STUDY OF MECHANICAL PROPERTIES AND DISSOLUTION OF GLASS AND GLASS- CERAMIC CALCIUM PHOSPHATE CONTAINING STRONTIUM OXIDE

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Abstract. *Bioabsorbable materials are desired components for applications such as temporary implants. Glass and glass-ceramics based on phosphate have properties that allow them to be used as substitutes for hard tissues, with the advantage of being similar in composition to the inorganic component of bone. In addition, several studies have been conducted on the use of strontium (Sr) in the composition of biomaterials. The aim of this study was to characterize the mechanical properties and dissolution of glass and glass-ceramic calcium phosphate containing strontium oxide. The glass system P_2O_5.Na_2O.CaO.SrO was prepared by conventional method and heat-treated glass-ceramic obtained from the family of phosphates. To identify the crystalline phases was obtained using the X-ray diffraction. The bioactivity was tested immersing samples in simulated body fluid (SBF) for 15 days. The mechanical properties evaluated were hardness and fracture toughness. The dissolution was tested from the solution to Tris-HCl, for 7, 14, 21, 28 and 90 days, both for glass as for the glass-ceramic.*

Keywords*: Glass-ceramic, bioresorbable glass, temporary implants, phosphate based glass, strontium.*

1. INTRODUCTION

Bioceramic materials, especially those based on the calcium-phosphate system it's been used as bone substitutes due to its biocompatibility, low density, chemical stability, high wear resistance, and mainly due to their similar composition to the mineral phase of bone [Kalita et al (2007), Sinha et al (2001)]. Particularly, phosphate based glasses have been widely studied owing to their characteristics of being bioabsorbable [kalita et al (2007), Santos (2000)], allowing them to be used as temporary implants.

Temporary implants have some advantages over the traditional metallic implants, including reduction of the charge distribution and elimination of a second surgery necessary to remove the implants. However, bioabsorbable implants have three main disadvantages when compared to metallic ones: lower resistance, higher cost and in some cases, undesirable biological response as observed for silicate based glasses [LeGeros et al (2002), Hench et al (1972)].

The mechanical properties of bioactive glasses can be improved through its crystallization, that is, converting them into glass-ceramic [Peitl et al (2001). Glass-ceramics are materials obtained from a controlled heat-treatment above the glass transition temperature. The glass crystallization may change also the rate of degradation. An ideal temporary implant should have its degradation rate similar to the rate of new tissue growth [Zhang et al (2011), Dias et al (2003)].

Besides the glass crystallization, the composition of phosphate based glasses can influence its properties. Recent studies show that the incorporation of strontium in the phosphate based glasses causes an increase of its density, and change its degradation rate. Strontium is already used in bone therapies and proved to increase bones strength, reduces bone resorption, and stimulates bone formation. Consequently, several studies have been conducted on the use of Sr in the composition of biomaterials. However, there are limited studies of strontium containing bioactive glass-ceramic [Bostman et al (2000), Dorozhklin et al(2010)].

Given the structural function that a temporary implant should have upon a solicitation, the mechanical properties are always taken into account, and particularly the fracture toughness, K_{IC}. In brittle materials, the use of the Vickers indentation test for the evaluation of the fracture toughness has become widespread because of the simplicity of the specimen preparation, requiring only the provision of a small polished and reflective plane surface from which a large quantity of data points can be generated rapidly. [Clement at AL (2001)].

The aim of this study was to evaluate the effect of crystallization on the indentation fracture toughness and on the in-vitro dissolution rate of a phosphate based glass containing strontium.

2. MATERIALS AND METHODS

Phosphate glass was prepared with a composition of $38CaO.35P_2O_5.24Na_2O.3SrO_2$ (mol%), using the following analytical chemicals: $CaCO_3$, Na_2CO_3, P_2O_5 and Sr_2O_3. The oxides were melted in an alumina crucible at 1000 °C for 1 h. The melt was quickly poured into a steel mould preheated at 300°C, and then annealed for 12 hours to avoid the residual stresses.

Differential thermal analysis (DTA) was performed to determine the glass transition temperature (Tg), and crystallization temperature (Tc). The analyses were carried out in a DTA-50 (Shimadzu) using an inert nitrogen atmosphere, a heating rate of 15 °C/min and a temperature scanning up to 1200 °C. The analysis was performed for bulk and powder samples.

Crystallization of glass samples was carried out in an electrical furnace with a controlled temperature (± 1 °C). Heat treatments were conducted at 490 ° C for 8 hours, obtaining a fully crystalline material. Crystalline phases were identified through X-ray diffraction using a XRD-7000 diffractometer (Shimadzu), with CuKα radiation, and Bragg-Brentano geometry. Spectra were recorded from 10 ° to 50 ° (2θ), continuous scan with speed of 2 deg/min.

