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Analysis of the structural changes of a phosphate glass during its dissolution in simulated body fluid

J. CLÉMENT, J.M. MANERO, J.A. PLANELL
Research Centre in Biomedical Engineering (CREB), Department of Materials Science and Metallurgical Engineering, Universitat Politécnica de Catalunya, Diagonal 647, 08028-Barcelona, Spain
E-mail: clement@cmem.upc.es

G. AVILA, S. MARTÍNEZ
Department Cristal-lografia, Mineralogia i Recursos Minerals, Universitat de Barcelona, Martí i Franqués s/n, 08028-Barcelona, Spain

The structural changes of two calcium–sodium metaphosphate glasses during its dissolution in simulated body fluid (SBF) have been analyzed by Fourier transform Raman spectroscopy (FT-Raman), scanning electron microscopy (SEM) and environmental scanning electron microscopy (ESEM). The results showed that no structural changes could be detected during the first week of dissolution. However, after approximately 4 weeks of dissolution the analysis of the glass surface revealed the presence of a thin orthophosphate layer. The elemental analysis of this layer by X-ray dispersive energy showed the presence of calcium phosphate ions, while almost no sodium was detected. The observation of the glasses by ESEM showed the formation of small crystals when the water vapor pressure of the chamber was decreased. This indicates that the layer analyzed by SEM and FT-Raman was related to a hydrated calcium phosphate layer.

1. Introduction

In the last two decades, phosphate glasses have been considered as potential materials for the repair and reconstruction of bone. Indeed, glasses in the system P_2O_5—CaO—Na_2O have a chemical composition similar to that of the inorganic phase of bone and present the unique property of being completely soluble [1, 2]. Phosphate glasses consist of PO_4 tetrahedra which can be attached to a maximum of three neighboring tetrahedra forming a three-dimensional network as in vitreous P_2O_5. The addition of metal oxide leads to a depolimerization of the network with oxygen atoms breaking the P—O—P links and creating non-bridging oxygens in the glass [3]. However, the modifying cations can provide ionic cross-linking between non-bridging oxygens of two different phosphate chains. Increasing the bond strength of this ionic link can improve the mechanical strength and chemical durability of these glasses. Thus, the properties of phosphate glasses are directly related to their chemical composition leading to an extensive range of materials with different mechanical properties and solubility [4]. The structure of phosphate glasses is usually described by the Q^n groups theory [3]. Q^n groups are PO_4 tetrahedra in which n is the number of bridging oxygen per PO_4 tetrahedron. It is known [5] that phosphate glasses containing nearly 50 mol % of modifying oxides consist mainly of Q^2 groups forming long chains or rings similar to organic polymers and linked by the modifying cations.

Considering the results reported for the dissolution of metaphosphate glasses in water [6], a recent study of the kinetics of dissolution in simulated body fluid (SBF) [7] led to the conclusion that a hydration mechanism at the surface of the glass controls the initial stages. Thus, totally hydrated phosphate chains disentangle from partially hydrated chains still attached to the surface and leach to the solution. The dissolution of the glass is then characterized by the formation of a hydrated layer and the progressive leaching of ions into the solution. The composition of this layer and its structural changes with time have not been determined.

The present study is focused on the analysis of the structural changes at the surface of a calcium–sodium metaphosphate glass during its dissolution in SBF.

2. Materials and methods

Two phosphate glasses in the system P_2O_5—CaO—Na_2O were elaborated using $NH_4H_2PO_4$, $NaCO_3$ and $CaCO_3$ as raw materials. The glasses were obtained by melting on a platinum crucible at a temperature of 1200 °C followed by rapid quenching on a metallic plate preheated to 350 °C. The materials were finally annealed during 30 min at a temperature corresponding to the respective glass transition temperature of the glasses, and then left for 8 h under gradual cooling conditions. The compositions and glass transition temperatures of the glasses are shown in Table I.

