Journal of Optoelectronics and Advanced Materials Vol. 7, No. 6, December 2005, p. 2827 - 2830

COREM COMPOSITE MATRIX BEHAVIOUR IN SIMULATED BODY FLUID

A. Griciuc, T. Popescu-Negreanu[a], R. Grecu[b], V. Simon*

Babes-Bolyai University, Faculty of Physics, 400084 Cluj-Napoca, Romania
[a]PONETI, 031307 Bucuresti, Romania
[b]Raluca Ripan Institute of Chemistry, 400294 Cluj-Napoca, Romania

This paper investigates the physical properties of the bioactive Corem composite matrix mainly consisting of fluorohydroxyapatite, wollastonite and collagen, as an effective scaffold material for bone restoration. Optical micrographs show the material building before and after immersion in simulated body fluid. X-ray diffraction patterns reveal the preponderance of hydroxyapatite and wollastonite crystalline phases. The functional silicate and phosphate groups were identified by Fourier transform infrared spectroscopy.

(Received August 22, 2005; accepted November 24, 2005)

Keywords: Hydroxyapatite, Wollastonite, Simulated body fluid, Microstructure

1. Introduction

Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, belongs to a family of isomorphic minerals called apatites, with practically identical crystallographic structure. Hydroxyapatite (HA) is an important biomaterial and is the principal inorganic constituent of bones and teeth. There is a great demand of this material in odontology and traumatology [1], together with others materials of the same family. Due to the biocompatibility of synthetic hydroxyapatite, it is used in the reconstruction of damaged bone or tooth zones. The inorganic part of bone consists in an amorphous phase of tricalcium phosphate, and a crystalline phase of HA with nanometric crystal sizes, while in the enamel of teeth, containing a 95% of HA, the crystals are bigger but still with submicrometric sizes. HA also finds applications in manufacturing of biocompatible ceramics.

The concept of bioactive materials defines a class of materials having ability to form tight chemical bonds with living bone. They are intermediate between resorbable and bioinert materials [2,3]. Composite matrix Corem is a scaffold obtained by lyophilisation and consists of type I collagen and PAW1 bioglass-ceramic granules. This biomaterial is used in stomatology, orthopaedy and neurosurgery for bone repair by direct filling of defects and support for bone cells culture [4].

In this work are investigated physical properties of composite matrix Corem before and after interaction with a simulated body fluid, keeping in mind the highly reactive physiological environment *in vivo*.

2. Experimental

The Corem composite matrix contains 40-80% bioglass-ceramic PAW1 powder and 20-40 % type I collagen. Bioglass-ceramic PAW1 consists in micro-crystalline fluorohydroxyapatite, $Ca_{10}(PO_4)_6(OH)F$, and wollastonite, $CaSiO_3$, phases dispersed into vitreous SiO_2-CaO-MgO phase. PAW1 is obtained from a glass powder of SiO_2-CaO-MgO-P_2O_5 system.

---

* Corresponding author: viosimon@phys.ubbcluj.ro

The Corem sponge sample was immersed in simulated body fluid (SBF) for several periods at 37 ^{o}C. X-ray diffraction patterns and optical micrographs were recorded before as well as after soaking in SBF.

The microstructure on randomly selected areas was observed with a stereo optical Nikon microscope. X-ray diffraction analysis (DRX) was carried out on a Bruker Avance diffractometer. The IR spectra were recorded on a FT/IR-610 JASCO spectrometer at room temperature in the wavenumbers range from 400 to 4000 cm^{-1} using the KBr disk technique.

3. Results and discussions

The X-ray diffraction pattern of the samples before immersion in SBF (Fig. 1a) confirms the presence in the Corem matrix of well developed crystalline phases of wollastonite and hydroxyapatite (HA) type. The main diffraction peaks [1,5] of HA appears at 2θ values of 25.9° for reflection (002), at 31.9° (triplet) for reflections (211), (112) and (300), and at 34.0° for reflection (200) while for wollastonite the main diffraction peaks occur at 27.7, 29.2 and 33.5°. Diffraction lines occurring at 2θ = 33.1^{O} are assigned to calcium phosphate silicate crystals.

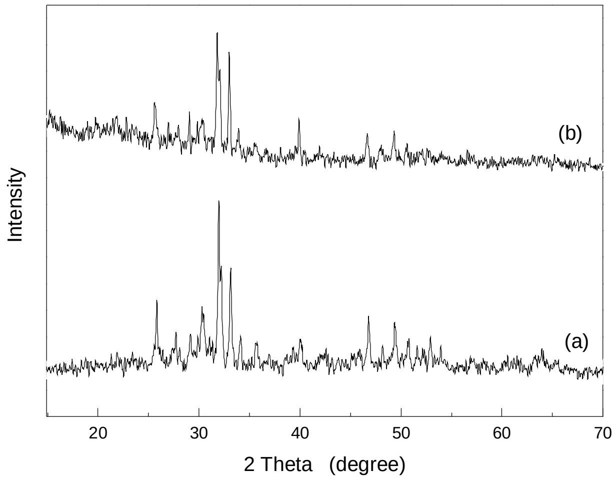
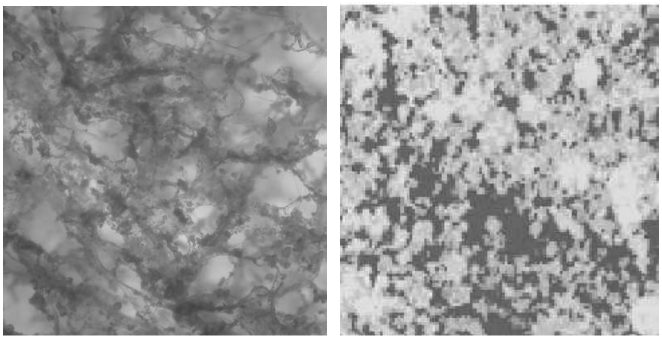


Fig. 1. DRX patterns before (a) and after five days soaking (b) in SBF.



