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Spectroscopic investigation of synergetic bioactivity behavior of some ternary borate glasses containing fluoride anions

A.M. Abdelghany[a,*], H. Kamal[b]

[a]Spectroscopy Department, National Research Center, 12311 Dokki, Cairo, Egypt
[b]Physics Department, Faculty of Science, Mansoura University, Mansoura 35516, Egypt

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Abstract

Ternary borate glasses containing LiF, ZnF_2, NaF or CaF_2 were prepared by full replacement of silica by borate in patented Hench′s bioglass. Prepared samples were examined for their corrosion behavior with the expected final formation of fluoroapatite after immersion in SBF (simulated body fluid). Characterization of the glasses was carried by FTIR (Fourier transform infrared) absorption spectra before and after immersion. DAT (deconvolution analysis technique) was used to identify the formation of fluoroxyapatite from FTIR data after immersion in SBF. X-ray diffraction analyses were done for all samples to identify the crystalline phases that were formed after immersion in SBF and also to determine the degree of crystallinity for each sample. Also, scanning electron microscopic (SEM) investigations were carried out to examine the morphological changes of the surfaces upon immersion and the effects of different individual fluoride additives. The solubility testing for glassy samples was performed and the changes in the pH of the leaching solution were measured and evaluated.

The overall combined spectral and solubility data were compared to evaluate the suitability of the prepared glassy samples to be used as bone bonding materials.

Keywords: Borate bioglasses; FTIR; Corrosion weight loss; Bone bonding; XRD

1. Introduction

Bioactive glass is one that elicits a specific biological response at the interface of the material which results in formation of a chemical bond between the tissues and biomaterial [1,2]. Bioactive glasses have numerous applications in the repair and reconstruction of diseased and damaged hard tissues (bone).

Certain compositions of glasses, glass–ceramics, and ceramics have been widely investigated for healing bone defects, due to their ability to enhance bone formation and to bond to surrounding tissues [3–5]. Hydroxyapatite and tri-calcium phosphate ceramics are biocompatible and produce few systemic toxicity or immunological reactions. However, stoichiometric hydroxyapatite resorbs slowly or undergoes little conversion into a bonelike material after in vivo implantation [6–8]. Day et al. have explored in 2003 [9] and then afterwards extensively studied [10–12] the use of borate glasses in biomedical applications. The potential bioactivity of borate glasses comes from their lower chemical durability and hence convert faster and almost completely to hydroxyapatite (HA) than the widely studied modified soda lime silicate Hench′s patented bioglass (45S5) when placed in the simulated body fluid (SBF).

A Ca–P layer was found to be formed on borate glass surface upon immersion in SBF at 37 °C; this Ca–P layer was formed more rapidly on the borate glass than on Hench 45S5 glass [13]. The formation of the Ca–P layer on the borate glass is believed to follow a set of dissolution–precipitation reactions similar in nature to those in the 45S5 bioactive glass system, but without the formation of a silica-rich gel layer [14]. Essentially, calcium ions dissolve from the glass, and because Ca–P often has the lowest solubility in the system, it precipitates onto the glass surface. Further dissolution of the glass, coupled with precipitation from the surrounding fluid leads to a thickening of the Ca–P layer and the conversion of

*Corresponding author. Tel.: +20 1221133152; fax: +20 2 33370931.
E-mail address: a.m_abdelghany@yahoo.com (A.M. Abdelghany).

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the glass to Ca–P. The ion exchange with the surrounding fluid during the conversion of the bioactive glass to Ca–P may influence cell proliferation and differentiation [14].

The present work reports the preparation of some selected ternary soda lime borate glass with some other glasses containing the substitution of parts of glass constituents by NaF, LiF, CaF_2 or ZnF to find out the effects of such different fluoride species on the bone bonding ability behavior upon immersion in SBF solution. The corrosion weight loss data of the prepared glasses in SBF solution were estimated. Also, the changes in the pH of simulated body fluid (SBF) leaching solution after immersion of the glasses within the leaching solution for a fixed time intervals were measured. A comparative structural characterization through Fourier transform infrared (FTIR) spectroscopic technique of the glasses before and after immersion was carried out to follow up the formation of hydroxyapatite (HA) within the studied samples. Also, scanning electron microscopic investigations of the glassy and crystalline derivatives were done before and after immersion to justify the bone bonding ability of these samples.