TABLE I Chemical composition and glass transition temperature of the glasses studied

Glass	BV-11	BV-f3
Mol% CaO	44.5	35
Mol% Na_2O	11	15
Mol% P_2O_5	44.5	50
T_g (°C)	445	405

Slabs of $5 \times 5 \times 10\,mm^3$ were cut from the glasses obtained with a diamond circular saw and then polished with 0.05 μm alumina particles. Samples were immersed in 25 ml of SBF prepared according to Kokubo [8], at a temperature of 37 °C and kept in polyethylene bottles. At different times, the glasses were removed from the solution and their surface was observed by scanning electron microscopy (SEM) and environmental scanning electron microscopy (ESEM). This latter technique is especially relevant because it allows observation of the samples in wet and in dry state. Energy dispersive X-ray analysis was performed to characterize the elemental composition of the surface of the glass. For SEM and Fourier transform Raman (FT-Raman) spectroscopy analysis, samples were rinsed in distilled water and allowed to dry to constant weight. FT-Raman spectroscopy was performed in the 90° configuration using the 514.5 nm argon ion laser line at frequencies between 300 and 1500 cm^{-1}. For ESEM analysis, samples were rinsed in distilled water and replaced in SBF after analysis. During the study, the solution was renewed weekly in order to prevent the saturation of the fluid.

3. Results

The FT-Raman spectra of BV-11 during the early stage of dissolution are shown in Fig. 1. In this figure, we can observe the spectra of the surface of the glass after 0, 4, 24 and 72 h of dissolution. It can be noticed that no structural changes are detected, as the spectra only showed the characteristic vibrational bands of the metaphosphate glasses: the $(P{=}O)_{sym}$ stretch at approximately 1260 cm^{-1}, the symmetric stretch of a non-bridging oxygen on a Q^2 tetrahedron, i.e the $(PO_2)_{sym}$ mode at 1170 cm^{-1}, and the $(POP)_{sym}$ stretch near 690 cm^{-1} [9]. Bands below about 500 cm^{-1} can be assigned to bending and torsional vibrations while bands at approximately 841 and 918 cm are due to fluorescence. At longer periods of dissolution, the FT-Raman spectra of the surface of BV-11 showed important differences with the reference spectra, indicating that structural changes at the surface of the glass may occur. Fig. 2 shows the spectra of the reference glass BV-11 and the spectra of the surface of the glass after 8 weeks of dissolution. First, it can be observed in this spectra that the intensity of the typical bands of the phosphate glass is highly decreased. Particularly, the decrease in the intensity of the $(PO_2)_{sym}$ band at 1170 cm^{-1} indicates the depolymerization of the glass due to the hydration of the phosphate chains. A new band at approximately 960 cm^{-1} also appeared. As can be observed in Fig. 2, by comparison of this spectra with the spectra of a commercial sintered hydroxyapatite, this band could be assigned to the symmetric stretch of the orthophosphate group PO_4^{3-} [10]. These changes could be detected from approximately 4 weeks of dissolution for both glasses and are related with the observation of a thin layer at the surface of the glass. The presence of this layer can be observed in Fig. 3, showing a SEM micrograph of the surface of BV-11 glass after 8 weeks of dissolution.

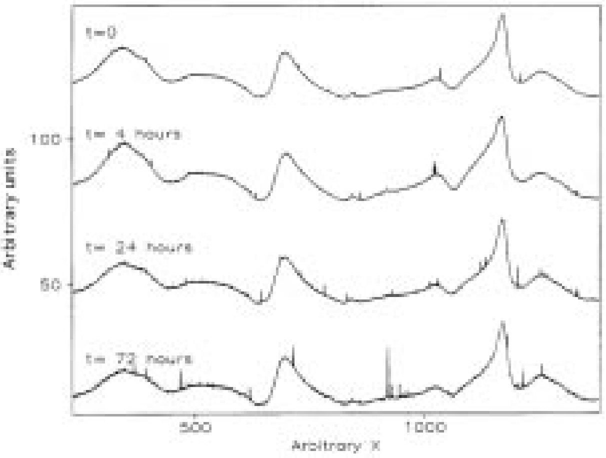

Figure 1 FT-Raman spectra of BV-11 after 0, 4, 24 and 72 h of dissolution in SBF.

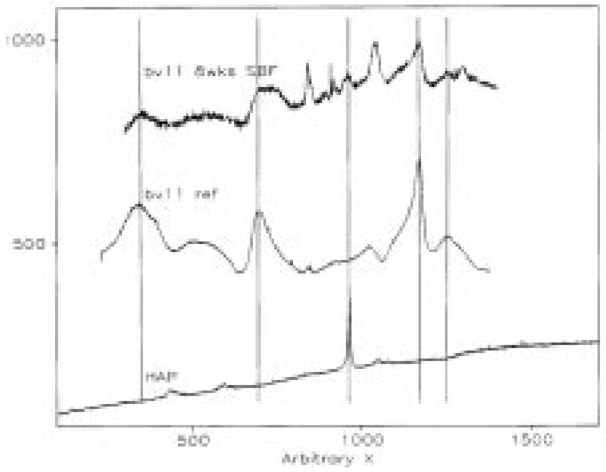

Figure 2 FT-Raman spectra of BV-11 after 0 and 8 weeks of dissolution and of a sintered commercial hydroxyaptite.

