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STRUCTURAL AND CHEMICAL INVESTIGATIONS ON SiO_2-CaO-P_2O_5 BIOACTIVE GLASS COMPOSITION

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Abstract:. *The glass obtained by the sol-gel method was immersed in a simulated body fluid solution, in order to observe the structural and morphological changes on its surface. Infrared spectroscopy - FTIR and electron microscopy SEM analyses showed the formation of apatite on the surface of the synthesized glass.*

1. INTRODUCTION

Glass with bioactive properties is obtained by mixing inorganic raw materials, by heating at high temperatures, depending on the composition obtained. The mixture of raw materials is transformed into a homogeneous, completely molten liquid, free of inclusions, of solid or gaseous nature. The liquid mass is transformed into an amorphous, solid substance. In these situations, crystallization is not allowed, and the viscosity increases to ambient temperature [1].

The first bioactive glasses were obtained experimentally in the early 1970s by L. Hench [2]. These glasses were based on a SiO2-Na2O-CaO system, more precisely the composition was the following: 45% SiO2 - 24.5% CaO - 24.5% Na2O - 6%P2O5. This product, known under the trade name 45S5, was produced by the company US Biomaterials. Similarly to other glasses, those used in medical applications also have in their composition a vitrification agent, silica (SiO2), a flux, soda (Na2O), a stabilizer, calcium oxide (CaO). What makes glass unstable in terms of interaction with fluids, in the sense that it can easily decompose in the presence of blood and plasma refers to the phosphorus (P2O5) content but also to the proportion of alkali and alkaline earth oxides, all of which accelerate the resorption process [2].

The sol-gel method allowed the synthesis of glasses with better bioactivity, compared to glasses obtained by melting raw oxide materials, due to the porous nature of the precursors.

The synthesis of bioactive glass compositions by the sol-gel process has been put into practice since the 1990s. This new class of bioactive materials is characterized by a wide range of biocompatibility; silicon-calcium-phosphate glasses can form a apatite film on their surface, for a silica percentage of less than 90%.

More specifically, the method involves the formation of an inorganic network by mixing metal alkoxide solutions, followed by several steps: hydrolysis, gelation, and finally, heat treatment at temperatures below 700^0C, to synthesize a glass [3].

Compared to the sol-gel method, glasses obtained by the classical method of melting oxide mixtures require working temperatures exceeding 1000 ^{0}C. The steps of the technological process are mostly like those of the classic glass synthesis. Given the conditions presented above, the structure of these glasses has a very low porosity, and the specific surface area is related to the granulometry of the raw materials used. In the case of large particles, the specific surface area can reach values below 1m^2/g [4].

The hydroxyapatite film forms much faster on the surfaces of bioactive materials synthesized by the sol-gel method, compared to glasses obtained by melting, in some cases the synthesized materials are resorbable, they are replaced over time by host tissue. Thus, the porous structure of the glasses obtained by the sol-gel method allows the formation of a hydrated layer inside the

material, on which, subsequently, biological tissue will form and grow.

Research by other authors [5] has shown the formation of a bone-like structure when using compositions such as 45S5 as implant material in rabbits. Trabecular bone structure developed on bioactive glass synthesized by classical processes but also portions not covered by tissue could be observed. In the case of glasses synthesized by the sol-gel process, these areas not covered by bone tissue were not highlighted.

Bioactive glasses obtained by the sol-gel process can be classified into different systems: binary, tertiary, quaternary: CaO – SiO_2 [6], SiO_2 – CaO – P_2O_5 [7] or SiO_2 – CaO – P_2O_5 – MgO [8]. By immersion in simulated body fluid, all these compositions show a certain degree of bioactivity.

This paper presents experimental results obtained for the 58% SiO_2-33%CaO – 9%P_2O_5 glass composition. Tests performed at different time intervals have highlighted the bioactive potential of this material.

2. MATERIALS AND METHODS

The glass was obtained by the sol-gel method, the precursors used were tetraethyl orthosilicate $Si(OC_2H_5)_4$ (TEOS), triethyl phosphate $(C_2H_5O)_3P(O)$ (TEP) and calcium nitrate tetrahydrate $(Ca(NO_3)_2 \cdot 4H_2O)$ [3, 9, 10].

The composition of the synthesized bioactive glass is detailed in Table 1.

