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EVALUATION OF THE BIOACTIVITY BEHAVIOR OF A 48 WT %SiO_2 BIOGLASS THROUGH EXPERIMENTS IN SIMULATED BODY FLUID

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Abstract. Among bioceramics materials, bioglasses which exhibits either a bioactive or resorbable behavior has been studied for many applications, such as bone substitutive and regeneration. When in contact with body fluid, the bioglasses can induce the formation of a hydroxyapatite surface layer. In this paper, we studied the bioactivity of a bioglass containing 48 wt %SiO_2, 27 wt% Na_2O, 19 wt % CaO and 6 wt %P_2O_5. After fusion and annealing, the samples were immersed in SBF for different periods, up to 14 days. The samples were characterized through XRD, DRIFT and SEM before and after bioactivity experiments. The overall results suggest the formation of a surface layer of consisting of hydroxyapatite, which was crystallized within seven days after in vitro experiments, leading to a suitable bioactivity. Moreover, the samples showed a glass network with high cohesion due to calcium addition, leading to materials with high corrosion resistance.

Introduction

In general, bioceramics can be used as reconstructive materials in order to repair a damaged part of living body or tissue. When implanted in biological enrironment, can present three distinct behaviors: inert; bioactive; bioresorbable.

The inert bioceramics do not show a superficial interaction layer on the surrounding tissues. However, they presented a good compatibility. Among the bioactive bioceramics, bioglasses and hydroxyapatite deserve particular attention. Bioglasses with a bioactive behavior are considered to cause specific physiological responses, since includes surface with silica, calcium and phosphate groups and an alkaline pH on the tissue/biomaterial interface. Bioglasses can be prepared containing different compositions of silica, and oxides of sodium, calcium and phosphorous. The commercial Bioglass® 45S5, firstly developed by Hench et al., has 45 wt% SiO_2, 24,5 wt% Na_2O, 24,4 wt% CaO and 6 wt% P_2O_5 and was the pioneer in biological studies [1,2,3].

In addition, according to Hench, a resorbable bioceramic develop the complete repair process of tissues, providing the damaged tissue with the same function as the new one. This is possible by a complete restoring of the tissue, specially bone, concerning not only functions, but also metabolic activities and biomechanical performance. These ceramics have controlled chemical decomposition, and are completely resorbable by living body. This fact helps to reduce the interface problems that are presented in many biomaterials [1,4].

The bioactivity of bioglasses is triggered when in contact with body fluid. Kokubo et. al. [5] developed a solution that simulated the body fluid compounds, so called SBF (Simulated Body Fluid). This solution contains inorganic ions in concentration similar as observed into human body. In their studies, Kokubo have described five stages of crystalline hydroxyapatite formation on bioglasses surface, after the immersion in SBF. In the first stage, sodium and calcium ions of the surface structure of bioglasses are exchanged with H^+ íons present in solution, forming a layer consisting of silanol groups; in the second stage, occurs the release of soluble silica [$Si(OH)_4$] of the bioglasses surface; in the third stage, occurs the condensation of the silanol groups forming a silanol-gel layer which is rich in calcium and sodium; in the fourth, due constant exchange and release of calcium and phosphorus ions of bioglasses, it is observed the saturation of these ions in SBF solution, causing the precipitation of these ions on bioglass surface, and, thus, forming an

amorphous calcium phosphate film; finally, in the last stage, crystallization of the amorphous calcium phosphate film and incorporation of hydroxyl and carbonate ions present in solution are observed, with the subsequently formation of crystalline hydroxyapatite [5].

Ogino et al. [6] have studied the influence of the silica amount on bioglasses composition, and, subsequently, on the formation of the hydroxyapatite surface. They concluded that, after in vitro tests, compositions with silica amount lower than 46 mol % lead to the simultaneously formation of both hydrated silica-rich layer and calcium phosphate based compounds layer; compositions with silica amount between 46 and 55 mol % lead to the formation of a silica layer on the hydroxyapatite layer, with a bilayer structure; finally, compositions with more than 60 mol % silica do not present the formation of any hydroxyapatite layer.

