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Effect of Nanohydroxyapatite Addition on the Pore Morphology And Mechanical Properties Of Freeze Cast Hydroxyapatite Scaffolds

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Abstract

In current study, the effect of nanohydroxyapatite (nHA) content on microstructural and mechanical properties of hydroxyapatite scaffolds fabricated using the water-based freeze casting method has been investigated. In the experimental procedure, the solidified samples were prepared by hydroxyapatite slurries containing different concentration of nHA followed by sintering procedure at 1350 °C. The characteristics of the initial powders, microstructure, and mechanical strength of the scaffolds were assessed by X-ray diffraction, scanning electron microscopy, and mechanical strength test, respectively. The results showed that, increasing of nHA leading to decrease in pore size, increase in inter structural bridges, reduce in porosity and increase in compressive strength of the hydroxyapatite scaffolds, which is believed to be more effective in bone tissue engineering applications.

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Keywords: Freeze casting; Nanohydroxyapatite; Scaffold; particle size.

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1. Introduction

As the most promising bone substitute materials, calcium phosphate (CP) compounds such as hydroxyapatite (HA) have been clinically used in dense, granular and porous forms due to their bioactivity, osteoconductivity, and similar composition to the natural hard tissues, Zamanian et al. (2010). Features affecting the performance of a scaffold for uses in the tissue engineering are pore size, porosity percentage and orientation, surface morphology, mechanical strength and porosity interconnectivity, Pourhaghgouy and Zamanian (2015). The porous forms of these materials have the possibility of tissue growth and the capability of being replaced by bone tissue, Oates et al. (2007). Several fabrication techniques such as polymer sponge method, Fook et al. (2009), pore-foaming, Zuo et al. (2011), infiltration of compression molded sponge, Corbin et al. (1999), gel casting, Meng et al. (2000), slip casting, Zhang et al. (2010), starch consolidation, Díaz and Hampshire (2004), microwave processing, Agrawal (1998), and freeze casting, Farhangdoust et al. (2013) have been used to produce porous structures. Among these techniques, freeze casting has attracted much attention due to its superior advantages such as simplicity, low shrinkage in forming process, possibility of controlling the porosity, interconnectivity, relatively good mechanical strength, environment-friendly and economic, Deville et al. (2006). Many factors such as powder content and size, and cooling rate affect porosity structure and studies about these parameters have been investigated by researchers, Lasalle et al. (2012). For example, Deville et al. (2010) investigated the influence of particle size on ice nucleation and growth during the ice-templating process. In our previous works, we explored the effects of powder particle size and nanoparticle size on the porosity size and mechanical properties of hydroxyapatite scaffolds, Ghazanfari and Zamanian (2014), Zamanian et al. (2014). Also in our previous work, the influence of freezing starting temperature on pore size and inter structure bridges of freeze-casted hydroxyapatite scaffolds were investigated. To our knowledge, surface morphology and inter structure bridges and mechanical properties of microhydroxyapatite/ nanohydroxyapatite scaffolds fabricated by this method has so far not been studied. Therefore, in the present study, microstructures and mechanical strength of microhydroxyapatite/ nanohydroxyapatite scaffolds were produced using the water-based freeze casting technique have been characterized. The results of this study can be beneficial to the promotion of hydroxyapatite scaffolds as candidates for bone tissue engineering.

2. Materials and methods

2.1. Scaffolds fabrication

In this study, hydroxyapatite scaffolds with 15vol% solid concentration have been produced by unidirectional freeze casting procedure. At first, dispersant (4 wt% of powder) (Dolapix CE 64, Zschimmer & Schwarz, Lahnstein, Germany) has been added to distilled water. Then, microhydroxyapatite (2196, Merck KGaA, Darmstadt, Germany) and nanohydroxyapatite (Sigma, USA) powders have been added to suspension, with weight ratios of 100:0, 50:50 and 0:100 (microhydroxyapatite:nanohydroxyapatite). Then, the prepared slurries were ball-milled for 20 h using alumina balls. After that, polyvinyl alcohol (PVA, Merck, Darmstadt, Germany) was added as a binder at 4 wt% of the solid content. Before casting, the slurries were de-aired in a vacuum desiccator for half an hour to remove the air bubbles. Freezing of the slurries was done by pouring them into a PTFE mold, placed on a Cu cold finger which the temperature is controlled using liquid nitrogen and a ring heater connected to a PID controller. The slurries were frozen with 1 °C/min cooling rate. Then, the solidified samples were placed in a freeze dryer (FD-10, Pishtaz Engineering Co., Tehran, Iran) for 48 h to sublimate the ice crystals. After sublimation, the green bodies were sintered at 1350 °C temperatures for 2 h.

