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Design of Highly Porous Hydroxyapatite Scaffolds by Conversion of 3D Printed Gypsum Structures – a Comparison Study

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Abstract

Hydroxyapatite (HA) is a bioceramic material with excellent biological properties. However, these properties are strongly dependent of its crystallinity degree, with high values of crystallinity associated to poor resorption rates and bioactivity. This work evaluates the properties of HA samples produced by two different free-forming conformation methods, CNC machining and 3D printing. In both cases, porous gypsum samples were produced and subsequently converted into HA in a reaction with di-ammonium hydrogen phosphate at 100°C and pH 8. A total conversion of the samples was achieved after 36 h independently of the conformation method used. The microstructure, however, before and after the conversion is showed to be dependent on the method used. After conversion the machined samples achieved a maximum compressive strength of 3.5 MPaforporosities of circa 80%, while 3D printed samples achieved a tensile strength of 2.0 MPa by porosities of 61%.

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*Keywords:*Hydroxiapatite; gypsum; 3D printing; CNC machining

1. Introduction

The Araripe region is a mountain range located on the northeast region of Brazil. This region is the greatest producer of gypsite in Brazil and responsible for 89% of all gypsite extracted from the country [1]. The purity of the sources located on this region is of ca 98%. However a great part of this amount is sold without processing or only after basic processing. Such unprocessed material with high purity is sold for a less than US$ 20/ton. Great part of the industries located in this region works with very basic conditioning methods, such as calcination, which does not necessarily aggregate value to the raw material (ca US$ 200.00/ton). Alternatively, the raw material has been used in the production of blocks forcivil building (US$ 400/ton) [1].

In this context, the development of new products and processing routes which could increase the added value and improve the commercial potential of the high purity gypsum extracted from Araripe region is an important way to promote the economic and social development of the region.

Hydroxyapatite (HA) is a biomaterial widely used for the preparation of substitute bone implants. Among the properties of HA are noteworthy the bioactivity, the osseoinductionand the similarity with the inorganic phase of the human bone, especially in the form of carbonated HA[2]. Many works have evaluated the mechanical properties of HA in order to produce porous scaffolds with enough mechanical strength to support the loads that acts during the first hours and days of the healing process. Porous HA scaffolds are only recommended to non load bearing applications. However the presence of pores on the scaffolds enhance the cell fixation and the growth of living tissue and blood vessels into the implant creating a strong interface between bone and implant with consequent improvementof the bone regeneration [3].

The production porous HA scaffolds from high purity gypsum bodies shows an interesting method to produce

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HAscaffolds with low crystallinity, similar as in human body, where the HA is crystallized at 37°C. The temperatures used in the thermal-bath conversion are reported to be between 100 and 120°C without need for a subsequent heat treatment [4,5].

Additive manufacturing (AM) technologies allow the fabrication of scaffolds in shapesmatching the ones of the patient's bone defect, by a direct conversion of a digital data into a 3D model. Among available AM processes, the powder-bed 3D-Printing operates with the successive addition of powdery material, layer-upon-layer, to form the final 3D model. The process allows, in this way, a better control of pore sizes, pore morphology and porosity of the matrix, if compared with other fabrication methods[6,7,8]. Studies have proved that layer thickness and binder saturation have a significant effect on the strength, integrity, and dimensional accuracy of 3D printed samples [9]. Recently, structures similar to the actual trabecular bone structure have been produced via 3D printing and characterized [10,11].

The aim of this work is a comparison of two different methods to produce form free scaffolds by conversion of high purity gypsum into HA. The bodies were produced via machining of gypsum blocs using a CNC device and via 3D printing of porous bodies from gypsum powder. After forming, the bodies were converted into HA. The structural and mechanical properties of the samples have been evaluated and compared before and after conversion into HA.

2. Materials and Methods

2.1. Preparation of Gypsum Structures by CNC machining

B-Gypsum (calcium sulfate hemihydrate, $CaSO_4 \cdot 0.5H_2O$,95% of purity, Gesso Mineral AG) and PVA (99% hydrolyzed, Sigma-Aldrich, USA) have been mixed using different proportions of polymer (0, 1, 5, 10 and 15wt.%). Gypsum/PVA slurrieshave been prepared using water/solid masse ratio of 0.7. Porous bodies were prepared by casting of the slurry in molds. Gypsum/PVA bodies were machined in a CNC lathe (Nardini, MS.220.G F2 KJL 919) using Solid Works based CAD models. After machining the gypsum/PVA bodies were immersed in water for approximately 2 hours, at a temperature of 90°C, in order to extract the polymer from the ceramic bodies.

2.2. Production of 3D printed gypsum structures

Gypsum hemihydrate powder with an average particle size of 10 µm was produced via calcination of high purity gypsite rocks at 180°C for 4 hours. The gypsite was provided from Araripe region located in Brazil.After calcination,the powder presented a Hausner ratio of1.65, indicative of poor flowability. The powder has been printed in a PrometalR1 (ExOne, USA), operating with a vacuum device for stabilization of the power bed [12]. Double distilled water containing 1 vol-% binder (Aqueous-Based Binder, ExOne, USA) was used to regulate the surface stress of the water particles during the printing process. After printing the samples were cleaned and subsequently immersed in water to ensure a complete dihydrate formation.

2.3. Conversion of gypsum into HA

The structures were submersed in 200 mL of $(NH_4)_2HPO_4$0.5 $mol.L^{-1}$ solution in a three-neck flask at a temperature of 100°C for 36 hours. The pH of the medium was controlled by adding NH_4OH 6.0 $mol.L^{-1}$ solution. At the end of the reaction time, the blocks were washed in de-ionized water until reaching neutral pH and then dried in an oven at 50°C for approximately 4 hours.

2.4. Characterization

The samples before and after conversion were characterized by X-ray diffraction (XRD) (Diffract ACT series 1000 SIEMENS, radiation Cu-Kα) and Scanning Electron Microscopy (SEM) ZEISS Gemini Supra 40 equipped with a EDS Bruker Quantax 400. Compressive strength of the machined samples (σ_c) were carried out using a Universal Mechanical Testing Machine (EMIC-DL 10000) in cylindrical samples of ø 11 mm x 22 mm. Mechanical strength of 3D printed samples was carried out in a universal mechanical test machine (Z005, Zwick/Roell) using the four spheres method.

3. Results

3.1. Machined gypsum bodies and conversion into HA

Fig. 1A shows the fracture surface of a gypsum structure without addition of binder. The microstructure consists of crystals in prismatic needle shape. The EDS analysis confirmed the high purity of the gypsum where only Ca and S peaks were observed.

The addition of PVA promoted a homogeneous distribution of the polymer resulting in a reinforcement of the samples, followed by a slight change in the size and form of the crystals. Due to the hydrophilic nature of PVA a larger interaction between the polymer and the hydration water was promoted. Consequently the crystals show better adherence to the PVA grains, causing greater interaction between crystals and polymer particles [1]. Macroscopically, the addition of PVA promoted an increase in the mechanical properties and the machining of the samples became possible. A minimum addition of 15%-masse PVA was necessary to permit the machining of the samples. Before the conversion into HA the amount of PVA was removed to prevent a negative interference of the PVA on the conversion process.

Fig. 1B shows the fracture surface of the samples after conversion HA for 36 hours. A great change on the morphology can be observed on the surface of the samples, in comparison to the gypsum morphology showed in Fig 1A. After conversion the surface presents particles of circular shape and a high porosity can be observed. The EDS analysis obtained for this sample confirmed the presence of the chemical elements Ca and P, which are characteristic for HA.