(a) (b)

Fig. 2. Optical microscopy images (a) before and (b) after five days soaking in SBF.

The microscopic image before SBF immersion (Fig. 2a) evidences both collagen and glass-ceramic components. After five days immersion in SBF the collagen peeled away (Fig. 2b). With reference to the triplet peaks occurring around 2θ=32°,

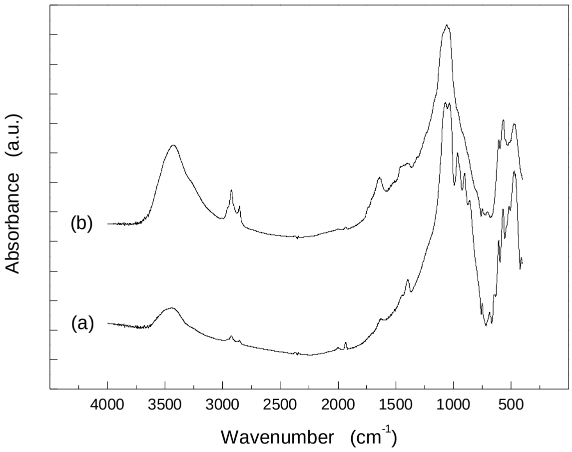


Fig. 3 FTIR spectra recorded from (a) bioglass-ceramic PAW1 unexposed to SBF and (b) from Corem matrix after 27 days exposure to SBF.

it may be seen a different preponderance of the three directions in the SBF reacted samples (Fig. 1b). This means that the orientation of the crystalline particles is more or less aligned to a certain direction. At the same time on the surface of the soaked bioglass-ceramic is formed a thin silica gel layer that provides favourable sites for HA nucleation, which is in agreement with the data reported by Kokubo [6]. The role of apatite crystals is critical for bone formation as well as it is an inhibition for bone resorption too [7]. It is also known that proteins bind to the apatite crystal surface of the ceramic favouring secondary nucleation, thereby affecting the dissolution and reprecipitation process on the ceramic [5].

The FTIR spectra (Fig. 3) show the presence in bioglass-ceramic PAW1 of different functional groups entering the phosphate and silicate structural units. A first indication by inspecting of the two spectra is that after SBF soaking the crystallinity is diminished, the absorption lines become larger or some of them are not more resolved. This result could be due also to the thin silica gel layer formed on glass-ceramic grains. The broad IR absorption bands between 2700 - 3400 cm^{-1} are due to OH stretching vibrations. The bands at 1066 cm^{-1} could be assigned to Si-O-Si(P) bonds vibrations, that centred around 1032 cm^{-1} to P-O stretching vibrations, while the bands under 1000 cm^{-1} are assigned to deformation vibrations of phosphate and silicate units. The peak around 471 cm^{-1} is assigned to Si–O–Si bending vibration [5]. Biological mineralization [8] generally incorporates both substitutions of HPO_4^{2-} into the hydroxyapatite structure for hydroxyl ions (A type apatite) and for PO_4^{3-} groups (B type apatite).

4. Conclusions

The collagen phase of composite matrix Corem immersed in simulated body fluid peels away after five days. The remained mineral phase consists of the same crystalline components of Corem matrix, but a larger amount of granules covered with a thin silica gel layer is observed. This provides favourable sites for HA nucleation.

References

[1] R. Z. Legeros, in: Calcium Phosphates in Oral Biology and Medicine, **15**, ed. H. M. Myers, Karger, Basel 1991, p. 4.

[2] L. L. Hench, in Bioceramics: Materials Characteristics Versus In Vivo Behavior, **523**, eds. P. Ducheyne and J. Lemons. Annals N.Y. Acad. Sci. 1988.
[3] V. Simon, Fizica Biomaterialelor, Presa Universitara Clujeana, 2002.
[4] D. Antonescu, T. Negreanu, M. Popescu, G. Stoica, St. Cristea, O. Vulpe, T. Ursu, Spitalul, **3**, 1 47 (1996).
[5] S. Abiraman, H. K. Varma, T. V. Kumari, P. R Umashankar, A. John, Bull. Mater. Sci. **25**(5), 419 (2002)
[6] T. Kokubo, in AW Glass-Ceramic, ed. by T Yamamuro, Kyoto, 1994, p 22-35.
[7] S. A. Nesbitt, M. A. Horton, Science **276**, 266 (1997)
[8] L. Lacout, in Biomaterials—Hard tissue repair and replacement, ed. D Muster, Amsterdam, Elsevier Science Publishers, 1992, p. 81.