The overall morphological study of the formation and development of a surface calcium phosphate layer on bioglasses, with particularly interest in the hydroxyapatite phase, are of fundamental importance in bioactivities studies of such materials. As example, Kim at al. [7] described the formation of a hydroxyapatite surface layer on Bioglass® 45S5 in first stages (up to 120 hs) after the samples immersion in a solution containing trishydroxymethyl amino methane and hydrochloric acid. The layer characterization was done by DRIFT analysis, in which functional groups could be identified. The results indicate the formation of an amorphous calcium phosphate layer with 2 nm thickness, after 2 min in vitro tests. Moreover, after 10 mins, there was also a silica-gel layer, which was formed between the samples and the amorphous calcium phosphate layer.

The objective of this paper was to perform the chemical, physical and biological bioglass of the system SiO_2-Na_2O-CaO with 6 wt % P_2O_5, containing 48 wt% silica. The study of such composition helps to better understand the behavior of the calcium phosphate formation on bioglasses that are chemically more stable than usual Bioglass® 45S5, after immersed in simulated body fluid.

Materials e Methods

Glass preparing

The powders of raw materials of studied glass, containing 48 wt% silica (XXX), 25 wt% sodium hydroxide (Casa Americana, Brazil), 19 wt % calcium oxide (Casa Americana, Brazil) and 6 % phosphorous oxide (Ventec, Brazil) were homogenized in an agate mortar and placed in a platinum crucible. The final composition were fused in an vertical furnace (Lindberg Blue CP 56724C, XX) at 1500°C/2h under a heating rate of 10°C/min in normal atmosphere. After melting, the samples were poured into brass molds and annealed at 500°C/2h in electric furnace (Quimis, XX), followed by natural cooling. After cooling, bioglasses samples were cutted into ~ 0.5 x 0.5 x 1,0 cm specimens (Isomet 4000, Buehler, Germany)

In vitro tests

In order to predict the bioactive behavior of bioglass, the samples (in duplicate) were immersed in 3 ml simulated body fluid (SBF) solution for different periods (1, 3, 5, 7 and 14 days). During the experiments, the SBF was changed every 2 days. The samples were kept at 37°C and 40 rpm (Shaker, SPLabor SP 222, Brazil) with a 7.25 pH.

Bioglass Characterization

The samples were characterized, before and after in vitro tests, through x-ray diffraction (XDR) analysis, infrared spectroscopy with diffuse reflectance (DRIFT) and scanning electron microscopy (SEM).

Results and discussions

Fig. 1 presents the x-ray diffraction pattern of the bioglass samples after in vitro tests for different periods. The results show the predominantly amorphous character of bioglass. Moreover, after 7 days of SBF immersion, it was possible to observe the formation of a hydroxyapatite

crystalline phase ($Ca_{10}(PO_4)_6(OH)_2$, ICDD 00-003 - 0747). After 14 days experiments, it is not possible to observe this phase, which suggests the detachment of this layer and the formation of new layer of an amorphous calcium phosphate phase on the surface of bioglass. This result can be confirmed comparing the morphological features of the surface micrographs of bioglass samples after in vitro tests for different periods (Fig. 2)

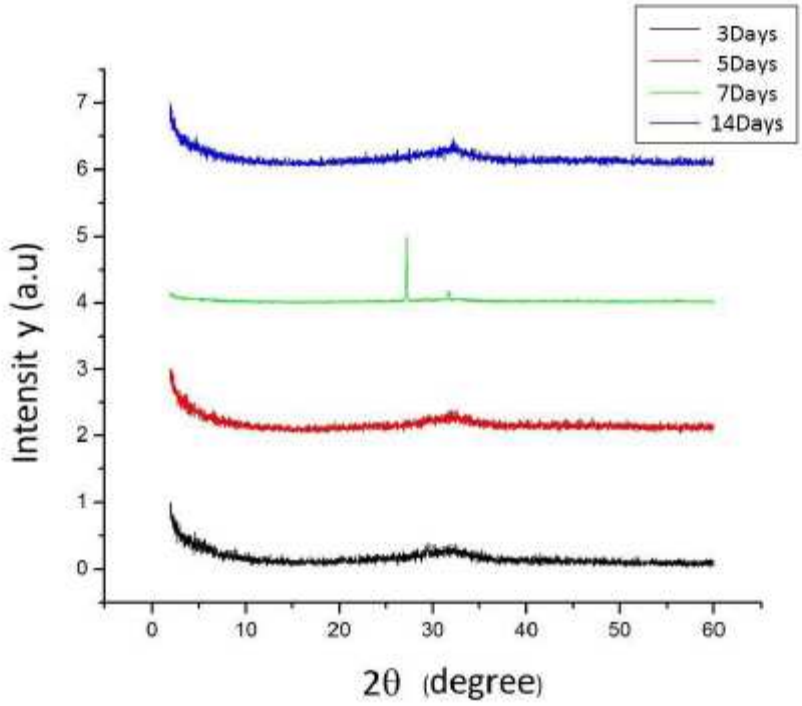

Fig. 1: X-ray diffraction patterns of the bioglass samples after in vitro tests in SBF for different periods

