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ANALYSIS OF MECHANICAL PROPERTIES AND SOLUBILITY OF PHOSPHATE GLASSES WITH DIFFERENT ADDITIONS OF MgO

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Abstract. *Bioresorbable materials are desirable components for applications such as temporary implants, as they degrade in a controlled manner until completion of the osseointegration of the bone, eliminating the need of a second surgery to remove them. Phosphate based glasses (PBG) have properties that allow them to be used as hard tissue substitutes with the advantage of being resorbable. Incorporation of strontium into PBG has been widely studied due to be considered a bone formation stimulator. Although strontium phosphate glasses have better cellular response, their degradation rate is higher. Some studies show that the addition of MgO significantly reduces the degradation rate of soluble phosphate glasses. Furthermore, the oxide interferes with the chemical structure of the glass, and consequently improve the mechanical properties of the same. Therefore, our aim was to evaluate the effect of different additions of MgO on a phosphate glass and, consequently, on its degradation behavior, hardness, elastic modulus and fracture toughness. Our results showed that the glass structure was modified by the dopant, becoming more rigid, and consequently, decreasing the glass dissolution, with an increase of hardness, elastic modulus, and fracture toughness.*

Keywords: *bioglass, phosphate glass, temporary implants, mechanical properties.*

1. INTRODUCTION

The Bioactive material is one that causes a biological response at the interface between the graft and the bone tissue, which results in the connection between both. Approximately 60% of bone implants available on the market involve ceramics, including glass. [1].

Bioactive glasses and glass-ceramics such as 45S5 Bioglass and other compositions based on phosphate systems represent an important group of inorganic bioactive biomaterials used for bone tissue engineering. Are a class of materials which have the ability to bond to bone tissue through the formation of a bone-like hydroxyapatite (HAP) layer on its surface, and so have great potential in applications such as temporary implants [2,3].

The growing interest in resorbable implants is that they play a temporary functional role. A new generation of biomaterials is being developed, in which implants are not only temporary, but are also metabolized gradually by naturally occurring processes in the body, taking an active part in the process of tissue regeneration [4].

The main purpose of a degradable implant is that it provides the correct amount of strength when needed and degrades harmlessly over time, until the load can be safely transferred to the cured bone [5].

This eliminates the need for a second surgery to remove the implant, reducing the total time of treatment and rehabilitation of the patient [6].

The phosphate-based glasses (PBG) solubility is a consequence of the P\O\P bonds presence, which are easily hydrated. Being so, the PBG have poor mechanical properties and this can limit their use in biomedical applications [7].

The addition of strontium oxide (SrO) to the phosphate glass has a fundamental role on the new bone formation and reduction of bone resorption, improving thus the bioactivity. To improve the chemical durability as well as the mechanical properties of phosphate glasses, several metallic oxides, including TiO₂, MgO, Fe₂O₃ and ZnO₂, have been added to the phosphate network without compromising its bioactivity [8].

The aim of this work was to investigate the effect of Mg dopants addition on the solubility, mechanical properties of a P_2O_5 –CaO–Na₂O–SrO glass for use as resorbable implant material.

2. EXPERIMENTAL PROCEDURE

2.1 Glass synthesis

Phosphate glasses in the system P_2O_5 –CaO–Na₂O–SrO were produced by using a conventional melt quench route, with nominal composition given in Table 1. Analytical grade chemicals calcium carbonate ($CaCO_3$, Biotec 99%), sodium carbonate (Na_2CO_3 , Vetec 99.5%), strontium carbonate (Sr_2CO_3 , Vetec 97%), magnesium oxide (MgO, Vetec 95%) previously dried (100 °C for 24 h), and phosphorus pentoxide (P_2O_5 —Vetec99%), were used as precursors. These precursors were weighed out and then placed into an alumina–zirconia ceramic crucible. The mixture was calcinated in an electric furnace (Jung, BTC-9090) at 700 °C for 1 h, then melted at 1100 °C for 1 h. The melted glass was poured and quenched between stainless steel plates and placed in an annealing furnace at 350 °C for 12 h in order to remove any residual stresses from the glass. The glass was then allowed to cool slowly to room temperature in the furnace. The amorphous state of the glasses was confirmed using powder X-ray diffraction (XRD; Shimadzu; 30 kV/40 mA, $CuK\alpha$). A Miniton diamond saw (Struers) was used to cut the glass into pieces with thicknesses of about 2 mm, using ethanol as the coolant and lubricant. Samples were then mechanically polished using 800, 1000 and 1200 grit SiC abrasive paper, followed by fine polishing with a CeO_2 aqueous solution.

