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Synthesis, characterization and bioactivity of a calcium-phosphate glass-ceramics obtained by the sol-gel processing method

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ABSTRACT

In this work, a calcium-phosphate glass-ceramics was successfully obtained by heat treatment of a mixture of 26.52 in wt.% of fluorapatite (Fap) and 73.48 in wt.% of 77S (77 SiO_2—14 CaO—9 P_2O_5 in wt.%) gel. The calcium phosphate-glass-ceramics was prepared by sol-gel process with tetraethyl orthosilicate (TEOS), triethyl phosphate (TEP), calcium nitrate and fluorapatite. The synthesized powders were characterized by some commonly used tools such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), ^{31}P magic angle spinning nuclear magnetic resonance (MAS-NMR), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and thin-film X-ray diffraction (TF-XRD). The obtained results seemed to confirm the nucleation and growth of hydroxyapatite (Hap) nano-phase in the glass. Moreover, an in-vitro evaluation of the glass-ceramic was performed. In addition, to assess its bioactive capacity, it was soaked in simulated body fluid (SBF) at different time intervals. The SEM, EDS and TF-XRD analyses showed the deposition of hydroxyapatite on the surface of the specimens after three days of immersion in SBF solution. The mechanical properties of the obtained material such as rupture strength, Vickers hardness and elastic modulus were measured. In addition, the friction coefficient of calcium phosphate-glass-ceramics was tested. The values of the composite of rupture strength (24 MPa), Vickers hardness (214 Hv), Young's modulus (52.3 GPa), shear modulus (19 GPa) and friction coefficient (0.327) were obtained. This glass-ceramics can have useful applications in dental prostheses. Indeed, this material may have promising applications for implants because of its content of fluorine, the effective protector against dental caries.

1. Introduction

Different processing methods could be used to produce glass: the sol-gel process and the melt-quenching process. The sol-gel process basically forms a three dimensional system of silica nanoparticles at room temperature [1]. Contrary to the melt-quenching glasses, the glasses derived from sol-gel process have an inherent nanoporosity while melt-quenched glasses are dense [2]. The resulted nanoporosity intensifies the solubility of the glass, which is in favor of the bioactivity. In addition, the sol-gel process has a great flexibility at room temperature. Bioactive glasses can be manufactured as: nanoporous powders, monoliths and nanoparticles [3]. Bioactive glasses and bioceramics were used as biomaterials for regeneration of bone defect in dental, orthopaedic and maxillofacial applications [4–8].

Some in vivo studies had shown the additional advantage of bioactive glasses in bonding with bone more rapidly than other bioceramics [9–13]. Therefore, their osteogenic properties, proved by in-vitro studies, resulted from their dissolution products exciting osteoprogenitor cells at the genetic level [14].

Among bioceramics, hydroxyapatite (Hap) and fluorapatite (Fap) were well chosen for biomedical purposes and scaffold construction in bone and teeth [15–17]. Because of the high biocompatibility and the similarity between the chemical composition of the synthesized Hap and the natural bone, Hap was considered as an excellent bone implant material [16,18].

Similarly, synthetic Fap was presented as an analogous material to Hap [19,20]. Even better, Driessens proved that this material is much more stable in acidic environments compared to Hap [21]. However, there is still a gap in materials design related to the invention of a bioactive glass that would encompass the advantages of both Hap and Fap. In addition, this works tried to adapt the sol-gel process in order to obtain a better homogeneity of the new material.

The purpose of this study was to elaborate a calcium-phosphate glass-ceramics with a new composition via the sol-gel method. The idea was to create ceramic coasters interpenetrating networks where hydroxyapatite and fluorapatite were dispersed homogeneously in the glass matrix. This homogenization was guaranteed by the germination and growth of a Hap nano-phase in the Fap-glass matrix that underwent

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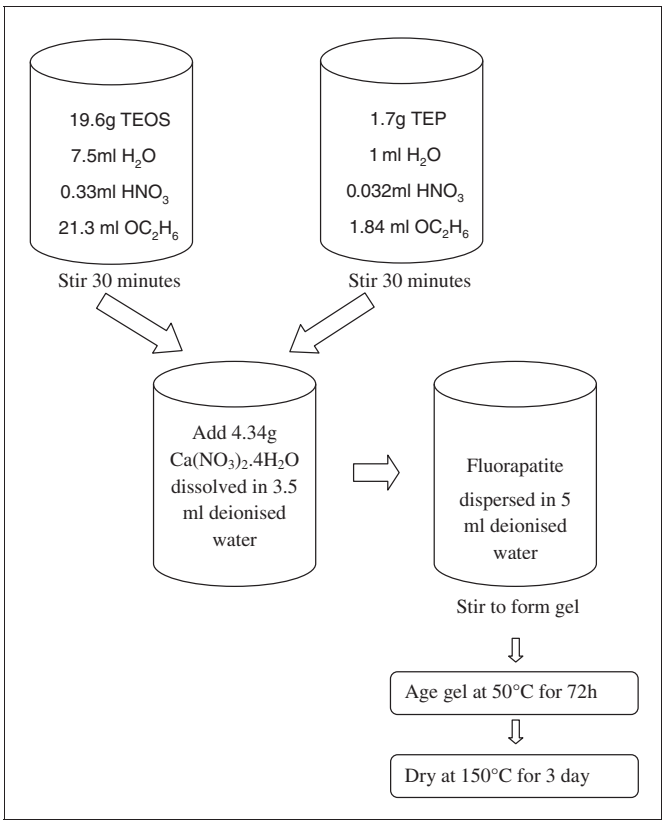

Fig. 1. Steps of the gel and composite synthesis.

an appropriate heat treatment. The bioactivity of the material was subsequently studied with an in-vitro test.

