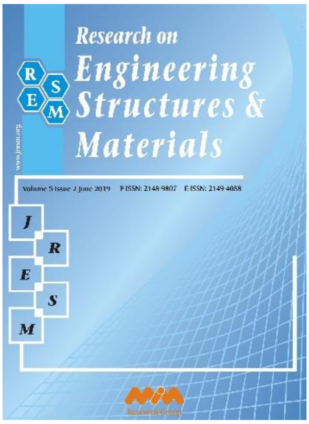
Research on
Engineering
Structures & Materials
journal homepage: http://jresm.org

RESEARCH
GROUP



Production and characterization of ternary sheep hydroxyapatite (SHA)-wollastonite (W)-commercial inert glass (CIG) biocomposite

Nermin Demirkol, Merve Turan

Online Publication Date: 25 Feb 2019
URL: http://dx.doi.org/10.17515/resm2018.68is0919
DOI: http://dx.doi.org/10.17515/resm2018.68is0919

Journal Abbreviation: *Res. Eng. Struct. Mat.*

To cite this article

Demirkol N, Turan M. Production and characterization of ternary sheep hydroxyapatite (SHA)-wollastonite (W)-commercial inert glass (CIG) biocomposite. *Res. Eng. Struct. Mat.*, 2019; 5(2): 167-174.

Research on Engineering Structures & Materials
journal homepage: http://jresm.org
Research Group

Research Article

Production and characterization of ternary sheep hydroxyapatite (SHA)-wollastonite (W)-commercial inert glass (CIG) biocomposite

Nermin Demirkol[*,a,1,2], Merve Turan[b,2]

[1]*Ceramic, Glass & Tile Program, Kocaeli University, Kocaeli, Turkey*
[2]*Department of Biomedical Engineering, Kocaeli University, Kocaeli, Turkey*

Article Info

Article history:
Received 19 Sep 2018
Revised 27 Jan 2019
Accepted 7 Feb 2019

Keywords:

Sheep bone;
Hydroxyapatite;
Mechanical Properties;
Composite;
Commercial Inert Glass;
Wollastonite

Abstract

Hydroxyapatite [HA] is the most widely accepted biomaterial for the repair and reconstruction of bone tissue defects. It has all the characteristic features of biomaterials such as biocompatible, bioactive, osteoconductive, nontoxic, non-inflammatory and non-immunogenic properties. It has low mechanical properties for load bearing applications. HA must be reinforced with other ceramics or metals to produce more load resistible composites. HA also can be produced from natural materials such as bovine, sheep, chicken, human bones, fish bones with simple calcination method. In this study, 5 wt% wollastonite and 5 wt% commercial inert glass were added to sheep hydroxyapatite together to improve mechanical properties. Mechanical properties of composite increased with increasing sintering temperature. The highest Vickers microhardness and compression strength values were obtained with SHA-5 wt% wollastonite- 5 wt % CIG composite sintered at 1300ºC as 197 HV and 94 MPa, respectively.

1. Introduction

Hydroxyapatite [HA; $Ca_{10}(PO_4)_6(OH)_2$] is biocompatible and bioactive material. It is replaced over a period of time. HA and its composites due to their absorption ability and biocompatibility are of interests for application in medicine [1,2]. However, the mechanical properties of HA are not good enough to be used as an implant in load-bearing applications. There have been many investigations aimed at improving the mechanical properties of HA, like preparing them as composite materials. Addition of second phase ceramic materials (e.g. alumina, titania) into HA matrix for enhancing strength has been an interesting research field in recent years. Wollastonite ($CaSiO_3$) generally has been used as a reinforcement phase to produce composites with improved mechanical properties. It has also been used as a biomaterial for artificial bones and dental roots because of its good biocompatibility and bioactivity [3].