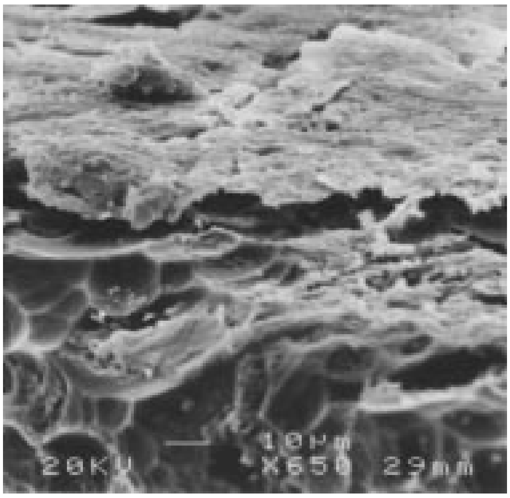

Figure 3 SEM micrograph of the surface of BV-11 after 8 weeks of dissolution in SBF (× 650).

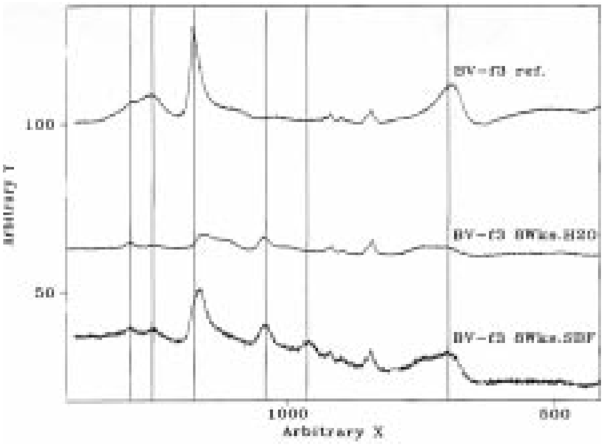

Figure 4 FT-Raman spectra of BV-f3 before dissolution and after soaking for 8 weeks in distilled water and in SBF.

Fig. 4 shows the Raman spectra of BV-f3 before dissolution and after 8 weeks of dissolution for both distilled water and SBF. It can be noticed that the two spectra after 8 weeks of dissolution show important differences compared to the reference spectra. The decrease in intensity of the typical phosphate bands of the glass appeared to be more important for the glass dissolved in water than in SBF, indicating that the dissolution may be more pronounced. On the other hand, the orthophosphate band at 960 cm^{-1} only appeared in the case of the glass dissolved in SBF. This fact indicates that the appearance of this band was related to the dissolution in SBF, and shows that an interaction between the hydrated layer at the surface of the glass and the surrounding medium occurs.

Fig. 5 shows the X-ray analysis of the surface layer of the glass BV-11 after 8 weeks of dissolution. It can be noticed that intense peaks correspond to Ca and P, while no peaks for Na were detected.

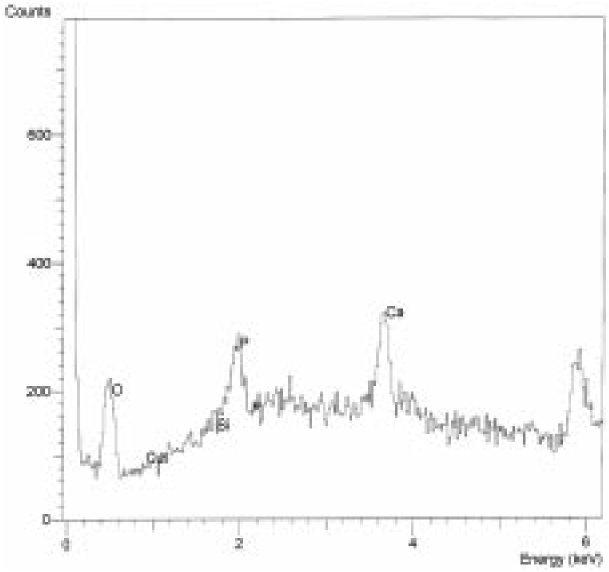

Figure 5 X-ray dispersive energy analysis of the layer on BV-11 after 8 weeks of dissolution in SBF.