Table 1. Composition of synthesized sol-gel glass

Composition	SiO_2	CaO	P_2O5
Mole, %	60	36	4
Weight, %	58	33	9

The technological process for obtaining bioactive glass involves, in the first stages, the performance of hydrolysis and condensation reactions. In this regard, 63 ml of TEOS (98%) was added to a solution of distilled water and hydrochloric acid in a glass vessel. Hydrochloric acid acts as a catalyst in order to initiate and, at the same time, accelerate the TEOS hydrolysis reaction. 7 ml of hydrochloric acid (HCl 2N) were used in 45 ml of distilled water.

After approx. 60 minutes, 4 ml of triethyl phosphate - $(C_2H_5O)_3P(O)$ (99%) was added to the reaction medium. In the next stage of the glass-making process, after approx. one hour, calcium nitrate tetrahydrate was added to the reaction medium. For the synthesis of this glass, approx. 38.5 g of $Ca(NO_3)_2 \cdot 4H_2O$ were used. The addition of the reagents involved in the glass synthesis was carried out under conditions of moderate mixing of the reaction medium. After approximately 75-90 minutes, the agglomeration process of the particles into a sol takes place.

In the second stage, the gelation process takes place, i.e. the interconnection of the particles that constitute the soil in a three-dimensional network. Various polystyrene molds were used where the soil was poured, later these molds were introduced into a glass container (Fig. 1), where under normal temperature conditions the gelation process of the soil occurs.

Figure 1. Polystyrene molds and glass container

In the next stage, the gel obtained by heating at a temperature of 60^0C, for a period of 54 hours, is matured in an oven. After this stage, the gel shrinks, and the liquid is removed from its pores. The process of forming the xerogel, i.e. a structure with interconnected pores without water and alcohol, takes place in approximately 4 days, following a heat treatment at a maximum of 175^0C. Figure 2 shows the gel matured in a cylindrical shape for 54 hours at a temperature of 60^0C.

Figure 2. Gel sample aged for 54 hours at 60 ^{0}C

In the last stage the xerogel is heated to a temperature of 600^0C. The stabilization process also aimed at eliminating some unwanted components from the structure of the synthesized glass. The heat treatment was carried out under normal conditions, in the air.

After this stabilization stage, the obtained glass was crushed in a mortar for further analysis (fig. 3).

Figure 3. Glass powders obtained by the sol-gel method, after the heat treatment applied to the xerogel at a temperature of 600 ^{0}C

The obtained glass was tested to study its bioactivity, by immersion in simulating body fluid, according to the procedure described in other works [3, 9].

3. MATERIALS CHARACTERIZATION

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) for the obtained material was performed on NETZSCH STA 449 F3 JUPITER. Temperature range: -150 ^{0}C … + 2000 ^{0}C, for a heating rate between 0.1 ^{0}C/min and 50 ^{0}C/min and a cooling time between 1500 ^{0}C and 50 ^{0}C in less than 30 min.

Information on the molecular groups in the structure of the bioactive glasses was obtained using a Bruker Tensor 27 FTIR spectrometer equipped with ATR equipment. Measurements were performed in transmittance - wavenumber (T, ν) coordinates in the range 4000 - 400 cm $^{-1}$ at a resolution of 2 cm $^{-1}$.

Scanning electron microscopy analysis was performed with a Carl Zeiss Auriga - FE-SEM (Field Emission - Scanning Electron Microscope - with the following characteristics: minimum resolution: 1 nm at 15 kV; 1.9 nm at 1 kV; magnification: 12x ... 1,000,000x; acceleration voltage of 0.1 - 30 kV with 10 V steps.

4. RESULTS AND DISCUSSIONS

Thermal analysis

For this analysis, a heating rate of 10 K/min was used in the range 25-1200 ^{0}C. From figure 4, thermogravimetric (TG) analysis suggests a mass loss of the glass powder in four stages corresponding to the following temperature ranges: (I) 25 – 250 ^{0}C, where a mass loss of 6.52% is observed; (II) 250 – 655 ^{0}C, in this stage the mass loss was 3.98%; (III) 655 – 790 ^{0}C, range in which the mass loss was 1.51% and (IV) 790 – 1200 ^{0}C, in this last stage the loss was 0.71%.