2. Experimental procedures

2.1. Preparation of bioactive glasses

Glass samples were prepared by subsequent introduction of B_2O_3 replacing SiO_2 in the patented Henche′s bioglass together with one of the fluoride cations using chemically pure H_3BO_3, $CaCO_3$, Na_2CO_3, CaF_2, ZnF_2, LiF and NaF. Using nominal composition ($45B_2O_3$, 24.5 Na_2O, 24.5 CaO, $6P_2O_5$) some bioglasses were prepared with additional 2% of each fluoride cation which was added separately.

The batches were accurately weighed out and then melted in Pt–2% Rh crucibles using an electric furnace at 1100 °C for 2 h and the melts were rotated two times to achieve homogeneity. Upon complete melting and homogenizing, the melts were cast into a preheated stainless steel mould of the dimensions required. The prepared glass samples were transferred immediately to an annealing muffle furnace adjusted at 380 °C. The annealing muffle after 1 h was left to cool slowly to room temperature at a rate of 25 °C/h.

2.2. X-ray diffraction analysis

The identity of the crystalline phases formed within the samples after immersion was analyzed by X-ray diffraction technique in order to identify the structural changes. The samples were ground and the fine powder was examined using a diffractometer adopting Ni-filter and Cu-target. The X-ray diffraction patterns were obtained using a Philips PW1390 X-ray diffractometer.

2.3. Solubility testing

The solubility of the studied borate glasses was determined by measuring the weight loss after immersion in SBF at human body temperature (37 °C). Samples were polished and refined with 600 girt polishing papers. The sample dimensions were measured accurately and washed in acetone for few minutes and then the sample was placed in a polyethylene beaker containing pre-calculated volume of SBF (ratio between geometric area of the glass sample and volume of the solution was fixed as 0.075 cm^{-1} in all cases for comparison and to avoid defects resulting from volumetric or supersaturation differences [15]). Samples were removed and excess moisture was removed by tissue paper at various time intervals and then reweighed. After immersion, the materials started to dissolve and the same was registered for every 24 h, until the end of 480 h. By knowing the initial weight (M_0) of each sample and the weight loss (M_t) at time t, the % of weight loss per unit area was obtained as:

$$\%\ \text{of weight loss} = \frac{M_o - M_t}{A} \times 100 \quad (1)$$

where A is the surface area in cm^2.

A regression method used for data fitting and dissolution rates in g m^{-2} h^{-1} was calculated according to the formula:

$$D_{rate} = (\text{slope} \times M_0/A) \quad (2)$$

where D_{rate} is the dissolution rates, M_0 is the initial weight and A is the surface area in cm^2

2.4. pH measurements

The pH changes for the attacking leaching solution after intervals were measured using a pH meter (pH 3L5i Germany). The measurements were conducted up to 480 h for the leaching solution at a time interval of 24 h for solubility studies. The percentage of error in the measurement of pH is ± 0.005 and calibration of the electrode against buffer solution was performed every 12 h. The same procedure was adopted by some authors [16]

2.5. FTIR measurements

Fourier transform infrared absorption spectra of the studied borate glasses were measured at room temperature (20 °C) in the wavelength range 2000–400 cm^{-1} using a computerized recording FTIR spectrometer (Mattson 5000, USA). Fine powdered samples were mixed with KBr in the ratio 1:100 for quantitative analysis and the weighed mixtures were subjected to a load of 5 t/cm^2 in an evocable die to produce clear homogenous discs. Then, the IR absorption spectra were immediately measured after preparing the discs to avoid moisture attack. The FTIR measurements were repeated after the samples were immersed in SBF.

2.6. Surface structural analysis using scanning electron microscopy

Scanning electron microscopic (SEM) investigations were performed on glass samples at room temperature using an SEM model Philips XL30 attached with EDX unit, with accelerating voltage 30 kV, magnification up to 400,000. All surfaces of studied samples were coated with gold for morphological investigations.