2. Materials and methods

2.1. Preparation of the gels

The synthesis of the samples of the 77S gel was established according to the nominal compositions of 77, 14, 9 wt.% of SiO_2, CaO, P_2O_5, respectively. The preparation of the gels involved hydrolysis and polycondensation reactions of stoichiometric amounts of tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$; Sigma-Aldrich, pureness ≥ 99,8%), triethyl phosphate (TEP, $OP(OC_2H_5)_3$; Sigma-Aldrich, pureness ≥ 99%), calcium nitrate ($Ca(NO_3)_2$, 4 H_2O; Sigma-Aldrich, pureness ≥ 99%) and Fap powder synthesized by the precipitation method as described by Brenzy and Green [22] and as given by the desired nominal composition stated above [23]. Fig. 1 shows the schematic flowchart of the synthesis procedure and outlines the procedures established for particulate gel preparations, which were later characterized and then subjected to thermal treatments to obtain the bioactive glasses and glass–ceramics. After the completion of the drying step, the gels and the Fap-gels were crushed manually in an agate mortar.

The powders were selected according to particle size (<100 μm) and reformed into pellets measuring 10 mm in diameter and 2.5 mm in thickness and pressed under 100 MPa.

Table 1
Initial compositions of biogels and Fap-biogels.

Samples	Fap (wt.%)	Gel (wt.%)	T (°C)[a]
GN	0	100	–
GN6	0	100	600
GN9	0	100	900
CN	26.52	73.48	–
CN6	26.52	73.48	600
CN9	26.52	73.48	900
CN12	26.52	73.48	1200

[a] Heat treatment temperature.

2.2. Conversion of the gels into glasses and glass–ceramics

The heat treatment of the gel and the composite Fap-gel were conducted in an electric oven (LabTech LEF-105P-1) at 600, 900 and 1200 °C for 3 h.

2.3. Characterization of the materials

2.3.1. X-ray diffraction (XRD) and thin-film X-ray diffraction (TF-XRD)

The X-ray diffraction (XRD) analysis was performed to analyze the glassy materials and crystalline phases that resulted from the heat treatments of the gels. The components phase of the sintered samples were identified by X-ray diffraction with Cu-Kα radiation (λ = 1.5406 Å) (XPERT-PRO powder diffractometer) and Co-Kα (λ = 1.7889 Å) (Bruker AXS D8 Focus). The diffraction patterns were obtained in the 2θ range from 5° to 65° in a continuous scan mode. The identification phase was conducted by comparing the experimental XRD patterns with the standard files compiled by the International Center for Diffraction Data (ICDD).

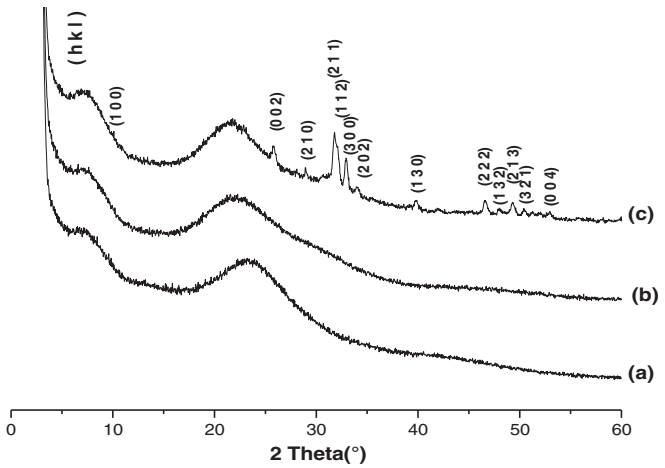

Fig. 2. XRD diagrams of GN (a), GN6 (b) and GN9 (c) (λ = 1.5406 Å).

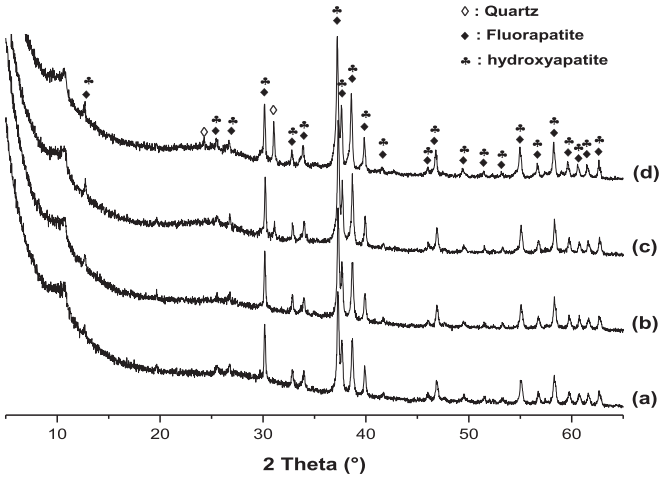

Fig. 3. XRD diagrams of CN (a), CN6 (b), CN9 (c) and CN12 (d) (λ = 1.7889 Å).