Materials Science and Engineering C 80 (2017) 45–53

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Interconnected porosity analysis by 3D X-ray microtomography and mechanical behavior of biomimetic organic-inorganic composite materials

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ARTICLE INFO

Article history:
Received 27 December 2016
Received in revised form 12 May 2017
Accepted 15 May 2017
Available online 17 May 2017

Keywords:
Hydroxyapatite
Mechanical characterization
Scaffold
Composite material
Porous material

ABSTRACT

Hydroxyapatite-based materials have been used for dental and biomedical applications. They are commonly studied due to their favorable response presented when used for replacement of bone tissue. Those materials should be porous enough to allow cell penetration, internal tissue growth, vascular incursion and nutrient supply. Furthermore, their morphology should be designed to guide the growth of new bone tissue in anatomically applicable ways. In this work, the mechanical performance and 3D X-ray microtomography (X-ray μCT) study of a biomimetic, organic-inorganic composite material, based on hydroxyapatite, with physicochemical, structural, morphological and mechanical properties very similar to those of natural bone tissue is reported. Ceramic pieces in different shapes and several porous sizes were produced using a Modified Gel Casting Method. Pieces with a controlled and 3D hierarchical interconnected porous structure were molded by adding polymethylmethacrylate microspheres. Subsequently, they were subject to a thermal treatment to remove polymers and to promote a sinterization of the ceramic particles, obtaining a HAp scaffold with controlled porosity. Then, two different organic phases were used to generate an organic-inorganic composite material, so gelatin and collagen, which was extracted from bovine tail, were used. The biomimetic organic-inorganic composite material was characterized by Scanning Electron Microscopy, Energy Dispersive X-ray Spectroscopy, X-ray Diffraction, Fourier Transform Infrared Spectroscopy and 3D X-ray microtomography techniques. Mechanical properties were characterized in compression tests, obtaining a dramatic and synergic increment in the mechanical properties due to the chemical and physical interactions between the two phases and to the open-cell cellular behavior of the final composite material; the maximum compressive strength obtained corresponds to about 3 times higher than that reported for natural cancellous bone. The pore size distribution obtained could be capable to allow cell penetration, internal tissue in-growth, vascular incursion and nutrient supply and this material has tremendous potential for use as a replacement of bone tissue or in the manufacture and molding of prosthesis with desired shapes.

1. Introduction

Hydroxyapatite (HAp) is widely utilized in medical fields due to its good biocompatibility, bioactivity, osteoconductivity, and/or osteoinductivity, noninflammatory behavior and nonimmunigenicity properties [1].

Porosity plays a decisive role for the behavior of biomaterials. A sufficient pore size and an interconnecting pore structure are required for osteoblast to grow into such a device. Also the porosity contributes to reduce final weight of the material [2,3].

The mechanical properties of an ideal bone scaffold should match host bone properties and proper load transfer.

The key factors for an ideal scaffold for bone tissue engineering are: (i) macro- (pore size > 100 μm) and micro-porosity (pore size < 20 μm); (ii) interconnected open porosity for in vivo tissue in-growth; (iii) sufficient mechanical strength and controlled degradation kinetics for proper load transfer to the adjacent host tissue, (iv) initial strength for safe handling during sterilizing, packaging, transportation to surgery, as well as survival through physical forces in vivo [4].

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http://dx.doi.org/10.1016/j.msec.2017.05.106
0928-4931/

Fig. 1. Hydroxyapatite objects molded in different sizes and shapes by the Modified GelCasting Process (scale in cm).

Since porous HAp is more reabsorbable and more osteoconductive than dense HAp, there is and increasing interest in the development of porous hydroxyapatite scaffolds as bone-replacement materials for the filling of both load-bearing and non-load-bearing osseous defects [5].

Porous HAp scaffold, due to its large surface area, simulates human bone structure for adhesion of biological tissue cell and growth of new bone phase [5].

The goal of recent biomaterials research is to accomplish an appropriate combination of chemical and physical properties to match those of the replaced tissue with a minimal foreign body response in the host [6].

