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Fluoride-containing bioactive glasses: Surface reactivity in simulated body fluids solutions

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Abstract

The issue of the contribution of the addition of F to glass bioactivity is not well resolved. This work reports on the surface reactivity in different solutions (DMEM and Tris) for some potentially bioactive glasses based on the composition of 45S5 glass, in which CaF_2 is substituted alternately for (part of) CaO and Na_2O. The reactivity of F-containing glasses has been compared with that of the reference 45S5 system. The aim of this study is to explain in detail the mechanism of formation of an apatitic crystalline phase at the interface between the inorganic material and simulated biological media. A multi-technique investigation approach proposes a set of reactions involving Ca-carbonate formation, which are somewhat different from that formerly proposed by Hench for 45S5 bioactive glass, and which occur when a F-containing glass surface is in contact with a SBF. The usefulness of IR spectroscopy in recognizing the starting step of apatite (and/or FA) formation with respect to XRD technique is well established here.
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1. Introduction

Some soda–lime–phosphosilicate glasses, such as Hench's Bioglass® 45S5, form bone-like apatite on their surface when in contact with the living body, and bond to living bone through this apatite layer [1]. This bone-bonding ability is called bioactivity. The mechanism proposed by Hench [2] for the bonding to bone of a bioactive glass is based on a long series of reactions occurring at the interface between the solid and the biological medium, which are supposed to lead, step by step, to the integration of the glass within the living system. The proposed process starts with an intense ion exchange between the solid and the contacting body fluid, and continues with the formation of a silica gel surface layer. On this silica layer, an amorphous Ca-phosphate phase is precipitated, which evolves with time in hydroxyapatite (HA) and/or hydroxy–carbonate–apatite (HCA) crystalline phases. This early set of step-like reactions is purely inorganic in nature, and occurs on a molecular nanometric scale.

Bioactive glasses of this kind are usually employed for coating either metallic prostheses or granules for bone defect repair. In particular, in granules, for which the surface/volume ratio is high, the degree of surface reactivity plays a determinant role. In fact, if the reactivity is high, most of the granules may quickly disappear, with no possibility of achieving the desired bone defect repair.

The degree of reactivity exhibited in the biological environment is related to the chemical composition of glasses. For instance, the addition of fluorides (CaF_2) to soda–lime–phosphosilicate bioactive glasses decreases the chemical reactivity, because F ions have been thought to act as a corrosion inhibitor and to promote the formation of a thin surface gel layer with a high silica concentration [3]. The same effect on chemical reactivity is observed by substituting CaF_2 for Na_2O in Bioglass 45S5, while the reverse effect is detected when CaF_2 is substituted for CaO. These

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different effects are explained by molecular dynamics simulation of glass structure. The replacement of Na_2O by CaF_2 reinforces the glass network because of the formation of Si–O–Ca–O–Si groups: the replacement of CaO by CaF_2 weakens the glass network because nano-aggregates of the Na^+F^- pair are formed beside those of $Ca^{2+}F^-$ [4,5] Moreover, *in vivo* study on short-term bone implants of a fluorinated glass showed that the silica gel layer formed is not as homogeneous as that formed on a similar F-free 45S5 glass, although the absence of a continuous Si-rich layer does not seem to affect the capability of the glass surface to become covered with a crystalline HA/HCA phase [6]. Ebisawa et al. [7] studied the compositional dependence of the bioactivity of glasses based on the binary system $CaO–SiO_2$ modified by Na_2O, MgO, B_2O_3, Fe_2O_3, P_2O_5 and CaF_2. The results obtained with CaF_2-modified glass showed that the velocity of HA formation in SBF decreased compared with the other systems (except for the Fe_2O_3-modified one), and that the silica gel layer is either small or not observed. And this behaviour was explained on the basis of lower Ca ion release from the F-containing glasses.

In contrast, other studies showed that the addition of fluorides to glasses used to produce glass ionomer cements disrupts the glass network, facilitating glass degradation and, in particular, the release of fluoride, which inhibits the formation of cavities in the mouth [8,9]. On the basis of these results, the contribution of F-addition to the bioactivity of bioactive glasses seems poorly resolved and, in particular, it may be possible that the mechanisms of HA and/or HCA phase formation are affected by the presence of fluoride.

