Applied Surface Science 256 (2010) 4586–4590

Contents lists available at ScienceDirect

Applied Surface Science

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

The influence of polymer concentrations on the structure and mechanical properties of porous polycaprolactone-coated hydroxyapatite scaffolds

J. Zhao, K. Duan, J.W. Zhang, X. Lu, J. Weng*

Key Laboratory of Advanced Technologies of Materials (Ministry of Education), Southwest Jiaotong University, Chengdu 610031, PR China

ARTICLE INFO

Article history:
Received 21 July 2009
Received in revised form 16 February 2010
Accepted 17 February 2010
Available online 25 February 2010

Keywords:
Porous scaffold
Hydroxyapatite
Composite
Polymer coating
Mechanical properties

ABSTRACT

Polycaprolactone (PCL)-coated porous hydroxyapatite (HA) composite scaffolds were prepared by combining polymer impregnating method with dip-coating method. Three different PCL solution concentrations were used in dip-coating process to improve the mechanical properties of porous HA scaffolds. The results indicated that as the concentration of PCL solution increases the compressive strength significantly increased from 0.09 MPa to 0.51 MPa while the porosity decreased from 90% to 75% for the composite scaffolds. An interlaced structure was found inside the pore wall for all composite scaffolds due to the penetration of PCL. The porous HA/PCL composite scaffolds dip-coated with 10% PCL exhibited optimal combination of mechanical properties and pore interconnectivity, and may be a potential bone candidate for the tissue engineering applications.

1. Introduction

Porous HA bioceramics scaffolds have been widely studied in bone tissue engineering field due to the importance of three-dimensional (3D) porosity for bone regeneration [1–4]. Numerous methods have been developed for fabricating porous HA scaffolds, such as pore forming, foaming, gel-casting, freeze-drying and polymer impregnating method (PIM) [5–9]. Of these, only PIM leads to high porosity (more than 90%) and great structure similarity to the natural bone, which supports faster rate of osseointegration and therefore leads to enhanced mechanical properties in vivo [10,11]. However, a high porosity is inevitably associated with a decrease in strength of the porous HA scaffolds. Therefore, it is significant to improve the strength of porous HA scaffolds with highly interconnected porosity to get better clinic results.

The introduction of polymers phase seems to be a promising choice to overcome low mechanical strength of porous ceramics because of its excellent toughness and plasticity by forming ceramics–polymer composite systems [12,13]. Among the most often utilized biodegradable synthetic polymers, PCL has been regarded as a preferable candidate in polymer–ceramics composite system due to its low cost and sufficient mechanical properties to serve as resorbable suture, drug delivery system, and bone graft substitutes [14,15]. As one of compound methods, polymer-coating method has attracted more attention owing to its quick and facile process and polymer diversity according to the clinical demands [16]. Kim et al. have reported the HA/PCL composite scaffold with antibiotic for drug delivery system while the compressive strength has been improved from 0.16 MPa to 0.45 MPa by different concentration of polymer solution [17]. Peroglio et al. adopted the PCL solution and PCL nanodispersion infiltrating into the porous alumina scaffolds with increased apparent fracture energy and fracture resistance [18]. However, our knowledge about the effect of polymer concentration on the microstructure and mechanical properties of composite scaffolds is still very scarce.

The present study concentrated on preparing a series of HA/PCL composite scaffolds and characterizing the influences of polymer concentration on the composite scaffold structure and mechanical properties. The concentration of PCL solution was optimized so as to obtain the composite scaffold with improved strength for potential scaffolds in bone tissue engineering.

2. Materials and methods

2.1. Materials

HA powder was synthesized by the wet chemical method in our laboratory. The size of HA particles was in the range of 0.1–8.0 μm with mean size of 2.1 μm by particle size analyzer (HOBRIBA La-920, Japan). Polyvinyl alcohol (PVA) with an average molecular weight of 75,000 was used as surfactant and dispersant additives. Polyurethane foams with pore size of 1 mm were used as duplicating template and cut into Ø 8 mm × 12 mm cylinder. PCL (Daicel Chemical Industries, Ltd., Japan) used in this study had an aver-

* Corresponding author. Tel.: +86 28 8760 1371; fax: +86 28 8760 1371.
E-mail addresses: zhaojing3526@126.com (J. Zhao), jweng@swjtu.cn (J. Weng).

0169-4332/$ – see front matter.
doi:10.1016/j.apsusc.2010.02.053

age molecular weight of 50,000. Chloroform was purchased from chemical engineering factory (China, Chengdu).

2.2. Scaffold fabrication

The porous HA scaffold was obtained by impregnating porous polyurethane foams with the slurry containing HA powder, distilled water and additives as our previous study [9]. PCL was used to enhance the strength and toughness of porous HA scaffolds. Three concentrations of PCL solutions were selected to investigate the influence of polymer solution concentration on the structure and mechanical properties of composite scaffolds. First PCL was dissolved in chloroform at different concentrations of 5%, 10% and 20% (w/v), respectively. Then the porous HA scaffolds were fully immersed in polymer solutions and treated by ultrasonic oscillation for 1 min each. PCL-coated HA composite scaffolds were centrifuged and then dried in vacuum drying chamber 48 h at room temperature. The names of composite scaffolds with 5%, 10% and 20% PCL were denoted as HA-5P, HA-10P and HA-20P, respectively.