The elimination of water adsorbed on the surface of the glass powders or from the precursors and catalyst (HCl), all used in the synthesis process, is confirmed by differential thermogravimetric analysis (DTG) through the endothermic peak located at 130 ^{0}C. The same phenomenon is also highlighted by differential scanning calorimetry (DSC) and derivative (DDSC) analysis, where the presence of endothermic peaks is located at 137.7 ^{0}C and, respectively, 109.2 ^{0}C is noted. Also, the endothermic peaks, corresponding to the DDSC and DTG analyses, are located at 660.3 ^{0}C and, respectively, 711.1 ^{0}C correspond to the decomposition of precursors such as calcium nitrate or of secondary products resulting from the synthesis process of bioactive glass.

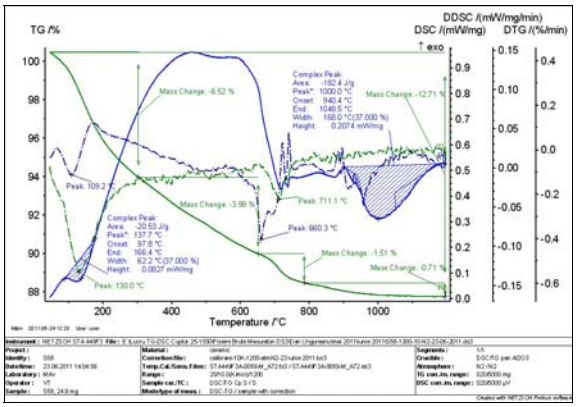

Figure 4. Thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis of the obtained glass powders

Chemical analysis FTIR

The FTIR spectrum of glass powders obtained from the SiO_2 –CaO – P_2P_5 system, stabilized at 600 ^{0}C, before immersion in simulated body fluid, is presented in figure 5. The presence of the three-dimensional silicate network is highlighted by this analysis by the peak located at 464 cm-1, typical for a Si – O – Si bond; the peaks at 800 cm $^{-1}$ and 875 cm $^{-1}$ are found in the case of Si – O bonds and the peak located at 1065 cm $^{-1}$, specific to Si – O – Si bridges. These peaks are also presented by other authors [11-12]. Also, the peak located at 3650 cm $^{-1}$ is characteristic of silanol groups (Si – OH), present in the structure of the analyzed glass. The phenomenon is also highlighted by Mabrouk et al. [13]. The peaks located at 1643 cm $^{-1}$ highlight the presence of crystallized water in the composition of the glass powders, and the peak at 1435 cm $^{-1}$ shows the presence of carbonate groups (CO_3^{2-}) in the structure of the same material. The incorporation of carbonate groups into the structure of the glasses occurred during the thermal stabilization treatment at 600 ^{0}C, since this process was not carried out in a protective atmosphere.

The presence of phosphorus in the structure of the synthesized glasses is highlighted by the peak located at 569 cm $^{-1}$ and the peak at 603 cm $^{-1}$ is also typical for the same type of P – O – P bond [11, 14].

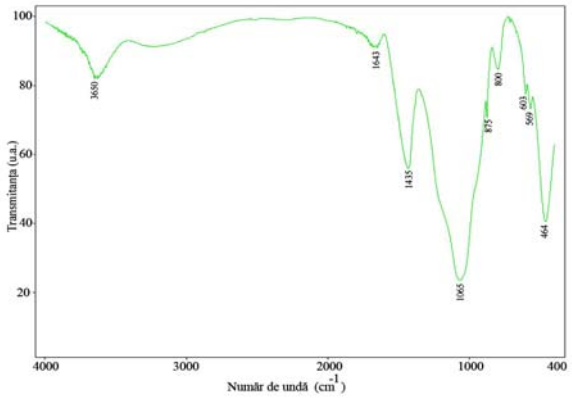

Figure 5. FTIR spectrum of glass before soaking in simulated body fluid

The FTIR spectrum of glass powders immersed for 7 days in simulated body fluid is shown in figure 6. The data in the spectrum below highlights the presence of silica at the surface of the immersed glass. Thus, the peak located at 1079 cm-1 is found in the case of Si – O – Si type bonds. The same type of bond is found for the peak located at 464 cm $^{-1}$. Si – O bonds are specific to the two peaks at 800 cm $^{-1}$ and 875 cm $^{-1}$ [11, 14]. The presence of silanol groups (Si – OH) in the structure of the glass powders is also highlighted in this stage of the analysis, at 3650 cm $^{-1}$ [13]. Regarding the presence of phosphate groups in the glass structure, they were identified in the spectrum by the three peaks characteristic of (PO_4^{3-}) group at 962 cm $^{-1}$, encountered in the case of P – O bonds, 603 cm $^{-1}$ and 567 cm $^{-1}$, typical of P – O – P bonds [212, 213 14, 15]. The two peaks at 1427 cm $^{-1}$ and 1643 cm $^{-1}$ are characteristic of the formation of both carbonate groups and the presence of crystallized water in the superficial structure of the analyzed glasses.