Demirkol [4] examined the physical and mechanical properties of hydroxyapatite-wollastonite-titania composites. Lin [5] et. all. worked on fabrication and characterization of hydroxyapatite/wollastonite composite bioceramics with controllable properties for tissue repair. In their study, the hydroxyapatite/wollastonite ($Ca_{10}(PO_4)_6(OH)_2/CaSiO_3$, HA/CS with different weight ratio were fabricated. The effects of composite ratio on sintering behavior, microstructure, mechanical properties, bioactivity, degradability behavior and the bone marrow mesenchymal stem cells (MSC) response to the composites were investigated. When the weight ratio of CS increased, the linear shrinkage of the

---

*Corresponding author: nermin.demirkol@kocaeli.edu.tr
[a]orcid.org/0000-0001-9088-023X; [b]orcid.org/0000-0002-9531-594X;
DOI: http://dx.doi.org/10.17515/resm2018.68is0919

ceramics decreased, while the porosity increased. Due to high porosity, mechanical properties of composite decreased. Harabi et.all. [6] prepared highly resistant wollastonite bioceramics using local raw materials. In their study, wollastonite-based ceramics were obtained by solid state reaction. The starting powders were sintered at different temperatures (850-1250°C) for 2 h. Moreover, different amounts of B_2O_3 (0.5-5.0 mass %) have been added. A relative density of about 97% of the theoretical was reached for samples sintered at 1050°C for 2 hours, containing 3 and 5 mass % B_2O_3. Excellent values of both three-point flexural strength (343±34 MPa) and micro hardness (4.8 GPa) for samples containing 5 mass % B_2O_3 sintered at 1050°C for 2 h. Besides this a relatively low mass loss ratio has been measured (1.1 %) for wollastonite samples containing 5 mass % B_2O_3, sintered under the same conditions, after soaking in lactic acid for 9 days. Finally, the bioactivity of wollastonite by the possibility of formation of apatite on the surface of wollastonite immersed in simulated body fluid was confirmed.

Glass compositions would be a good idea for doping apatite matrix. Demirkol [7] et. all. investigated influence of commercial inert glass addition on the mechanical properties of commercial synthetic hydroxyapatite (CSHA). In their study, CSHA powders were mixed with 5 and 10 wt.% CIG separately. The powder portions were pressed at 350 MPa between hardened steel dies. Pressed samples were sintered between 1000°C and 1300°C for 4 h. The physical and mechanical properties were determined by measuring density, compression strength, the Vickers microhardness. Structural characterization was carried out with X-ray diffraction and scanning electron microscopy studies. The highest mechanical properties and the highest density were obtained in CSHA-5 wt.% CIG composite sintered at 1300°C. Rocha [8] et. all. worked on production and characterization of hydroxyapatite/niobo phosphate glass scaffold for bone repair. The scaffolds were produced by hydrothermal deposition of monetite on polyurethane sponge substrates, further converted to hydroxyapatite in an alkali solution. In their study, after heat treatment, elimination of the organic sponge provides a three-dimensional (3D) structure. Niobo-phosphate glasses were added to the heat treated struts and the scaffolds were sintered. The samples incorporated with niobo phosphate glass showed a higher densification of the interconnections, when compared to samples without glass. This result may determine the development of an interface more resistant to the forces subjected on these scaffolds. Salman [9] et. all. investigated the sintering effects and mechanical properties of bovine hydroxyapatite-commercial inert glass composites. In their study, bovine hydroxyapatite containing 5 wt% CIG and 10 wt% CIG biocomposites were produced at different sintering temperatures, separately. Addition of glass components into the HA structure in small quantities is very popular for improving sinterability and improving the mechanical performance of HA biomaterials.

The objective of this study was to produce and to characterize ternary sheep hydroxyapatite (SHA)-wollastonite (W)-commercial inert glass (CIG) biocomposite for orthopedical applications.

2. Materials and Methods

In this study, materials and methods part includes experimental studies and characterization of ternary sheep hydroxyapatite (SHA)-wollastonite (W)-commercial inert glass (CIG) biocomposite.

2.1. Experimental Studies

The SHA used in this study was prepared from calcinated sheep bones. Firstly, fresh cut femurs were deproteinized with NaOH and after reirrigation the samples were subjected to calcination at 750°C. Then calcinated sheep bones were wet ball milled for 24 hours and they were dried at the drying oven. Mean particle size of obtained SHA powders were 10 µm. The SHA powder was mixed with 5 wt% wollastonite (W) and 5 wt% commercial inert glass (CIG) for 4 h together. Used wollastonite was obtained from Eczacibasi Company. The samples were prepared according to a British Standard for compression tests. The samples were pressed at 350 MPa because this is a British standard for the preparing mechanical test samples for bioceramic and ceramic materials (BS 7253) [10]. The powder portions were pressed at 350 MPa between hardened steel dies. Pressed samples sintered at different temperatures between 1000°C and 1300°C (with the heating rate of +5°Cmin^{-1}) for 4 h (Ozmak Furnaces, Istanbul, Turkey). According to my former studies and some literatures 4 hours sintering time is sufficient and suitable for this kind of biocomposite materials [7, 9].