To test the bioactivity of the glass, the samples were soaked into 20 ml of tris-buffered simulated body fluid (SBF) solution, which resembles the human blood plasma, at 37°C, for 15 days. The SBF was prepared by dissolving reagent grade NaCl, $NaHCO_3$, KCl, $K_2HPO_4.3H_2O$, $MgCl_2.6H_2O$, $CaCl_2$ and Na_2SO_4 in deionized water. The solution was buffered to pH 7.4 with tris-(hydroxyl methyl)-amino methane $[(CH_2OH)_3CNH_3]$ and hydrochloric acid. The immersed glass samples were taken out after 15 days soaked into SBF, washed with deionized water and finally air-dried, and observed by scanning electron microscopy (SEM) and composition determined by energy dispersive spectroscopy (EDS) (Jeol JSM6360-LV).

The solubility test was performed according to the ISO 10993-14 (Biological evaluation of medical devices – Part 14: Identification and quantification of degradation products from ceramics). The samples were weighed initially (Wi) and then soaked into a Tris[hydroxymethyl]aminomethane-HCl solution (Tris-HCl solution) with pH 7.4 at 37 °C, using triplicate samples. At the end of each period of immersion time (7, 14, 21, 28 and 90 days) samples were weighed again (Wf). A relative weight loss percentage of samples was calculated using the following equation:

$$\text{Weight loss (\%)} = \left[\frac{Wi - Wf}{Wi} \right] \cdot 100 \tag{1}$$

Fracture toughness of glass and glass-ceramic samples were obtained through Vickers indentation technique, using a microhardness tester (HVS-2, Shimadzu), applied load of 100 gf during 30 s. Five indentations were made on each sample. The radial cracks lengths were measured using an optical microscope (BX-61, Olympus) and an image analyzer software (AnalySIS, Olympus). The fracture toughness was calculated according to equation proposed by Anstis et al (1981).

$$K_{IC} = 0.016 \cdot \left(\frac{E}{HV} \right)^{1/2} \cdot \frac{P}{c^{3/2}} \tag{2}$$

Where:
K_{IC} = fracture toughness
E = elastic modulus (GPa)
P = applied force (N)
HV = Vickers hardness (GPa)
c = length of radial crack (m)

Elastic modulus were measured trough instrumented indentation, using a nanoindenter (MTS), with Berkovich tip, applied load of 400 mN, and one load-unload cycle. Values of elastic modulus were obtained from an average of 9 indentations on glass and glass-ceramic samples, calculated with the method of Oliver and Pharr (1992).

3. RESULTS AND DISCUSSION

A typical DTA curve obtained for powder and bulk samples is shown in figure 1. It is observed two exothermic peaks due to crystallization phenomena (520 °C for powder and 570 °C for bulk samples), and two endothermic peaks corresponding to the melting temperature (715 °C and 740 °C). The temperature of glass transition (Tg) for both samples is almost the same (390 °C). It is observed that the exothermic peak occurs at a lower temperature for powder samples. This indicates that the surface crystallization is preferred than volume crystallization, as the relative surface area is higher. The chosen crystallization temperature was of 490 °C, the onset temperature for powder samples. Higher temperatures were also tested, and although they have produced fully crystalline samples, it also caused its deformation.

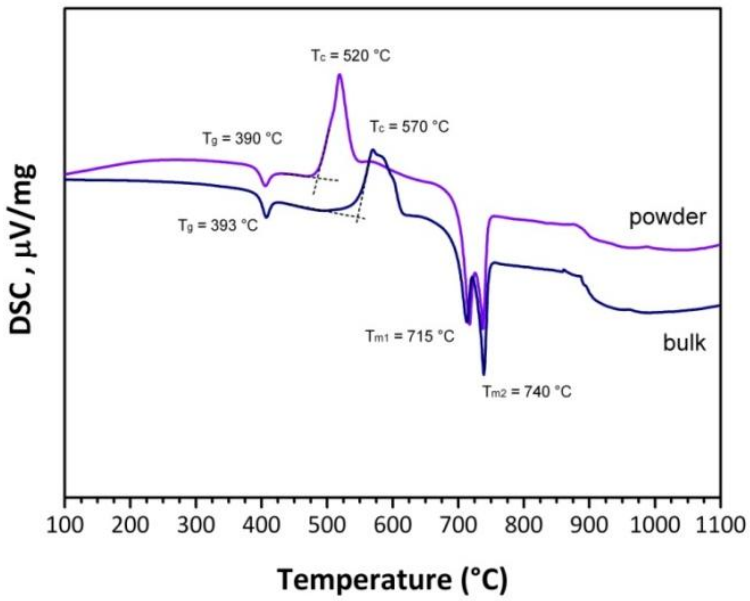

Figure 1. DTA curves of powder and bulk samples, obtained with a heating rate of 15 °C/min.