Table 1. Nominal glass composition in mol%.

Glass	P_2O_5	CaO	Na ₂ O	SrO	MgO
PCNSr	40	30	25.0	5	-
PCNSrMg2.5	40	30	22.5	5	2.5
PCNSrMg5	40	30	20.0	5	5.0
PCNSrMg7.5	40	30	17.5	5	7.5

2.2 Degradation studies

The degradation tests were performed based on ISO10993-14. Tests were carried out in Tris (hydroxyl methyl) amino methane–HCl (Tris– HCl) solution (pH 7.4) at 37 °C, using triplicate samples. At the end of each period of immersion time (7, 14, 21, 28 and 42 days), samples were washed in deionized water, and then dried and weighted using an analytical scale (AG200, Gehaka). A relative weight loss percentage (WL), after a certain time of immersion, t, of the samples was calculated using the following equation:

$$W_L = [(W_o - W_t) \div W_o] \times 100 \quad (1)$$

where W_o and W_t stand for initial and final weight after a specific immersion time, respectively.

2.3 Mechanical Properties

2.3.1 Instrumented indentation

Hardness and elastic modulus were obtained by instrumented indentation, where an indenter of known geometry is pressed into the material and the penetration depth (h) is continuously recorded as a function of the applied load (P) for both the loading and unloading cycles. The hardness (H) and elastic modulus (E) from the P-h curves were determined by the Oliver and Pharr method. [9]

2.3.2 Indentation fracture toughness (K_c)

The fracture toughness (K_c) was determined by the Vickers indentation technique using a microhardness tester (HVS-2, Shimadzu). Polished samples were indented using a load of 0.981 N (100g) applied for 30 s. Ten indentations were made in each sample, and three samples were made for each composition. The size of the cracks emanating from the corners of the Vickers indentations was measured immediately after each indentation by using an optical microscope (BX-61, Olympus). For all indentations from the three glasses, the ratio l/a (crack length generated by indentation divided by half of the length of the indentation diagonal) is between $0.25 \leq l/a \leq 2.5$, thus it was assumed that the crack geometry is of Palmqvist type. The fracture toughness values were calculated using a modified version of the Evans and

Charles relationship described by Lankford, that was applied to phosphate glasses and had good agreement with the K_{IC} values obtained by a conventional method [10,11].

$$K_{IC} = \frac{\xi(E)^{2/5}}{H} \times \left(\frac{P}{a\sqrt{l}} \right) \quad (2)$$

where K_{IC} is the fracture toughness, ξ is $0,016 \pm 0,04$, H is the Vickers hardness, E is Young's modulus, a and l are defined as the crack length and indentation length measured from the center of the Vickers indentation, and $l=c-a$.

3. RESULTS AND DISCUSSION

The results of the mechanical properties are presented in Figures 1 to 3. In general, the hardness values of the analyzed glass do not present significant differences, and that the glass with 7.5% of MgO presented the highest average value. With respect to the fracture toughness and modulus of elasticity, it is possible to observe a significant increase in the average values for the glasses with the addition of the 5% of MgO oxides, while the PCNSr glass presented the lowest average value.

Fig. 1. Hardness (GPa) values obtained by nanoindentation for the phosphate glass with different additions of Mg.