The present paper is dedicated to the experimental detection of the physico-chemical behaviour of some potentially bioactive glasses towards different simulated biological media, based on the composition of 45S5 bioactive glass, in which CaF_2 is substituted alternately for (part of) CaO and Na_2O, so as to produce two series of F glasses: one with a constant Na/Ca ratio, and another with a decremental Na/Ca ratio as a function of F content.

The study aims to explain in some detail the degree of reactivity of the glasses immersed in the biological environment on the basis of the different compositions, in order to indicate the mechanism and the rapidity of formation of a HA and/or HCA crystalline phase at the interface between the inorganic material and the simulated biological medium.

2. Experimental

2.1. Synthesis

Two series of F-containing glasses, based on the molar composition of Bioglass® 45S5 ($46.2SiO_2–24.3Na_2O–26.9CaO–2.6P_2O_5$; hereafter referred to as H-glass), were synthesized. In the first series, termed $HNaCaF_2$, CaF_2 replaces Na_2O, and the general compositional formula is: $46.2SiO_2–(24.3-x)Na_2O–26.9CaO–2.6P_2O_5–xCaF_2$ (where $x = (0), 5, 10, 15$). The second series, in which CaF_2 replaces CaO, is named $HCaCaF_2$, and its general compositional formula is: $46.2SiO_2–24.3Na_2O–(26.9-x)CaO–2.6P_2O_5–xCaF_2$ (where $x = (0), 5, 10, 15$). The glasses' synthesis procedures were reported in detail in a previous work [4].

For characterization purposes, the solid samples were ground in agate mill jars and sieved, in order to produce and isolate particles <26 μm in size. The powders obtained were first analysed, in order to verify the expected (theoretical) glass composition because, during the fusion process, P and F compounds could be partly volatilized. Compositional data, reported in previous work [4], showed that the deviation is ±0.2 mol.% (as oxide) for each constituent. Particles size distributions were determined using a laser granulometer (Fritsch, model Analysette 22).

The analysis showed that all the starting glassy powders presented a particle size distribution where 90 vol.% of the powder had a dimension <26 μm (see Fig. 1a), and the maximum was ~20 μm. It is interesting to note the presence of a maximum of some 5 vol.% of fine particles (<5 μm; Fig. 1b) and that the analysis confirmed that all the starting samples presented a very similar particle size distribution. (For the sake of clarity, data relative to 5%, 10% $HCaCaF_2$ and 5%, 10% $HNaNaF_2$ are not shown in Fig. 1.) The measurements of particles distribution were performed in triplicate, and data are presented as a mean ($\sigma_{Freq.Dist.} = 0.1\%$).

2.2. SBF

Of the various buffered simulated body fluids solutions (SBF) that are currently adopted to test *in vitro* the reactivity of bioactive materials, the following two were used in the present study: Dulbecco's modified Eagle's medium (DMEM) and tris(hydroxymethyl)aminomethane solution (Tris).

2.2.1. DMEM solution

DMEM (Sigma–Aldrich) contains inorganic ions (like those present in simulated body fluids (SBF) solutions, and mimicking the inorganic ion composition of human plasma, the main difference between SBF and DMEM being the HCO_3^- concentration, which is 4.2 and 44.0 mM, respectively) [10] as well as amino acids, vitamins, glucose, L-glutamine and Na pyruvate. The use of this complex solution, mimicking the cells' environment, allows the reactivity usually tested with SBF solutions and all side reactivity effects that may be possibly produced during cellular tests to be monitored at the same time. The pH is set to 7.4.

2.2.2. Tris buffer solution

Tris buffer solution, i.e., solution of tris(hydroxymethyl)aminomethane, used mainly for comparison purposes in (some) experiments, is a suitable reference

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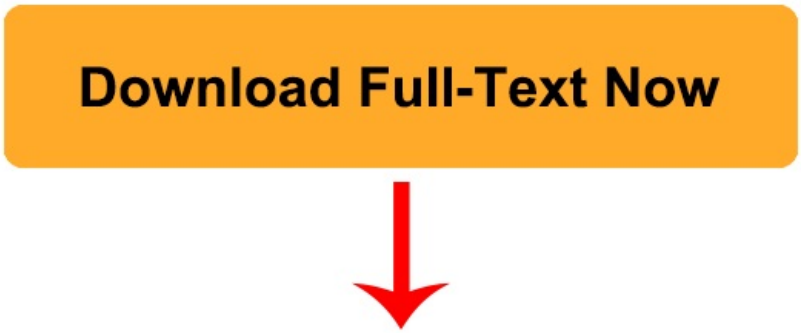

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