment first. Then 28 g HA nano powder gradually dispensed in the SA solution with continuously stirring to get uniform HA–SA composite slurry.

The HA–SA scaffolds were fabricated by a micro-syringe extrusion freeforming system (MAM Micro-Droplet Jetting, Shanghai Fochif Mechatronics Technology Co., Ltd, China) using the previous HA–SA composite slurry. Then these scaffolds were cross-linked in 5% $CaCl_2$ solution for 24 h.

In order to effectively demonstrate the better performance of the new slurry system, some scaffolds have been fabricated using HA-glycerol slurry referring to our previous works [7,11] as a control group. To simplify the presentation of the study results, the scaffolds with new slurry system were named as HA–SA and the controlled ones named as HA-G. Both HA–SA and HA-G scaffolds were dried at room temperature for 24 h.

The HA–SA and HA-G scaffolds with different layers (2, 4, 6 and 8 layers, ø14 mm) were made to investigate the cracking phenomenon when dried at room temperature. The macro-morphology of HA–SA and HA-G scaffolds was measured by a portable USB Digital Microscope (A005+, Shenzhen D&F Co., Ltd). 3D cubic scaffolds with the size around 10 mm × 10 mm × 4 mm were fabricated and then sintered at different temperatures.

2.3. Properties of HA–SA scaffolds after sintering

The thermal behaviors of the synthesized HA–SA scaffolds were characterized by thermo-gravimetric and differential scanning calorimetry (TG/DSC). TG/DSC analysis was performed using a NETZSCH, STA 499F3 device. 19.24 mg of HA–SA scaffolds was heated from the ambient temperature to 1400 °C at a rate of 10 °C/min in an alumina pan. A staged sintering process was used to sinter the HA–SA scaffolds. In short, 3D cubic HA–SA scaffolds obtained in Section 2.2 were pre-sintered at 400 °C for 1 h and then sintered at 1000, 1100, 1200 and 1300 °C for 2 h using a commercial chamber furnace (KSL-1700X S, Hefei Kejing Materials Technology Co., Ltd, China).

The size of HA–SA scaffolds before and after sintering was measured by a microcaliper to calculate the linear shrinkage of scaffolds on firing. The water absorption tests were carried out by soaking samples in distilled water for 3 h and then tapered with a soft paper towel to remove excess water from the specimen surface. The water absorption (WA(%)) was calculated according to the following equation [12,13]

$$\mathrm{WA}(\%) = \frac{W_1 - W_2}{W_1} \times 100 \quad (1)$$

where W_1 and W_2 are weights of the sintered HA–SA scaffolds before and after immersing in distilled water of 3 h, respectively. At least 5 scaffolds were used for each sintering temperature during linear shrinkage and water absorption testing.

The phases of the original HA powder and sintered scaffolds were characterized by X-ray diffraction (XRD, X'Pert PRO, the Netherlands). The microstructures were studied using scanning electron microscopy (SEM, Nova NanoSEM 450, FEI, the Netherlands).

3. Results and discussion

3.1. Performances of the new slurry in the fabrication of composite scaffolds

The macro-morphology of HA-G and HA–SA scaffolds with different layers (2, 4, 6 and 8 layers) after drying is shown in Fig. 1. The HA-G scaffolds suffer obvious macro-cracks in several places. With the decrease of the scaffold layers, the cracking phenomenon becomes more serious. By comparison, no cracks are found in the HA–SA scaffolds, only a warping is occurred in two layer one. Thus, under the same drying process and condition, HA–SA scaffolds show better crack resistance performance than HA-G scaffolds.

To optimize the pore structure, two types of HA–SA scaffold models, named as XY model and XXYY model, were designed. Fig. 2 shows the top view, left side view and sectional view of XY model scaffold and XXYY model scaffold. As shown in left side view, 50% transversal pores are replaced by slurry because of fiber depositing path due to continuous fiber depositing [14]. From Fig. 2 it also can be seen that both XY model scaffold and XXYY model scaffold have regular vertical pores, whereas transversal pores tend to fuse together due to the downward relaxation of the slurry caused by gravity. Compared with XY model scaffold, the transversal pores of XXYY model scaffold are much more regular. Unlike HA-glycerol slurry system, the scaffolds made

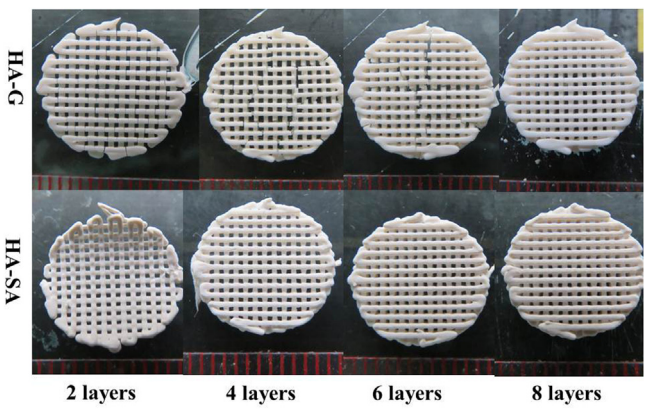

Fig. 1. Macro-morphology of HA-G and HA–SA scaffolds after drying.