2.2. Property Characterization

2.2.1. Phase analysis

The X-ray diffraction (XRD, Philips PW3710) was used to investigate the effect of sintering temperature on the phase transformation in initial hydroxyapatite powder. The comparison of XRD patterns with JCPDS standards was carried out to identify the crystalline phases.

2.2.2. Microstructural characterization

In order to evaluate the morphology and the particle size of the nanohydroxyapatite powders, the powders were ultrasonically dispersed in ethanol to form a diluted suspension and then a few droplets were dropped on carbon coated copper grids. Then, the images were taken using a transmission electron microscopy (TEM, GM200 PEG Philips) operating at 200 kV. In addition, microstructure observation of the scaffolds was conducted with scanning electron microscope (SEM, Stereoscan S360, England).

2.2.3. Mechanical testing

The compression tests of scaffolds were carried out on a testing machine (Santam, STM- 20, Iran) on five samples, with a crosshead speed of 0.5 mm/min.

3. Results and discussion

3.1. Phase analysis

Figure 1 shows The XRD patterns of the initial powder and the sintered scaffold at 1350 °C, which can be completely indexed with HA (JCPDS#76-0694). HA was the only phase, and no secondary phase was found.

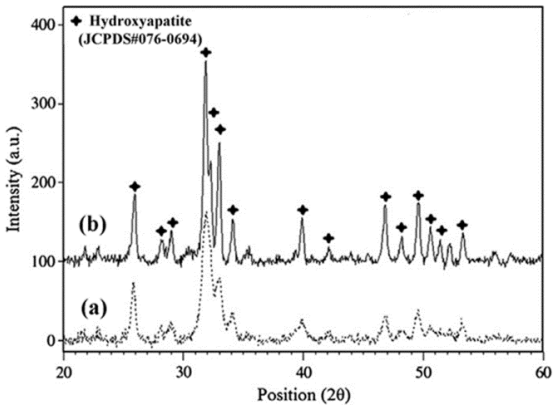

Fig. 1. XRD spectra of (a) initial; (b) sintered powders at 1350 °C.

3.2. TEM diffraction

Figure 2 shows the TEM photograph of nanohydroxyapatite powders. As can be seen, Morphology of nanohydroxyapatite particles is irregular-rod-like structure with length and diameter of less than 100 nm and 50 nm, respectively.

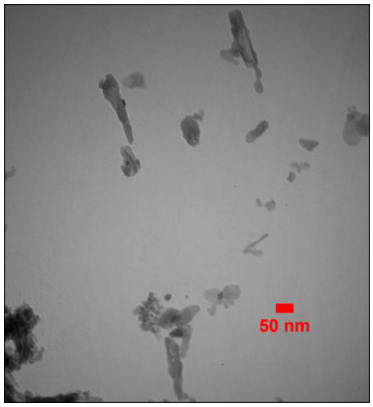

Fig. 2. TEM image nanohydroxyapatite powder.

3.3. Microstructural characterization

Figure 3 shows SEM micrographs of the hydroxyapatite-sintered scaffolds. As can be seen, the microhydroxyapatite scaffolds have thicker walls and larger pores. By adding nHA, porosity and walls size were reduced. The reason is that, by increasing the nanoparticles and simultaneously increasing the specific surface area, ice crystal nucleation sites increase. As a result, the number of formed ice crystals increase and the distance between them decrease. Therefore, the width of the ceramic walls and porosity size decrease. It also, inter structure bridges density greatly increased with increasing weight percent of nHA, so that the porosity surfaces were completely covered with the created bridges in the cross section image of nanohydroxyapatite scaffold (fig. 3f).