The overall micrographs (Fig. 2) suggest the formation of a globular amorphous hydroxyapatite on the bioglasses samples surface. It can be seen the hydroxyapatite with a higher density distribution after 7 days experiments (Fig. 2c) as compared to 14 days (Fig.2d).

The results of mass variation of the bioglass samples after different periods in SBF solution (Fig. 3) confirm the greater deposition of hydroxyapatite after 7 days as compared to 14 days. This behavior suggests that the bioglass surface layer, below the hydroxyapatite layer, consists of poorly alkaline materials due to leaching process. This layer, which is rich in silanol group, does not provide mechanical strength and tends to detach. Thus, the bioglass surface is now exposed as a non-treated one. On this new surface, it was possible to observe the formation of the hydroxyapatite, through the calcium and phosphorous percolation. This mechanism also reveals that under the formation of the amorphous hydroxyapatite is the crystalline hydroxyapatite earlier formed.

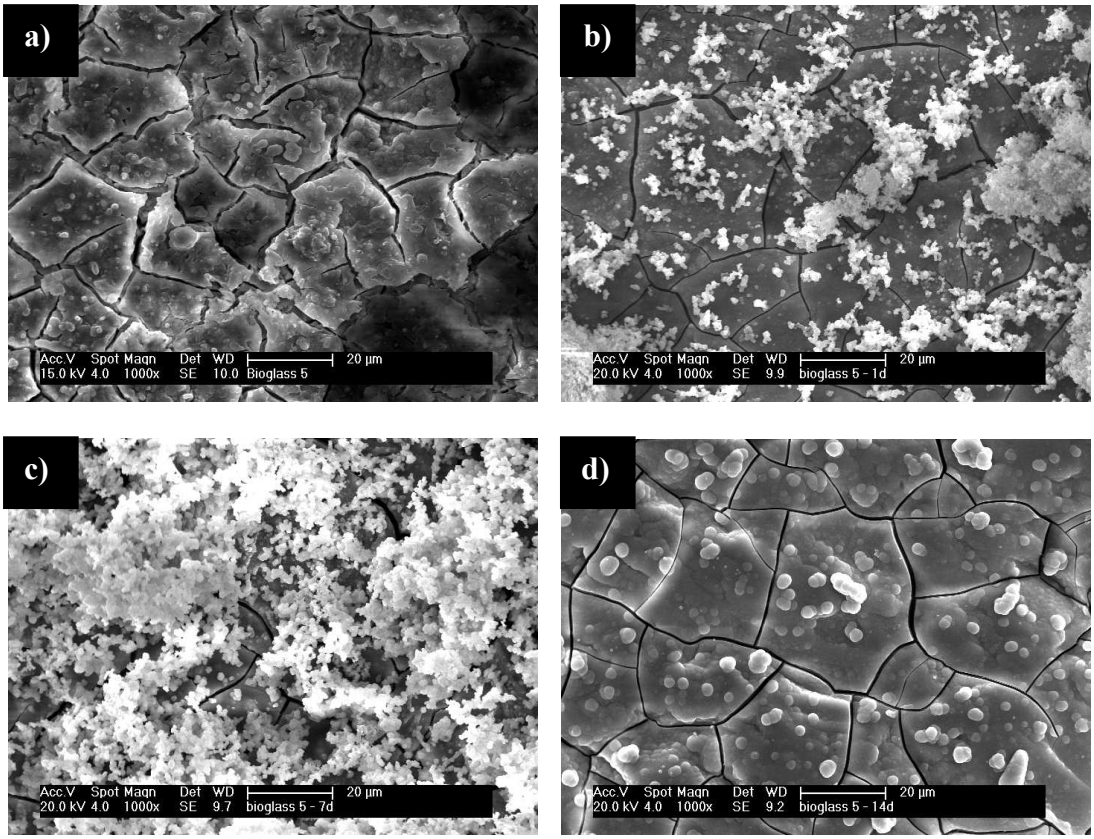

Fig. 2 : Scanning electron micrographs of bioglasses surface. (a): before in vitro tests; (b): after 1 day immersion; (c): after 7 days immersion; (d): after 14 days immersion