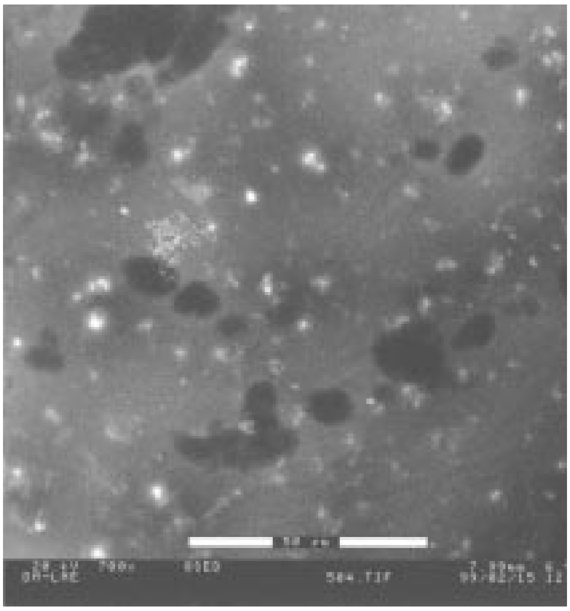

Figure 6 ESEM micrograph showing the wet surface of BV-11 after 20 days of dissolution in SBF.

Figs 6 and 7 show two ESEM micrographs of the surface of a BV-11 sample after soaking for 20 days in SBF. The pictures represent the same area of the glass. The surface of the glass was first observed as retrieved from SBF, as shown in Fig. 6, and then the surface was slowly dried by reducing the vapor pressure in the chamber, as shown in Fig. 7. First, it can be noticed in the two micrographs the presence of small etch pits at the glass surface, indicating the corrosion of the glass. On the other hand, it can be seen in Fig. 7 that small crystallites have precipitated. These crystallites appeared as the humidity of the samples decreased at the surface of the glass. This fact indicates that the layer analyzed in its dry state was related to the formation of a hydrated calcium phosphate.

4. Conclusion

The analysis of the surface changes of the phosphate glasses studied revealed the formation of a hydrated layer

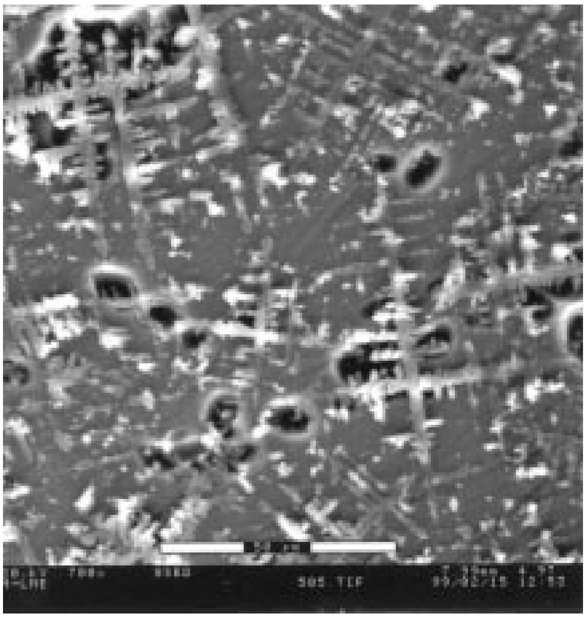

Figure 7 ESEM micrograph showing the dry surface of BV-11 after 20 days of dissolution in SBF (× 700).

as the dissolution proceeds. The Raman spectroscopy and the X-ray analysis showed that this layer was composed of calcium orthophosphate groups. This indicates the formation of an apatitic phase at the surface of the glass. However, this layer could not be assigned to the formation of a hydroxycarbonate apatite layer, as no bands corresponding to the CO_3^{2-} group vibration could be observed during the Raman analysis. The ESEM observations confirmed the hydrated characteristics of the layer. The SBF seemed to play an important role in the formation of this calcium phosphate layer as it could not be detected when the dissolution is carried out in distilled water.

These observations can be related to the mechanisms of dissolution described by Bunker *et al.* [6]. In this work, the formation of a hydrated layer during the dissolution of the glass was demonstrated. Then, the dissolution consists of the leaching of the phosphate chains into the medium. As the dissolution time increases, the concentration of orthophosphate groups of the surrounding medium increases. Thus, in a leaching solution with a high ionic strength, such as SBF, the saturation of the medium will occur rapidly, and may lead to the precipitation of an apatitic phase at the level of the hydrated layer.

Acknowledgments

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