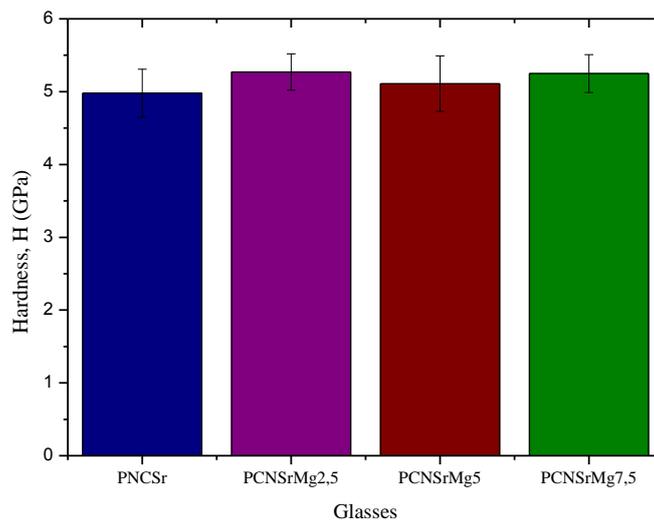


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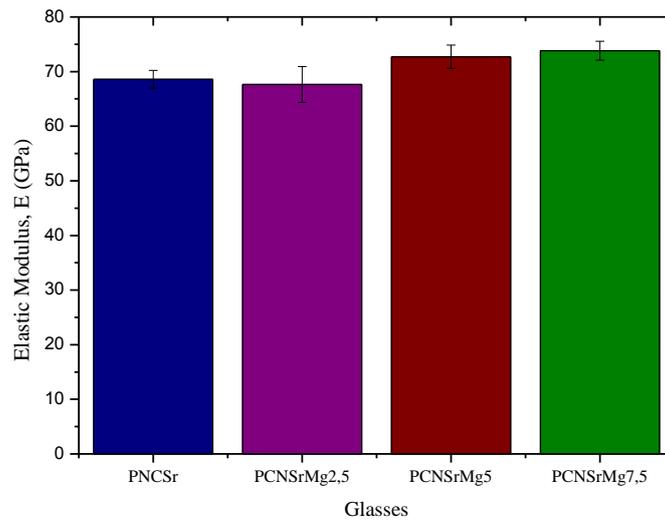


Fig. 2. Elastic modulus (GPa) measure by nanoindentation for the phosphate glass with different additions of Mg.

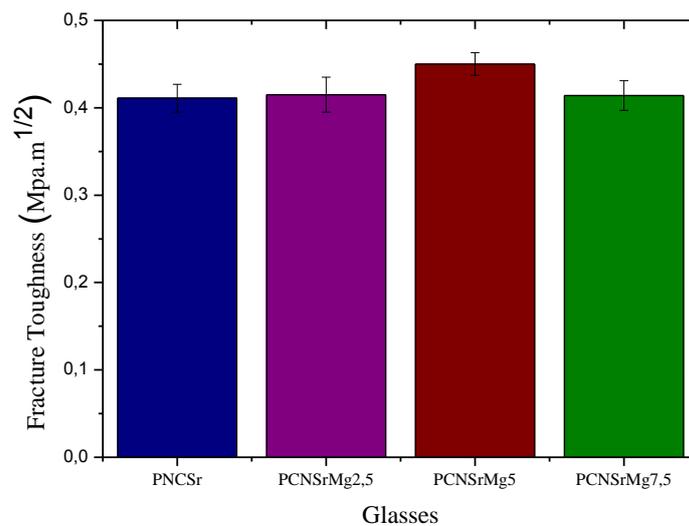


Fig. 3. Fracture toughness values (Mpa.m^{1/2}) obtained by Vickers indentation for the phosphate glass with different additions of Mg.

The addition of Mg in PCNSr glass alters the glass structure, making it more rigid, as verified in the results of mechanical properties. However, the same dissolution behavior was not observed, as observed in figure 4. For, the glass with the highest MgO addition was the one with the highest dissolution value.

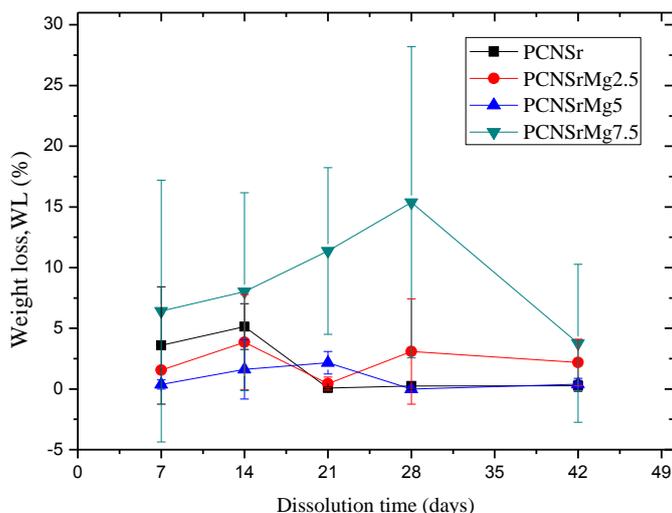


Fig.4. Weight loss as a function of time for the phosphate glass with different additions of Mg.

4. CONCLUSION

The glass structure was affected by the addition of MgO, that acted as a network modifier increasing the binding strength between the phosphate chains. This increase in stiffness improved the mechanical properties of Sr-phosphate glass and decreased solubility. For glass with 7.5% MgO the solubility increased. However, for application as a temporary implant, the glass must remain mechanically stable during the healing period and then be absorbed by the body. Based on the results, the most suitable glass for these applications is glass with 5% MgO.

5. REFERENCES

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