2.2. Characterization

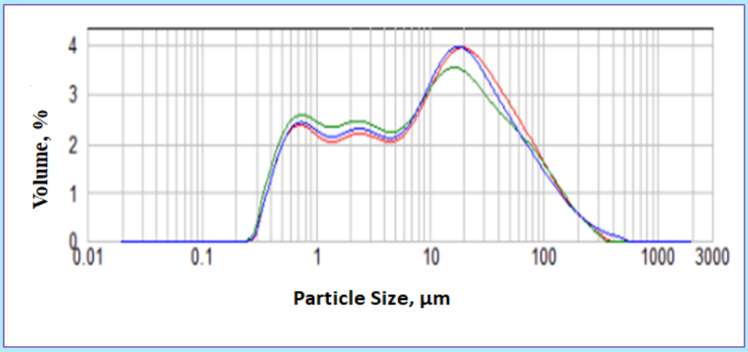
Chemical analysis of used commercial inert glass was determined by XRF. Compression strength, Vickers microhardness, as well as density were measured. The density of composites was gauged with the Archimedes method. Scanning electron microscopy (SEM) was used to characterize the microstructure of the composite. Scanning electron microscopy (SEM) images were taken with scanning electron microscope (FEI NovaNanoSEM650 attached with EDAX Trident System). The compression tests were done with a universal test apparatus, at the crosshead speed of 3 mm/min. Microhardness values were determined under 200 g load for 15 s (HMV Shimadzu JP).

3. Results and Discussion

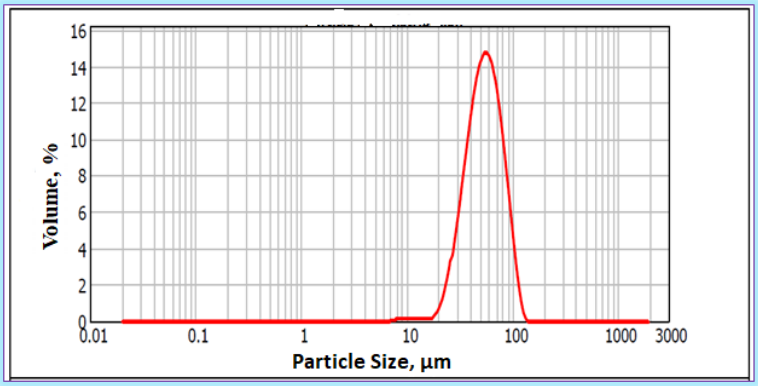
Table 1 Chemical Analysis of Used Commercial Inert Glass (CIG).

Oxide	**wt%**	**Oxide**	**wt%**
SiO_2	68.80	TiO_2	0.017
Na_2O	17.02	Al_2O_3	2.15
CaO	9.25	Cr_2O_3	0.012
MgO	1.77	CuO	0.0036
Fe_2O_3	0.084	Others	Trace

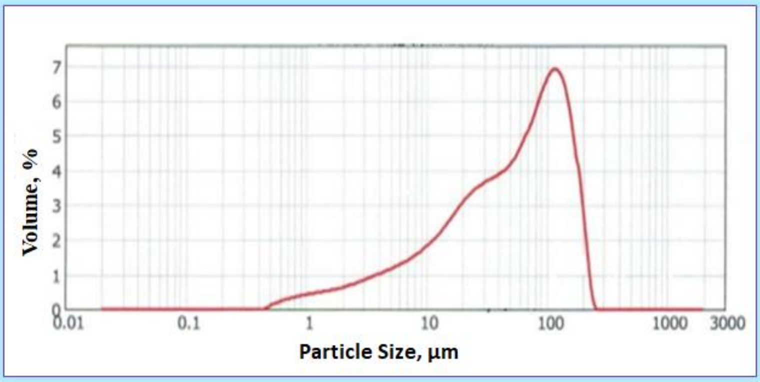
Table 1 shows the chemical analysis results of used commercial inert glass (CIG). Quartz is the major element as expected. Used CIG is typically soda lime silica window glass.



(a)



(b)



(c)

Fig. 1 Particle size distribution of (a) used sheep hydroxyapatite(SHA) (b) used wollastonite (W) (c) used commercial inert glass (CIG) [11].

