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Bioactivity evolution of calcium-free borophosphate glass with addition of titanium dioxide

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ABSTRACT

The addition of titanium dioxide in the bioactive phosphate glass composition is intended to control the rate of dissolution, but nevertheless, the TiO_2 presence may affect the glass bioactivity. Therefore, in this study the bioactivity response of the calcium-free borophosphate glasses by varying the titania content was evaluated. The glass system belonging to the compositional range $(100 - x)[10B_2O_3 \cdot 30Na_2O \cdot 60P_2O_5] \cdot xTiO_2$, with $0 \leq x \leq 12$ mol%, was obtained by the conventional melt quenching method and the structural changes were assessed by performing X-ray diffraction, Raman and Fourier Transform Infrared measurements. The Raman and Fourier Transform Infrared spectra show the presence of Ti – O – P bonds once the titania was added to the glass composition. This result indicates that structural rearrangements take place in the main phosphate network due to the replacing of P – O – P by Ti – O – P bonds. Regarding in vitro assessment of bioactivity, the results obtained by analysing the information derived from X-ray diffraction, Fourier Transform Infrared, Scanning Electron Microscopy and Energy Dispersive X-ray spectroscopy point out that the increase of titanium dioxide content has as consequence the occurrence of a more pronounced apatite layer. However, in the case of the samples with the highest TiO_2 content, the crystallization of apatite layer does not occur in the first 14 days. The solubility test data indicated a clear decrease of glass solubility for titania amounts of 8 and 12 mol%.

1. Introduction

Titanium alloys and composites containing titanium dioxides are used in orthopaedic and dental applications, due to their good biocompatibility, corrosion resistance and mechanical properties [1–3]. Phosphate-based glasses represent an important group of biomaterials due to their high solubility in aqueous media. The dissolution rate can be tailored by changing the glass composition, thereby the degradation rate varies from hours to several weeks [4–6].

With B_2O_3 addition to batch composition the phosphate network of the glasses becomes bioresorbable [7,8], and the thermal and mechanical durability becomes better than in the case of the pure phosphate glasses [9,10]. However, if the rate of dissolution of a material is too fast, it will be resorbed by passive dissolution in the physiologic fluids without giving rise to tissue remodelling. The addition of TiO_2 in the calcium phosphate glass system resulted in a slower degradation [6]. In this view, Neel et al. [11] and Guedes et al. [12] reported that 5 mol% TiO_2 glass represents the optimal TiO_2 content in terms of biocompatibility, but they did not see evidence of apatite layer formation after immersion in simulated body fluid (SBF). It is known that the formation of a calcium phosphate layer on the material surfaces after immersion in SBF is a marker in the bioactivity assessment [13,14].

The application of bioresorbable materials includes temporary implants, obviating the need for removal surgery [5], and drug delivery systems as they could deliver the drugs within the body in a controlled way [7].

In the previous study conducted by our group it was demonstrated that calcium free borophosphate glasses exhibit bioactive character [15]. In order to assess the degradation rate of the glass, titanium dioxide was added in different molar ratios [6] but, this may affect the material's bioactivity. It was reported that by increasing the TiO_2 content in $CaO–P_2O_5$ glass matrices the bioactivity diminished [16]. Accordingly, the aim of this study is to evaluate the influence of the addition of titania to the $10B_2O_3 \cdot 30Na_2O \cdot 60P_2O_5$ glass composition, in a relatively high amount (0–12 mol%) on samples' bioactivity. In the first step, the structural characterization was performed by involving various techniques such as X-ray diffraction analysis (XRD), Raman spectroscopy and Fourier Transform Infrared (FT-IR) spectroscopy. Further, in vitro bioactivity was evaluated using XRD, FT-IR, Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) spectrometer.

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2. Materials and methods

2.1. Glass formation

The bioactive glasses belonging to the following compositional range: $(100 - x)[10B_2O_3 \cdot 30Na_2O \cdot 60P_2O_5] \cdot xTiO_2$, with x = 0; 1; 4; 8 and 12 mol%, were prepared using as starting materials H_3BO_3, Na_2CO_3, P_2O_5 and TiO_2 of reagent purity grade. The mixtures corresponding to the desired compositions were melted in air, in sintered corundum crucibles, in an electric furnace at 1200 °C for 15 min. The melts were quickly cooled at room temperature by pouring and pressing between two copper plates. Prior characterization the obtained glasses were milled.

2.2. Solubility testing

The solubility of glasses was determined by measuring the weight loss during immersion in deionised water [17]. Measuring the initial weight (M_0) of each sample and the weight (M_t) at time t, the weight loss per unit area was obtained as follows:

$$\text{weight loss}\left[\frac{g}{cm^2}\right] = \frac{M_0 - M_t}{A}.$$

The surface area of the investigated samples was measured before immersion in distilled water. For each sample the exposed surface area to the surrounding liquid was 1 cm^2/ml.

2.3. Assessment of the bioactivity

In order to check the bioactivity, the obtained powders were immersed in SBF in closable conical polypropylene flasks placed in an incubator at a constant temperature of 37 °C under static condition and analysed after immersion for 14 days. The SBF was prepared according to Kokubo's protocol [13]. The solution was buffered at a pH of 7.4 at 37 °C. The SBF was replaced once a week due to the well-known decrease of cation concentration during the course of the experiments as a result of the changes in the chemistry of the samples [18]. The weight of glass per volume of SBF used was 10 mg/ml for each sample. After 14 days the powders were filtrated, rinsed several times with distillate water and dried.