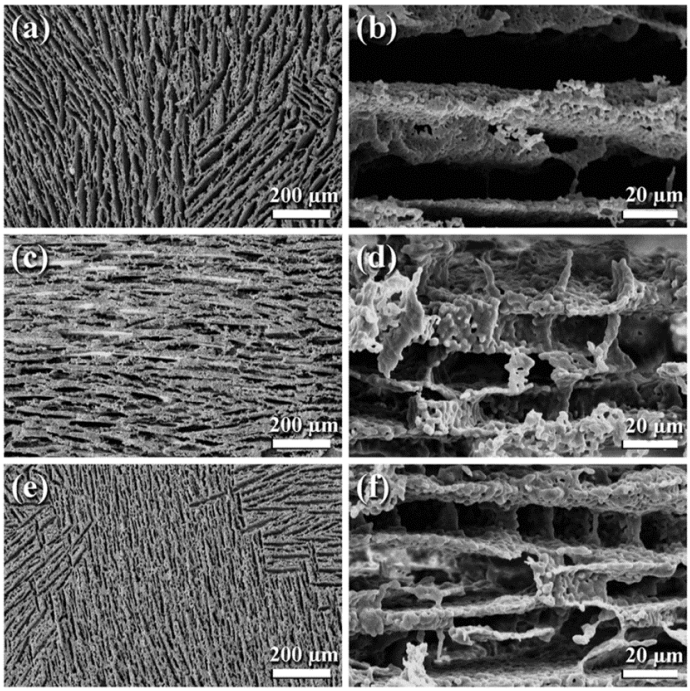

Fig. 3. SEM images hydroxyapatite scaffolds: (a, b) 100% microhydroxyapatite; (c, d) 50/50 microhydroxyapatite/ nanohydroxyapatite; and (e, f) 100% nanohydroxyapatite; perpendicular to the ice growth direction, with magnifications X100 (left) and X1000 (right).

3.4. Evaluation of mechanical strength

Figure 4 shows shrinkage, porosity and compressive strength of the hydroxyapatite scaffolds with different nHA concentrations. The compressive strength of the samples is affected by the porosity size and amount. The compressive strength of the samples increases by increasing the nanoparticles and with a simultaneous decrease in porosity size and percentage. Moreover, increasing the number of inter structural bridges in the nanohydroxyapatite scaffolds greatly increased the strength. The increase in strength was much more than the increase in shrinkage because of the presence of these bridges. These bridges were not observed in the microhydroxyapatite scaffolds.

4. Conclusions

In this paper, the influence of nHA on the microstructure and mechanical properties of freeze-casted hydroxyapatite scaffolds was studied. As the nHA increasing from 0 to 100 vol.%, the porosity decreased from 73% to53%, while the compressive strength increased from 2 MPa to 17 MPa. Furthermore, the pore channel size decreased and inter structural bridges increased. Thus rendering them suitable in bone tissue engineering.

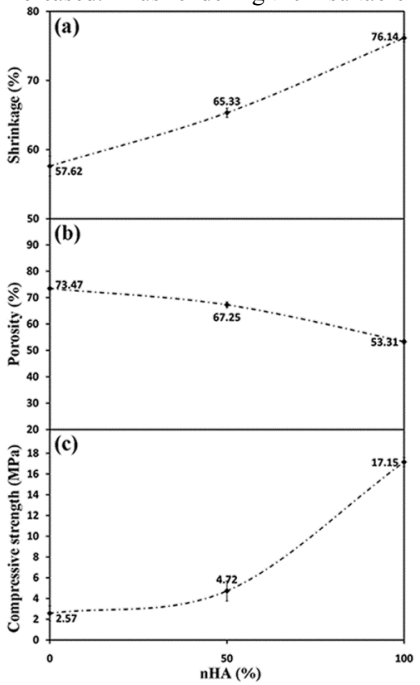

Fig. 4. Effect of nHA concentration on the (a) shrinkage; (b) porosity; (c) compressive strength of hydroxyapatite scaffolds.

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