Some studies have been reported on the use of HAp-collagen and HAp-gelatin [7,8]. In one of them, they report obtaining the composite material by 3D printing. This material showed a positive reaction for regeneration of bone tissue, both in vitro and in vivo tests [7]; however, they make no study on porosity or mechanical performance. In other work, the authors show a successfully osteointegration of a HAp foams coated with gelatin tested in rabbits, those foams were obtained by the sol-gel method with the aid of a surfactant for generating macropores and including gelatin [8]. However, despite the good results obtained, they did not conduct a study of the porosity or the mechanical properties of the material.

Gelcasting is a well-established colloidal processing method for making high quality, complex shaped ceramic parts by means of in situ solidifying through which a macromolecular network is created to hold the ceramic particles together. During gelcasting, the macromolecular gel network results from the in situ polymerization of organic monomers added in the suspensions to hold the ceramic particles together, and the strong particle gel can develop sufficient strength to support their own weight and thus can be handled without shape distortion [9].

In this work, the synthesis of a hydroxyapatite-based, organic-inorganic composite material, with controlled 3D hierarchical porosity and with physicochemical properties similar than those present in natural bone tissue, is reported along with their mechanical performance characterization and 3D X-ray microtomography studies to study the pore interconnection.

X-ray microtomography (X-ray μCT) is a technique introduced for the analysis of materials that allows obtain images of the inside of a sample in high resolution (micrometers) and high contrast, without destroying it, allowing to reconstruct the sample in a 3D digital object with a sub-micrometric resolution (up to 0.7 μm), which allows visualizing and handling the virtual solid within a computer. An X-ray beam passes through different materials depending on their densities, producing an image with high contrasts [10]. Numerous 2D slices are captured to reconstruct the object in 3D with the highest precision and detail, allowing the study and measurement of all its textural attributes, such as porosity or permeability, that are of great importance for research in many Materials science fields. This technique is used for geothermal and oilfield geology research; it is also useful in archeology, in electronics, in the study of ceramics, composites, metallic foams, etc. [10,11,12] In the present work, this technique was used to study the interconnected porosity of the composite material obtained, which is relevant to determine its possible application as biomaterial. Although other techniques exist for the study of porous materials, such as nitrogen adsorption-desorption isotherms (SBET), it was decided to use this technique due to the interest of visualizing the macro porosity of the samples without destroying them. The SBET technique is useful for analyzing porosities at micro and mesoscopic scales, but it is not suitable to analyze macropores such as those observed with X-ray μCT.

2. Materials and methods

2.1. Preparation of the composite material

Inorganic scaffolds were molded following the Modified GelCasting Process (MGCP) described in previous works [13,14] using synthetic hydroxyapatite powders [Aldrich] and Polyethylene glycol [Fluka], Polyvinyl butyral [Acros] and Polyacrylic acid [Fluka] as plasticizer, binder and dispersant, respectively. In this new modification of the process, PMMA

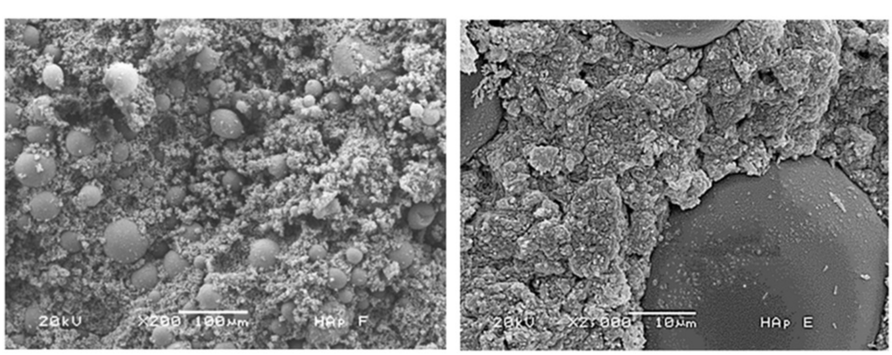

Fig. 2. SEM micrographs of HAp particles with the polymers used to mold the sample and the distribution of PMMA micro spheres.