BOLETIN DE LA SOCIEDAD ESPAÑOLA DE
Cerámica y Vidrio
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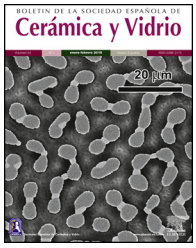

Different *in vitro* behavior of two $Ca_3(PO_4)_2$ based biomaterials, a glass-ceramic and a ceramic, having the same chemical composition

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ARTICLE INFO

Article history:
Received 26 August 2015
Accepted 5 October 2015
Available online 11 October 2015

Keywords:
Simulated body fluid
Tris–HCl
Tricalcium phosphate
Wollastonite
Bioceramics

ABSTRACT

In this work, the influence of the nature of two materials, with the same chemical composition, on their *in vitro* behavior has been studied. Two routes were used to obtain these materials with the composition 45% CaO, 22% SiO_2, 28% P_2O_5 and 5% MgO (wt.%). The first material is a glass-ceramic obtained by melting and quenching on cold water and the second one is a ceramic obtained by conventional solid state sintering. In both cases, the raw materials used were tricalcium phosphate, talc and wollastonite.

The reactivity in simulated body fluid and Tris–HCl solutions was studied. Both materials showed bioactive behavior, but the glass-ceramic dissolved faster, releasing large proportion of Ca and P ions, which afterwards nucleated and precipitated. However, the ceramic was more stable under the same conditions in these solutions. Glass-ceramic composite has a more open structure and allowed the faster formation of a bone-like apatite layer than the ceramic.

Diferencias en el comportamiento *in vitro* entre 2 biomateriales basados en $Ca_3(PO_4)_2$, un vitrocerámico y una cerámica, con la misma composición química

Palabras clave:
Suero fisiológico simulado
Tris-HCl
Fosfato tricálcico
Wollastonita
Biocerámicas

RESUMEN

En este trabajo se estudia la influencia de la naturaleza de 2 materiales con la misma composición química en su comportamiento *in vitro*. Se han empleado 2 métodos para obtener estos materiales con una composición del 45% de CaO, 22% de SiO_2, 28% de P_2O_5 y 5% de MgO en peso. El primer material, un vitrocerámico, se obtuvo mediante fusión y colado sobre agua fría. El segundo, una cerámica, se consiguió mediante sinterización convencional en estado sólido. En ambos casos las materias primas fueron fosfato tricálcico, talco y wollastonita.

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http://dx.doi.org/10.1016/j.bsecv.2015.10.001

Se estudió la reactividad frente a suero fisiológico simulado y solución Tris-HCl. Ambos materiales han mostrado comportamiento bioactivo pero el vitrocerámico evidencia una reactividad más alta, liberando cantidades mayores de iones Ca y P, los que posteriormente nuclean y precipitan. La muestra cerámica tiene un comportamiento más estable bajo las mismas condiciones en estas soluciones. El material vitrocerámico tiene una estructura más abierta y conduce a la formación más rápida de una capa de hidroxiapatita.

Introduction

The materials, which are used to replace or supplement the functions of living tissues, are known as biomaterials. Ceramics, glasses and glass-ceramics have succeeded for several decades for bone repairing applications [1–4]. They are capable to bond tightly to bone but they are not fully replaced by new bone. The first bioactive biomaterial was developed by Hench et al. in 1969 [5]. It consists of a silicate glass incorporating sodium, calcium and phosphorous ions, known as Bioglass®. In their studies, Hench et al. [6] showed that Bioglass® forms a calcium phosphate layer on its surface and through that layer joins to living bone. They found that the calcium phosphate layer on the glass can be formed in solutions buffered to pH 7.4 Tris (hydroxymethyl) aminomethane and hydrochloric acid (Tris–HCl buffer solution). Hench et al. [7] showed that some glass was adhered to living bone spontaneously, without formation of fibrous tissue at the surface. They found that in glasses of calcium phosphates, a layer can be formed *in vitro* in buffered solutions. Since then, it has been found that various ceramic materials, such as hydroxyapatite, β-tricalcium phosphate sintered, apatite-wollastonite glass-ceramic [8], join to living bone.

In the first years of study of biomaterials, bioactivity was determined by *in vivo* animal tests. In 2006, Kokubo et al. [9] showed that the *in vivo* bone bioactivity of a material can be predicted from the apatite formation onto surface in simulated body fluid solution (SBF which is close to human plasma). Thus, when new materials are obtained, bioactivity is checked through *in vitro*, prior to use *in vivo*.

The bioactive behavior of glasses and ceramic is identified as their ability to react chemically with living tissues, forming with them mechanically strong bonds. These bone bondings are attributed to the formation of an apatite-like layer on the glass surface, with composition and structure equivalent to the mineral phase of bone.

A lot of different materials have been developed and, in order to evaluate their goodness, compared with Bioglass® [6,7,9–11].

Material biodegradation does not depend exclusively on its physical and chemical properties but also on biological mechanisms. However, dissolution rate significantly affects the behavior of the material *in vivo*. If the material has an appropriate degree of solubility, resorption will take place, i.e., cells interact with the material and leading the process of bone regeneration.

The purpose of this paper is to explore the influence of the material structure (fully crystalline or glass-ceramic) on the bioactive behavior. For this, two materials were prepared with the same chemical composition within SiO_2-P_2O_5-CaO-MgO quaternary system. *In vitro* studies were evaluated on two kinds of solutions, simulated body fluid (SBF) and Tris–HCl pH 7.4. The specimens were characterized by X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). The solutions were examined for changes in the concentration of Ca, Mg, Si and P ions using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

Experimental

In the present work, a glass-ceramic (G-TCP60) and a ceramic (C-TCP60) with the same chemical composition, corresponding to 61 wt.% $Ca_3(PO_4)_2$ (Tricalcium Phosphate: TCP in short), 24 wt.% $CaSiO_3$ (Wollastonite: W in short) and 15 wt.% $3MgO{\cdot}4SiO_2$ (Talc: T in short), were selected in the $Ca_3(PO_4)_2$–$CaSiO_3$–$3MgO{\cdot}4SiO_2$ (TCP-W-T) pseudo-ternary system.

The starting materials were a high-purity synthetic precursor of $Ca_3(PO_4)_2$ from Carlo Erba Reagents, a reagent-grade high-purity Hydrous magnesium silicate, Talc, $3MgO\ 4SiO_2{\cdot}H_2O$, from Sigma–Aldrich, and a high-purity natural Wollastonite, $CaSiO_3$, NYAD® 1250 from NYCO®.

Glass-ceramic powders were obtained by melting stoichiometric mixtures of the raw materials. The powder mixture was melted in an electric furnace for 2 h in a Pt crucible at 1500 °C. The molten glass was poured in water to obtain a frit (G-TCP60). Volumetric specimens of the glass-ceramics were selected for SBF studies and powder samples were used to test the biodegradability in Tris–HCl.

Polycrystalline bioceramic powder samples were obtained by conventional solid state sintering route. Raw materials were mixed by attrition milling in ethanol for 1 h and the powder was sieved to obtain a powder smaller than 100 μm. Disks of 10 mm in diameter and 5 mm in height were uniaxial pressed (1000 kg/cm^2) and sintered at 1050 °C for 2 h. These pieces were ground with tungsten carbide mortar and sieved to a size between 45 and 100 μm. Ceramic powders obtained were used to test biodegradability in Tris–HCl. On the other