Four different times of crystallization at 490 °C were tested: 1, 2, 4, and 8 hours. Surface crystallization was observed for the studied composition. X-ray diffraction results showed that only for 8 hours, it was obtained a fully crystalline sample, with the presence of the following phases: CaP_2O_6, $Ca_3(PO_4)_2$, $Sr(PO_3)_2$, $Ca_2P_2O_7$, $Sr_4P_2O_9$. The calcium pyrophosphate $Ca_2P_2O_7$ is known to be bioactive (Dias et al. 2007). The biocompatibility of the other phases CaP_2O_6, $Ca_3(PO_4)_2$, $Sr(PO_3)_2$, $Sr_4P_2O_9$ was not reported in the literature.

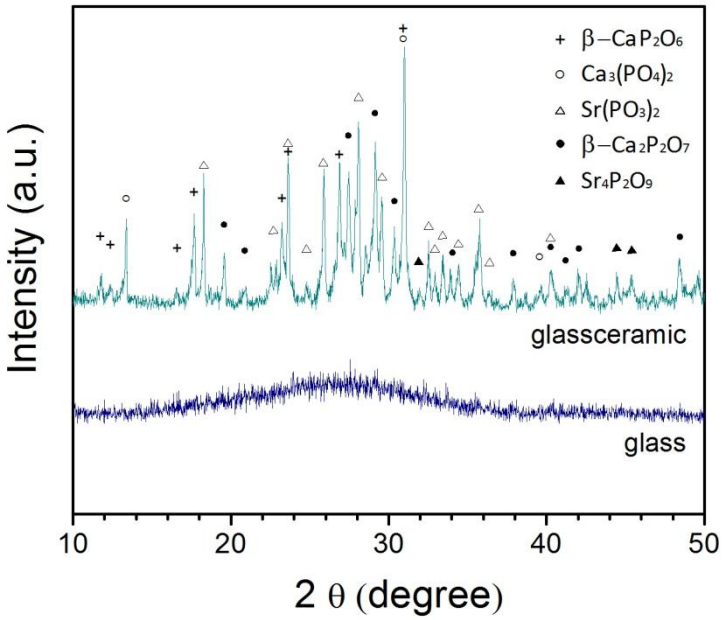

Figure 2. XRD patterns of glass and glass-ceramic samples heat-treated at 490 °C for 8 hours.

SEM results of the glass-ceramic after soaking into SBF during 15 days showed the nucleation of hydroxyapatite, as shown in figure 3.

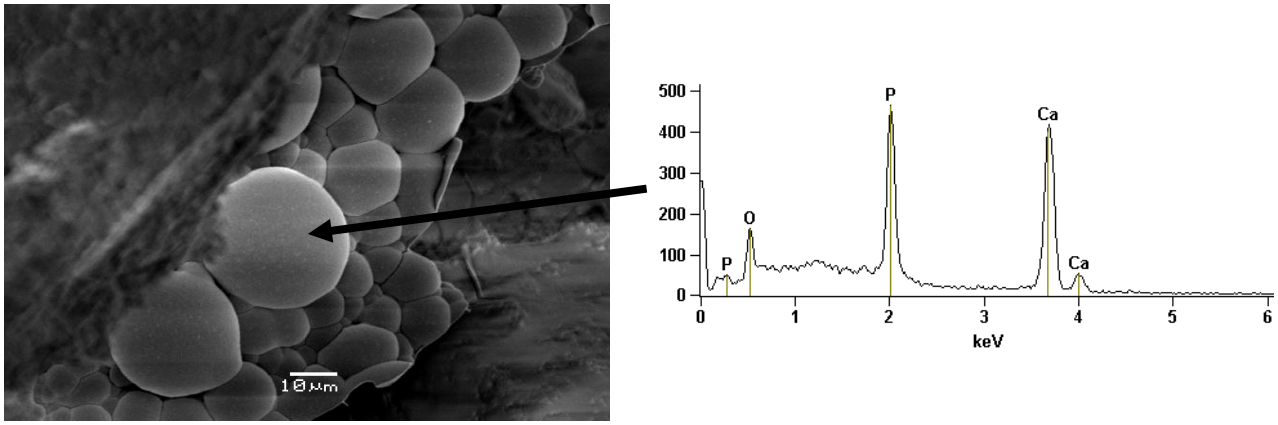

Figure 3. SEM micrograph showing the apatite formation on glass-ceramic in SBF after 15 days at 37 °C, and the correspondent EDS spectra, showing the presence of Ca, P, and O.