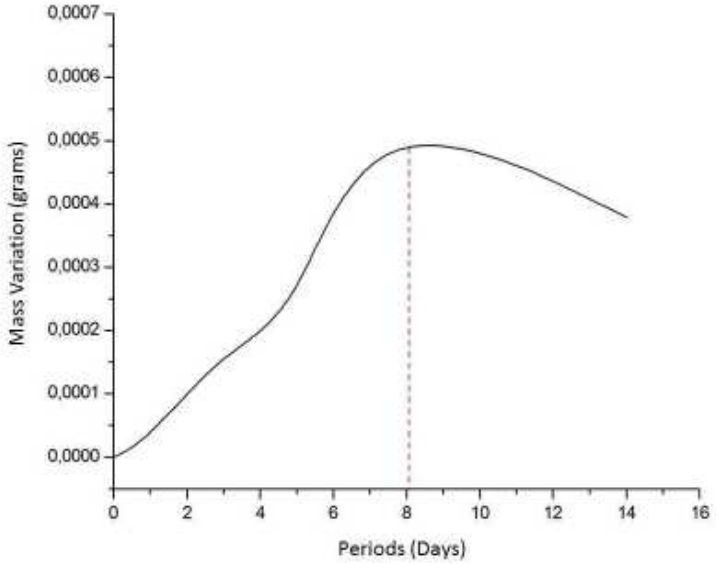

Fig. 3: Mass variation of bioglasses samples after different periods in SBF

Fig. 4 shows the DRIFT spectra of the bioglasses samples after diferente periods in SBF immersion. The results indicate that for longer periods it is observed the formation of peaks near 515-530 and 600-610cm^{-1}, corresponding to the crystalline P-O bonding [8]. Moreover, the peaks near to 550-560cm^{-1}, related to vitreous P-O bonding [8], were with lower intensity. These observations suggest that the phosphorous of the glass network is percolated to the surface as SBF solution effect. This ion is finally precipitated together with calcium, deposited on the bioglass surface. During this deposition phenomenon, these ions react with calcium presented in SBF solution, or even with dissociated calcium of vitreous network, forming crystalline compounds of based calcium phosphate on the bioglass surface.

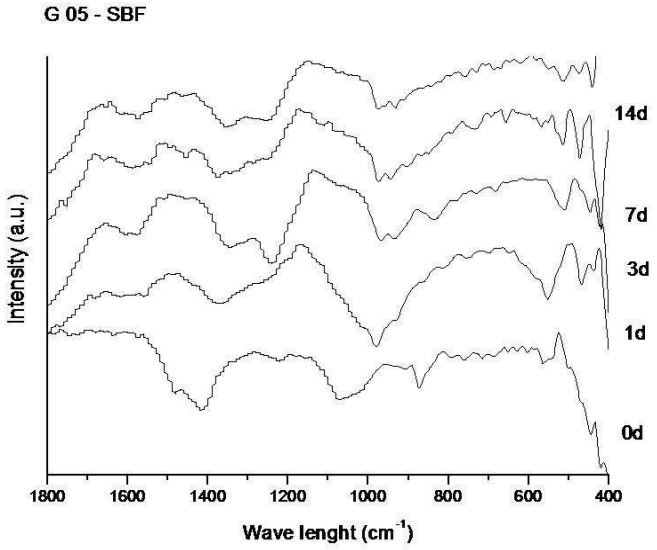

Fig. 4: DRIFT spectra of bioglasses samples after different periods in SBF immersion

Conclusions

The studied bioglasses containing 48 wt %SiO_2 have a suitable overall composition to promote the formation of an amorphous calcium phosphate layer on their surface after 1 day in SBF immersion. However, the stability of such layer is shown only after 7 days experiments, when the layer is presented as a crystalline phase. After this period, there is the detachment of this layer and the subsequent formation of other calcium phosphate layer. Such behavior may be of interest in situations when a higher integration of the implant with soft tissues is needed.

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