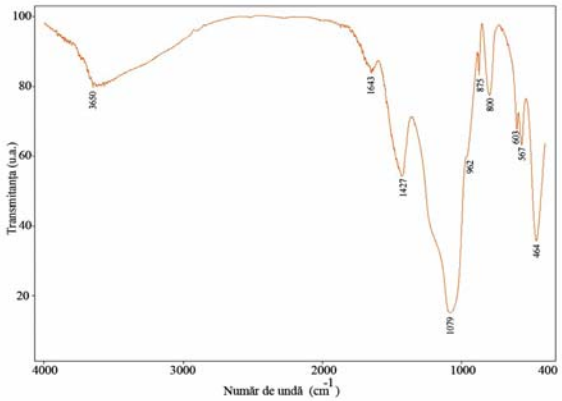

Figure 6. FTIR spectrum of glass immersed for 7 days in simulated body fluid

Microscopy analysis

The morphology of the glass powders after 7 days of immersion in human simulant fluid is shown in Figure 7. Regarding the topography of the glass particles, their irregular appearance can be observed. Thus, optimal conditions are created for the germination and growth of apatite on the surface of the obtained glass.

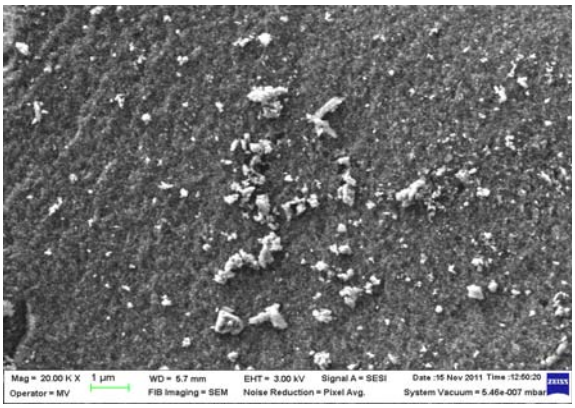

Figure 7. SEM morphology of glass powder, immersed for 7 days in simulated body fluid (Magnification: 20,000 X)

The SEM micrograph taken at 100,000 X (Fig. 8) highlights the presence of apatite that forms clusters with a size of 200 nm.

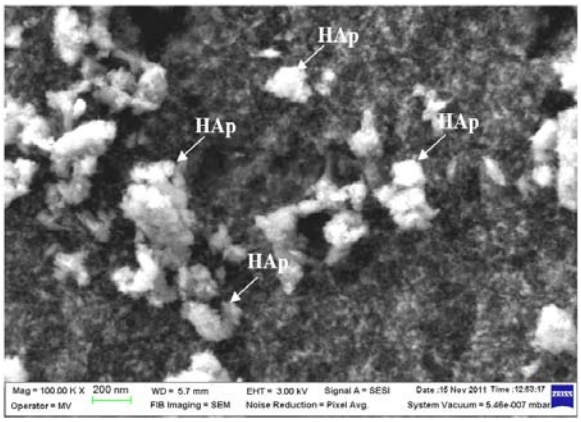

Figure 8. SEM morphology of glass powder, immersed for 7 days in simulated body fluid (Magnification: 100,000 X)

5. CONCLUSIONS

In this work, a glass with a composition of 58% SiO_2 – 33% CaO – 9% P_2O_5 was synthesized by the sol – gel method.

The bioactivity of this material was tested in vitro, in a SBF solution. The glass obtained in powder form was analyzed in terms of thermal stability, composition and morphology by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy analysis, and scanning electron microscopy – SEM.

FTIR tests performed after 7 days of immersion in a simulant body fluid solution highlight the formation of new molecular groups of phosphate (PO_4^{3-}) and carbonate (CO_3^{2-}), both specific to carbonatite

hydroxyapatite. Electron microscopy analysis – SEM, at the same time interval (7 days), reveals new crystalline formations on the glass surface, attributed to hydroxyapatite.

The results obtained confirm the synthesis of a material with bioactive potential.

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