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Manufacturing of calcium phosphate scaffolds by pseudomorphic transformation of gypsum

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ABSTRACT

Carbonated hydroxyapatite (CHAp) and β-tricalcium phosphate (β-TCP) have been employed for decades as constituents of scaffolds for bone regeneration because they chemically resemble bone mineral. In this study, the feasibility to manufacture CHAp/β-TCP scaffolds by pseudomorphic transformation of casted blocks of gypsum was investigated.

The transformation was carried out by immersing the precursor gypsum block in 1 M $(NH_4)_2HPO_4$/1.33 M NH_4OH solution with liquid/solid ratio of 10 mL/g and autoclaving at 120 °C and 203 kPa (2 atm) for 3 h at least. Neither shape nor dimensions significantly changed during transformation. The composition of scaffolds treated for 3 h was 70 wt.% CHAp and 30 wt.% β-TCP, and their compressive and diametral compressive strengths were 6.5 ± 0.7 and 5.3 ± 0.7 MPa, respectively. By increasing the time of treatment to 6 h, the composition of the scaffold enriched in β-TCP (60 wt.% CHAp and 40 wt.% β-TCP) but its compressive and diametral compressive strengths were not significantly affected (6.7 ± 0.9 and 5.4 ± 0.6 MPa, respectively).

On the basis of the results obtained, it was concluded that this route is a good approach to the manufacturing of biphasic (CHAp/β-TCP) scaffolds from previously shaped pieces of gypsum.

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Fabricación de andamios de fosfato de calcio mediante transformación pseudomórfica del yeso

Palabras clave:
Hidroxiapatita carbonatada
β-Fosfato tricálcico
Yeso
Pseudomorfismo
Implante óseo

RESUMEN

La hidroxiapatita carbonatada (CHAp) y el β-fosfato tricálcico (β-TCP) han sido utilizados durante décadas como constituyentes de los andamios para regeneración ósea, debido a su semejanza química con la sustancia mineral del hueso. En este trabajo se investigó la viabilidad de fabricación de andamios de CHAp/β-TCP mediante transformación pseudomórfica de bloques de yeso previamente moldeados. La transformación se realizó sumergiendo el bloque precursor de yeso en una disolución 1 M $(NH_4)_2HPO_4$/1,33 M NH_4OH en proporción líquido/sólido de 10 mL/g, y autoclavando a 120 °C y 203 kPa (2 atm) durante al menos 3 h. Ni la forma ni las dimensiones de la pieza cambiaron significativamente durante la transformación. La composición de los andamios obtenidos con 3 h de tratamiento fue 70% m/m CHAp y 30% m/m β-TCP, y sus resistencias a la compresión y a la compresión diametral fueron de 6,5 ± 0,7 y 5,3 ± 0,7 MPa, respectivamente. Incrementando el tiempo de tratamiento a 6 h, la composición del andamio se enriqueció en β-TCP (60% m/m CHAp y 40% m/m β-TCP), pero su resistencia no varió significativamente (resistencia a la compresión 6,7 ± 0,9 MPa y resistencia a la compresión diametral 5,4 ± 0,6 MPa). Sobre la base de los resultados obtenidos se concluyó que esta ruta resulta adecuada para la fabricación de andamios bifásicos a partir de piezas de yeso previamente moldeadas.

Introduction

Modern approach to bone regeneration is based on the use of scaffolds and osteoinductive factors. Scaffolds are temporary tridimensional and macroporous structures made of biocompatible and resorbable materials which are intended to attract and support the colonization of mesenchymal stem cells and their differentiation into osteoproductive cells. Ideally, the scaffold resorption rate should match the rate of new bone growth [1].

The use of additive manufacturing (AM) processes for the fabrication of 3D scaffolds for bone regeneration has received great attention in the last decade [2]. Among the several AM techniques available 3D-Printing (3-DP) on powder layer is particularly interesting because of its simplicity and low cost [3].

Some of the available commercial systems employ a powder mainly consisting in Plaster of Paris ($CaSO_4{\cdot}(1/2)H_2O$, CSH) and an aqueous binder ink. During printing, the setting of powder takes place according to the hydration reaction of Eq. (1) and, after removing unreacted powder; solid pieces made of gypsum ($CaSO_4{\cdot}2H_2O$, CSD) are obtained.

$$CaSO_4 \cdot \frac{1}{2}H_2O_{(s)} + 1\frac{1}{2}H_2O \rightarrow CaSO_4 \cdot 2H_2O_{(s)} \quad (1)$$

CSD was the first ceramic material used for bone repairing. It was successfully employed by Dreesmann [4] in 1892 for filling bone cavities of different etiologies (tuberculosis, osteomyelitis, enchondroma) in 8 patients. Seventy years later Peltier demonstrated that CSD implants in dogs were biocompatible and totally resorbed within a few weeks to a few months, but they failed to stimulate osteogenesis [5]. Nevertheless, CSD has been clinically used to date to fill bone defects, alone or in combinations with osteoinductive factors or antibiotics, because of its low cost, availability, easy handling, injectability and moldability [6].

The *in vivo* resorption rate of CSD is considerably higher than the rate of growth of new bone. This is the main concern for using CSD scaffolds for bone regeneration procedures in clinics, especially when large defects are involved. Instead, materials with lower resorption rates, such as the less soluble apatite-like calcium phosphates, are generally preferred for manufacturing scaffolds for bone engineering [7–14].

Pseudomorphing is the phenomenon by which one mineral is replaced by another while preserving the macroscopic shape, but changing the chemical composition and microstructure. It occurs in nature as consequence of weathering during millions of years [15]. At the beginning of the seventies, coral ($CaCO_3$, calcite) was pseudomorphically transformed into HAp by hydrothermal reaction with aqueous $(NH_4)_2HPO_4$ at 180–350 °C and 103 MPa for 12–48 h [16]. Since then, a lot of coralline HAp-based materials became commercially available and has been successfully applied for bone regeneration procedures in clinics.

More recently, the pseudomorphical transformation of CSD monoliths into HAp by treatment in alkaline phosphate solutions have been reported [17–22]. According to the published results, previous dehydration of CSD to CSH is required in order to strengthen the scaffold and to speed off the hydrothermal reaction. Minor amounts of more acidic calcium phosphates ($CaHPO_4{\cdot}2H_2O$, DCPD or $CaHPO_4$, DCP) were formed along with HAp.

The purpose of this study was to investigate the manufacturing of calcium phosphate scaffolds by direct hydrothermal transformation of CSD monoliths, without previous