2.3. Characterization

2.3.1. Phase composition

X-ray diffraction analysis (XRD) was used to characterize the phase composition of the PCL coatings on scaffolds. In order to observe the phase composition of PCL coating with different concentrations, pressed HA sheets were dipped into varied PCL solutions to form a PCL coating and then dried in air for 24 h. XRD instrument is a Phillips X'Pert, using CuKα radiation at 35 mA and 45 kV. Scans were performed with a 2θ range of 10–60° with 0.033° steps.

2.3.2. Porosity

The mass variations before and after dip-coating process were recorded to study the effect of coating concentration on mass. The mass variation of porous HA scaffolds with varied coatings was measured with a precise electronic balance (BS224S, Sartorius) with a sensitivity of 5×10^{-4}. The total porosity for HA scaffold and PCL-coated HA scaffolds were calculated by Archimedes method and Gravimetry method, respectively [19,20]. Six scaffolds of each group were determined and averaged.

2.3.3. Microstructure

Before and after the dip-coating process, the microstructures of varied scaffolds were observed by scanning electronic microscopy (SEM, Quanta200). Clearly, the boundary of PCL and HA would be influenced by the ductility of PCL. Therefore, it is necessary to keep the real interface between the scaffold and PCL coating and investigate the interaction. The composite scaffolds were firstly placed in liquid nitrogen, and then rapidly fractured by brittle failure in order to overcome the polymer effect on the boundary. The cross section of porous scaffolds were fixed on a copper stud and coated with gold for SEM observation to investigate the polymer morphologies and distributions.

2.3.4. Mechanical properties

In compression tests, cylindrical samples (Ø 8 mm × 12 mm) were used. The tests were carried out in ambient atmospheric condition (20 ± 5 °C and 50 ± 5% RH) using an INSTRON 5567 mechanical tester (USA) with 30 kN load cell. The crosshead speed was set at 0.5 mm/min and the load was applied until the scaffold was fractured. At least five samples of each scaffold were measured and the results were averaged.

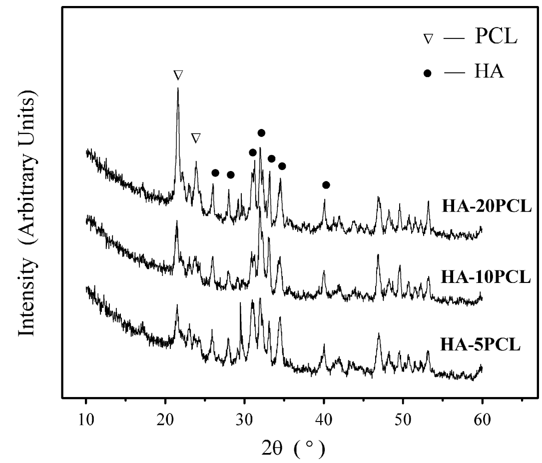

Fig. 1. XRD patterns for three PCL-coated HA samples.

3. Results and discussion

3.1. Phase composition of composite scaffolds

The XRD patterns of PCL coatings containing different concentration are shown in Fig. 1. The XRD peaks for three composite samples show typical PCL and HA peaks without additional peaks for other phases or peak shifts, which indicated that no chemical reactions occurred during the sintering process. After dip-coating process, the increase in the concentration of PCL solutions increased the peak intensities of PCL.

3.2. The effect of PCL concentrations on porosity

The sintered porous HA scaffold showed excellent interconnectivity and porosity (Fig. 2). Porosity is one of the most important factors affecting the morphological properties of biomaterials scaffold in bone regeneration process. Higher porosity favors tissue ingrowth, bone formation and forming biological fixation with surrounding tissue [20]. Therefore, the prepared scaffold is competent for nutrient diffusion, metabolite elimination, cell migration and bone ingrowth into the interior scaffold in vivo [21].

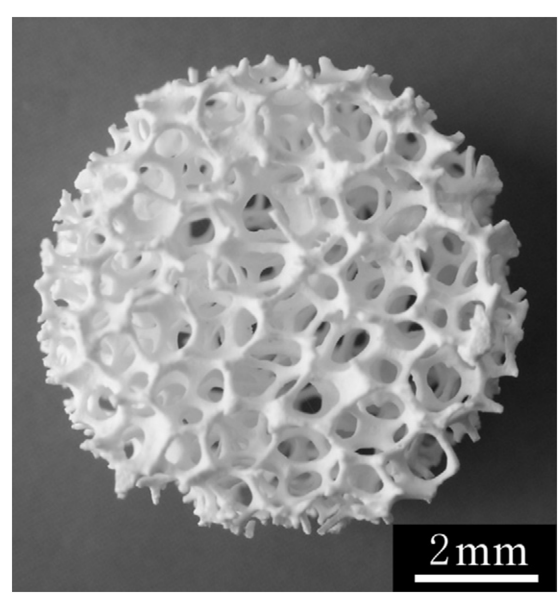

Fig. 2. The appearance of sintered HA porous scaffold.