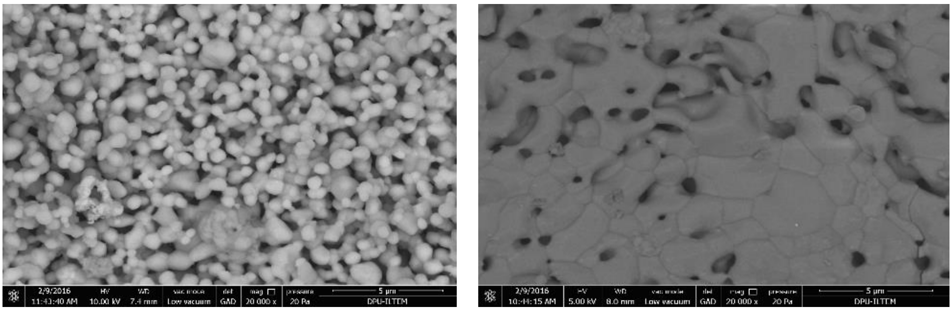
Figure 1 exhibits the particle size distribution of used raw materials in this study. Demirkol [11] determined the mean particle sizes of used raw materials in her former study. The mean particle sizes of sheep hydroxyapatite, wollastonite and commercial inert glass are 10, 65 and 68 µm, respectively.

Table 2 Density, compression strength and Vickers microhardness results of SHA-5W5CIG biocomposite sintered at different temperatures.

Sintering Temperature (°C)	Density (g/cm^3)	Compression Strength (MPa)	Vickers Microhardness (HV)
1000	2,38±0,05	58±8,10	77±4,81
1100	2,57±0,11	72±5,70	101±5,75
1200	2,73±0,22	81±9,93	181±8,93
1300	2,81±0,15	94±4,88	197±9,97

Table 2 summarizes the experimental results of density, compression strength and the Vickers microhardness of the samples sintered at different temperatures.

Density, compression strength and Vickers microhardness values increased with increasing sintering temperatures. As seen as also Bulut [12] et. all.'s study with increasing sintering temperature, the density of the composite increased while their porosity decreased. The highest density, compression strength and Vickers microhardness values were obtained with SHA-5W5CIG biocomposite sintered at 1300°C as 2,81 g/cm^3, 94 MPa and 197 HV, respectively.



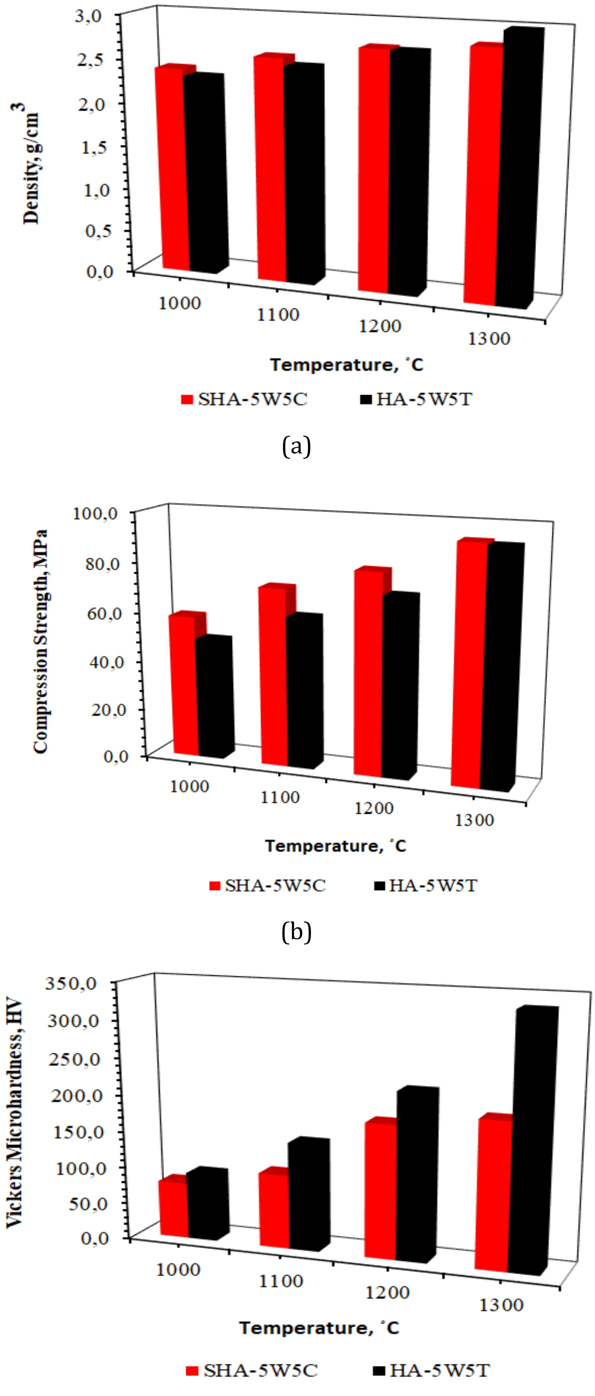
(a) (b)