2.4. Methods

2.4.1. X-ray diffraction

The X-ray diffraction analysis was carried out on a Shimadzu XRD-6000 diffractometer using CuKα radiation (λ = 1.54), with an Ni-filter. The diffractograms were recorded in 2θ range from 10° to 80° with a speed of 2°/min.

2.4.2. Near infrared-Fourier Transform-Raman spectroscopy

NIR-FT-Raman spectra were recorded using a Bruker Spectrometer (model RFS 100) equipped with a Neodymium:Yttrium Aluminium Garnet (Nd:YAG) laser, emitting at 1064 nm, and a germanium detector cooled with liquid nitrogen. When sample fluorescence is a problem, which was the case with our samples, 1064 nm FT-Raman analysis with near infrared excitation is frequently the solution. Spectral data of the bioactive glasses were accumulated from 300 scans with a spectral resolution of 2 cm^{-1} in the range of 0–3500 cm^{-1} with a laser power of 800 mW.

2.4.3. FT-IR spectroscopy

The FT-IR absorption spectra were recorded with a JASCO 4100 (Jasco, Tokyo, Japan) spectrometer, at room temperature, in the range of 400–4000 cm^{-1}, and spectral resolution of 4 cm^{-1} using the well-known KBr pellet technique.

2.4.4. Scanning Electron Microscopy

The SEM images were recorded using an FEI Quanta 3D FEG scanning electron microscope operating at an accelerating voltage of 30 kV, equipped with an Energy Dispersive X-ray (EDX) spectrometer. The powders were covered with Au to amplify the secondary electron signal. Energy Dispersive X-ray (EDX) micro-analysis was carried out using the same instrument operating at an accelerating voltage of 30 kV. The EDX analyses were performed on different and big areas (around $200 \times 300\ \mu m^2$) and the recorded values were closed to each other for each measured sample (no more than 5% between the average value and the maximum and minimum values). On each EDX spectrum, a matrix correction method (ZAF correction) was applied. The accuracy of the ZAF corrections of the recorded intensities have a relative standard deviation of a maximum of 2% for major peaks in the spectrum and 5% for a particular minor element peak.

3. Results and discussion

3.1. Structural characterizations

The obtained samples with different titania contents were transparent, but their colour changes, from colourless to light violet, with the addition of TiO_2. The recorded XRD patterns are illustrated in Fig. 1 and show a very broad peak at around 2θ = 22° that confirms the vitreous character of all samples.

Considering the amount of the two glass formers (B_2O_3/P_2O_5: 1/6), it is expected that most of the identified structures to be specific to ultraphosphate glasses ($[P_2O_5]$ > 50 mol%), the matrix of the ultraphosphate glasses mainly consisting of Q_2 and Q_3 tetrahedral units [15,19]. The recorded Raman spectra are presented in Fig. 2 and show two very intense bands at 690 and 1160 cm^{-1} that occur as a result of the symmetric stretching vibrations of P – O – P bonds in Q_2 structural units and to the symmetric stretching vibrations of non-bridging oxygens in Q_2 tetrahedron, respectively [8,15,19–23]. The weak band at 1280 cm^{-1} may be due to the symmetric stretching vibrations of phosphoryl (PO) groups [15,19,22]. The presence of P – O – B bridges is indicated by the signal located around 630 cm^{-1} [15,20,24,25]. With the TiO_2 addition to the batch other Raman bands can be observed at 1310 and 522 cm^{-1} and attributed to the $B-O^-$ stretching vibrations of $B-O^-$ bond in BO_4 units [26] and bending vibrations of P – O bonds, respectively [27,28]. The relative intensities of the signals at 1040, 1010 and 920 cm^{-1} increase as the TiO_2 content becomes higher. The first band is due to the motion of the non-bridging oxygen (PO_3) in Q_1

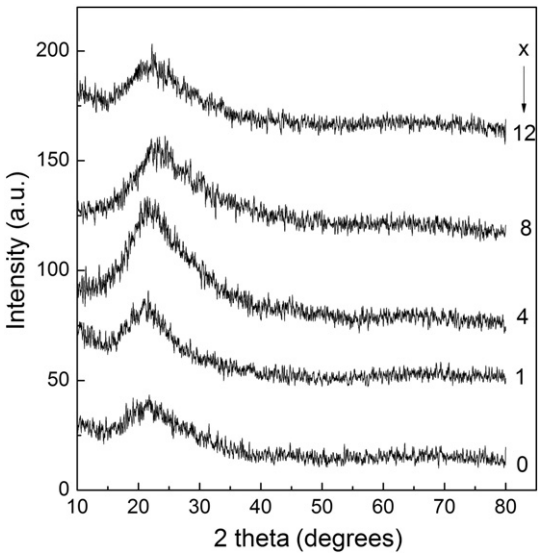

Fig. 1. XRD patterns of the $(100 - x)[10B_2O_3 \cdot 30Na_2O \cdot 60P_2O_5] \cdot xTiO_2$ glass samples.