Dissolution studies were carried out in order to investigate the degradation of these glass-ceramics and the results confirmed that by controlling the crystallization of the initial glass, glass-ceramics with high degree of degradation may be obtained. In fact, the level of chemical degradation observed for these materials is well-above that reported in literature for bioactive ceramics that are clinically used, namely hydroxyapatite (HA), and tricalcium phosphate (TCP). [Chun et al. (2002)] reported that the level of calcium and phosphorus leached from HA and TCP ceramics under similar degradation testing are usually in the range of 6.1-0.36 ppm and 13-5.5 ppm, respectively [Chun et al (2002)]. The glass-ceramic prepared in this work seem to be capable of combining a bioactive behavior in-vivo, due to the bioactive and bioresorbable phases existing in the microstructure.

The variation in mass loss as a function of immersion time is shown in figure 4. It is observed that the dissolution is higher for the glass-ceramic than for glass for all times studied. In addition, both the glass and glass-ceramic has the weight loss increased gradually as a function of immersion time.

This indicates, according to Lettuec et al (2000) and Laurencin et al (2003), that a higher rate of degradation of the material is a result of their phase composition and its degree of crystallinity, in which each phase has a unique degradable characteristic. The solubility of glass-ceramics is influenced by several factors related to the crystalline phases: structure and density, volume fraction and grain size, and also by the content of the residual glassy phase.

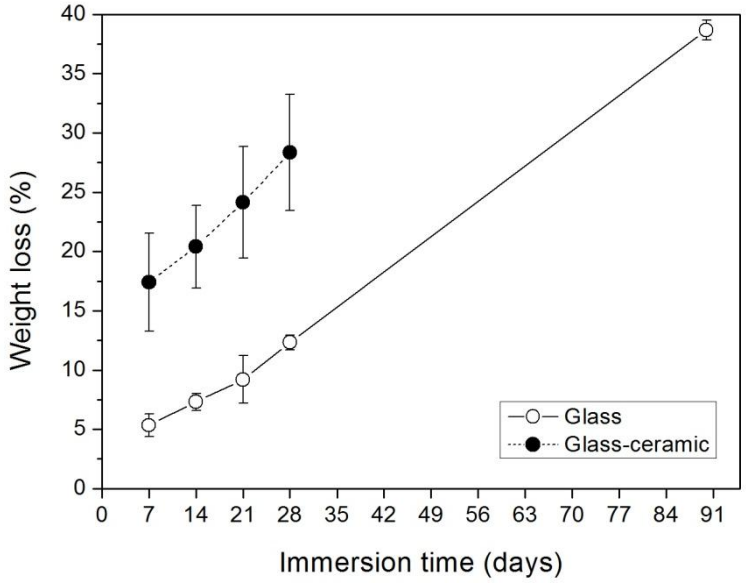

Figure 4. Degradation of glass and glass-ceramic in Tris-HCl solution.

Table 1 shows the average values of Vickers hardness found for both glass and glass-ceramic samples, before and after the dissolution tests. Note that there is a great influence of crystallization on the hardness of glass and ceramics. The crystallization produced a decrease of hardness and did not produced cracks even with higher loads (2 kgf), not allowing the determination of fracture toughness. The elastic modulus values obtained trough nanoindentation were 67 GPa for glass.

Table 1: Average values of hardness for glass and glass-ceramic before and after dissolution tests.

Glass			Glass ceramic		
Time (days)	HV (kgf/mm²)	K_{IC} (MPa.m$^{1/2}$)	Time (days)	HV (kgf/mm²)	K_{IC} (MPa.m$^{1/2}$)
0	442 ± 50	0.5 ± 0.02	0	162 ± 44	-
7	407.2 ± 98	0.51 ± 0.01	7	15.6 ± 2.5	-
14	449 ± 59	0.48 ± 0.01	14	15.5 ± 1.4	-
21	344.2 ±29	0.49 ± 0.03	21	20 ± 1.5	-
28	379 ± 44	0.52 ± 0.03	28	18.8 ± 2	-

4. CONCLUSIONS

The effect of crystallization on the mechanical properties and dissolution of calcium-phosphate-strontium glass and glass-ceramic was evaluated. The results shows that the crystallization had an effect on the hardness of the glass, as this decreased considerably, mainly after the dissolution test. The fracture toughness was measured only for the glass samples because the glass-ceramic presented no cracks. The dissolution increased with the immersion time, being greater for the glass-ceramic. This effect is attributed to the composition of the phases obtained by crystallization.

4. ACKNOWLEDGEMENTS

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