Fig 2. SEM micrographs of SHA-5W5C biocomposite sintered at (a) 1000°C and (b) 1300°C

Figure 2 exhibits the scanning electron microscopy photos of SHA biocomposites containing 5 wt% wollastonite and 5 wt% commercial inert glass (SHA-5W5C) sintered at 1000 and 1300°C.

When Figure 2a compared with Figure 2b, grain growth occurred and amount of porosity is also decreased with increasing sintering temperature. The composite sintered at 1300°C is more compact than the composite sintered at 1000°C.

Bulut [12] et. all investigated biocompatibility of hydroxyapatite-alumina and hydroxyapatite-zirconia composites including commercial inert glass (CIG) as a ternary component. In their study, grain growth occurred with increasing sintering temperature similar to this study.



(a)

(b)

(c)

Fig 3. Comparison of (a) density (b) compression strength (c) Vickers microhardness of SHA-5W5C and HA-5W5T composites sintered at different temperatures

Demirkol [4] investigated physical and mechanical properties of commercial synthetic hydroxyapatite (CSHA)-wollastonite-titania composites. In her study, CSHA-2.5 wt% wollastonite-2.5 wt. % titania and CSHA-5 wt% wollastonite-5 wt. % titania (HA-5W5T) composites prepared and sintered at 1000-1300**°C.** The physical and mechanical properties were determined by measuring density, compression strength and Vickers microhardness (HV). Density, compression strength and Vickers microhardness results of SHA-5W5C and HA-5W5T biocomposites sintered at different sintering temperature were compared in Figure 3.

As can be seen in Fig. 3, density, compression strength and Vickers microhardness results of both composites increased with increasing sintering temperature. Both addition of 5 wt.% titania and 5 wt.% commercial inert glass to hydroxyapatite containing 5 wt.% wollastonite showed similar compression strength value with the samples sintered at 1300°C. But, Vickers microhardness values of HA-5W5T composites higher than SHA-5W5C composites for all sintering temperatures. As a result in this study, increasing the temperature resulted in higher compression strength and density for 5 wt% glass addition to SHA-W composite similar to Oktar et.all's study [13].

Titania also improves the biocompatibility properties like commercial inert glass [14].

5. Conclusion

In this experimental study; 5 wt% wollastonite and 5 wt% commercial inert glass were added to sheep hydroxyapatite together to improve mechanical properties. From the results of this study, the following conclusions can be drawn:

- Commercial inert glass (CIG) and wollastonite (W) are suitable for making hydroxyapatite biocomposite with high mechanical properties.
- Density, compression strength and Vickers microhardness values increased with increasing sintering temperature.
- Porosity level of SHA-5W5C decreased with increasing sintering temperature. The compact structure was obtained with the biocomposite sintered at 1300°C.
- The highest density, compression strength and Vickers microhardness values were obtained with SHA-5W5C composite sintered at 1300°C as 2,81 g/cm^3, 94 MPa and 197 HV, respectively.
- Addition of 5 wt.% wollastonite and 5 wt.% CIG to sheep hydroxyapatite increases the density, compression strength and Vickers microhardness values up to 8,49%, 36,23% and 19,39%, respectively.
- Addition of 5 wt% CIG to SHA-5 wt% wollastonite increases the compression strength value as well as 5 wt% titania addition to HA-5 wt% wollastonite with the composite sintered at 1300°C.
- Titania addition to hydroxyapatite- wollastonite composite increases the Vickers microhardness more than commercial inert glass (CIG) addition to hydroxyapatite-wollastonite composite.
- While wollastonite improves the mechanical properties, commercial inert glass (CIG) improves both mechanical properties and bioactivity.
- Using natural sources hydroxyapatite (sheep, fish, chicken, bovine bones etc.) is more economic than the synthetic hydroxyapatite.
- Biocompatibility studies are going on.
- Sheep hydroxyapatite-5W5C composite will be a good candidate for orthopedical applications after biocompatibility test results.

References

[1] Stipniece L. Salma-Ancane K. Putnins A. and Berzina-Cimdina L. Evaluation of Sr-and/or Mg-containing Hydroxyapatite Behavior in Simulated Body Fluid, Key Engineering Materials, 2015; 631: 61 – 66. https://doi.org/10.4028/www.scientific.net/KEM.631.61

[2] Skwarek E. Bolbukh Y. Janusz W. and Tertykh V. Hydroxyapatite Composites with Multiwalled Carbon Nanotubes. Adsorption Science & Technology, 2017; 35(5-6): 534 – 544. https://doi.org/10.1177/0263617417700637

[3] Encinas-Romero MA. Aguayo-Salinas S. Valenzuela-Garcia JL. Payan SR. and Castillon-Barraza FF. Mechanical and Bioactive Behavior of Hydroxyapatite-Wollastonite Sintered Composites. Int, J. Appl. Ceram. Technol., 2010; 7(2): 164-177. https://doi.org/10.1111/j.1744-7402.2009.02377.x

[4] Demirkol N. Physical and Mechanical Properties of Hydroxyapatite-Wollastonite-Titania Composites. Journal of Turkish Ceramic Federation, 2016; 49: 102-109.

[5] Lin K. Zhang M. Zhai W. Qu H. Chang J. Fabrication and Characterization of Hydroxyapatite/Wollastonite Composite Bioceramics with Controllable Properties for Hard Tissue Repair. Journal of the American Ceramic Society, 2011; 94(1): 99-105. https://doi.org/10.1111/j.1551-2916.2010.04046.x

[6] Harabi A. Chehlatt S. Preperation Process of a Highly Resistant Wollastonite Bioceramics Using Local Raw Materials. Journal of Thermal Analysis and Calorimetry, 2013; 111(1): 203-211. https://doi.org/10.1007/s10973-012-2242-5

[7] Demirkol N. Oktar F.N. Kayali E.S. Influence of Commercial Inert Glass Addition on the Mechanical Properties of Commercial Synthetic Hydroxyapatite. Acta Physica Polonica A, 2013; 123(2): 427-429. https://doi.org/10.12693/APhysPolA.123.427

[8] Rocha D.N. Oliveira Cruz L.R. Prado Neto J.L. Elmassalami Ayad N.M. Gobbo L.A. and Silva M.H.P. Production and Characterization of Hydroxyapatite/Niobo Phosphate Glass Scaffold. Key Engineering Materials, 2014; 587: 128-131. https://doi.org/10.4028/www.scientific.net/KEM.587.128

[9] Salman S. Oktar F.N. Gunduz O. Agathopoulos S. Ovecoglu M.L. Kayali E.S. Sintering Effect on Mechanical Properties of Composites Made of Bovine Hydroxyapatite(BHA) and Commercial Inert Glass (CIG). Key Engineering Materials, 2007; 330-332: 189-192. https://doi.org/10.4028/www.scientific.net/KEM.330-332.189

[10] British Standard Non-metallic materials for surgical implants. Part 2. Specification for

[11] Demirkol N. Production and Characterization of Sheep Hydroxyapatite Composites, Yalın Publication, 2016; 59-62.

[12] Bulut B. Erkmen Z.E. Kayali E.S. Biocompatibility of Hydroxyapatite-Alumina and Hydroxyapatite-Zirconia Composites Including Commercial Inert Glass (CIG) as a Ternary Component. J. Ceram. Sci. Tech. 2016; 07[03]: 263-276.

[13] Oktar FN. Goller G. Sintering Effects on Mechanical Properties of Glass-Reinforced Hydroxyapatite Composites. Ceramics International. 2002; 28: 617-621. https://doi.org/10.1016/S0272-8842(02)00017-2

[14] Sidane D. Rammal H. Beljabbar a. Gangloff S.C. Chicot D. Velard F. Khireddine H. Montagne A. Kerdjoudj H. Biocompatibility of Sol-Gel Hydroxyapatite-Titania Composite and Bilayer Coatings. Materials Science and Engineering: C, 2017; 72: 650-658. https://doi.org/10.1016/j.msec.2016.11.129