INVESTIGATIONS REGARDING STRUCTURAL CHARACTERISTICS OF SOME CERAMIC POWDERS HEAT-TREATED AT LOW TEMPERATURES

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Abstract. *Hydroxyapatite is one of the most widely used ceramic biomaterials in medical applications. This is due to the similarity in terms of chemical structures with mineal structures from the body tissue (teeth and bone). In this paper experimental results are presented in case of hydroxyapatite powders synthesized by chemical coprecipitation, after applying a heat treatment at low temperature. X-ray diffraction, Fourier transform infrared spectroscopy, particle size distribution analysis, as well as the morphology of the powders - all these investigations have revealed the synthesis of a material with appropriate characteristics clinical applications that might serve later.*

Keywords: *hydroxyapaite, XRD, Fourier transform infrared spectroscopy, scanning electron microscopy*

1. INTRODUCTION

Hydroxyapatite is one of the most studied ceramic materials with medical applications in the reconstruction and regeneration of bone structures, for which researchers have shown great interest since the 1970s. The varieties of technological routes by which the material can be synthesized are many, from the processing of hard tissue of mammals or coral [1, 2] to laboratory synthesis [3-5] (chemical co-precipitation method, the solid state synthesis reactions, hydrothermal methods, sol-gel processes etc.).

Thus, this material can be obtained in the form of powders and used in well established conditions or can be used as a coating on various substrates made by biocompatible alloys such as the stainless steel (316L) [6], Co - Cr alloys, pure titanium or titanium alloy (TiAl4V6). At the same time have been developed a series of biocomposite such as collagen - hydroxyapatite [7], polyethylene - hydroxyapatite, polymethyl-methacrylate - hydroxyapatite, polylactic acid - hydroxyapatite [8] etc.

2. SYNTHESIS METHOD

Hydroxyapatite synthesis was made by chemical co-precipitation, in accordance with the technological process described in other papers [9, 10]. The precursors used were calcium hydroxide and orthophosphoric acid. The chemical reaction behind this synthesis is as follows:

$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O$$

Raw materials and technological parameters involved in synthesis of hydroxyapatite powders are presented in Table 1.

Table 1. Raw materials and technological parameters used in hydroxyapatite synthesis

Raw materials	**Concentration**, [M/l]
Calcium hydroxide	0,3
Ortophosphoric acid	0,18
Technological parameters	
Temperature synthesis, [^oC]	60
Acid addition rate, [ml/min.]	0,5
pH	10,5
The stirrer speed, [rpm]	1200
Ripening time of precipitate, [h]	48

2.1 Sample characterization

Phase characterization, average crystallite size and crystallinity degree were achieved by X-ray diffraction. For this purpose have been used a Bruker AXS Advance D8 diffractometer ($Cu_{K\alpha}$, λ = 0.15406 Å, U = 40 kV, A = 30 mA). Information regarding molecular groups of hydroxyapatite structure was obtained by a FTIR-spectrometer Bruker Tensor 27. The measurements were carried out in the coordinate transmittance - wave number (T, ν) in range of 4000 - 400 cm^{-1} with a resolution of 2 cm^{-1}.
Dimensional analysis and particle size distribution of nanopowders were performed by using the dynamic light scattering (DLS) analysis (Brookhaven Instruments Zetasizer Plus 90). Morphology and topography of the analyzed particles have been determined by using scanning electron microscopy technique Auriga FE-SEM (Field Emission - Scanning Electron Microscope) model manufactured by Carl Zeiss, which has the following characteristics: minimum resolution of 1 nm at 15 kV or 1.9 nm at 1 kV, magnification: 12x ... 1,000,000 X, accelerating voltage 0.1 - 30 kV in steps of 10 V.

3. RESULTS AND DISCUSSION

3.1 XRD analysis

Figure 1 shows the X-ray diffraction spectrum of hydroxyapatite powders synthesized in according to technological process and thermal treated at 200^0C. As we expected, XRD spectrum reveal a major proportion of amorphous phase, evidenced by the lower diffraction peak. After heat treatment at high temperatures (over 800 ^{0}C), the diffraction peaks become more sharp.

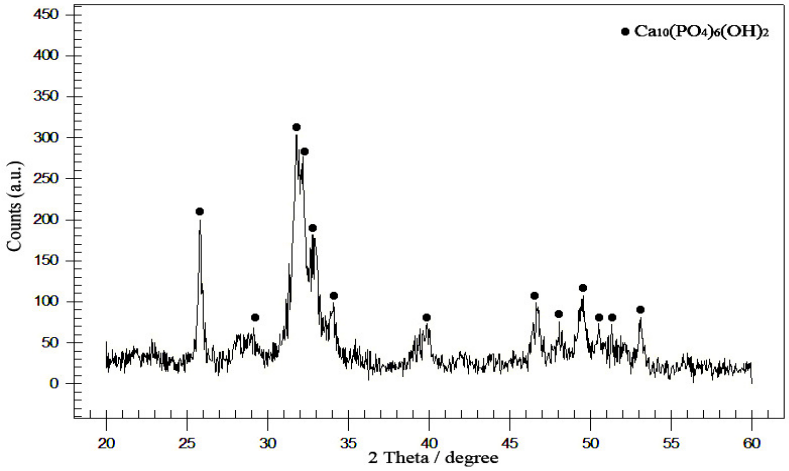

Fig. 1. X-ray diffraction spectrum of the synthesized hydroxyapatite powders heat treated at 200^0C

The informations above presented are supported by data obtained regarding crystallinity degree of hydroxyapaite powders synthesized in accordance with procedure described in other papers [9, 10] where C_R factor was 23.13%.

As regards the purity of crystalline phases in Figure 1 and Table 2 it appears that single-phase present in the powders structure analysed was hydroxyapatite. The presence of hydroxyapatite was evidenced by the characteristic peaks of this phosphocalcic compound, including 2θ values: 25.773, 29.048, 31.771, 32.09, 32.929, 34.007, 39.813, 46.69, 49.488, 53.089. After calculations, the average crystallite size of the powder heat treated at 200^0C was located around 20 nm, this size is typical hydroxyapatite undergone heat treatment at low temperatures.

Table 2. Estimated crystallite size of hydroxyapatite sample heat treated at 200^0C

2θ [^{0}]	d [A]	I [%]	Phase	Miller indices			FWHM [^{0}]	τ [nm]
				h	k	l		
25.773	3.4539	28	$Ca_5(PO_4)_3(OH)$	0	0	2	0.327	26.0
29.048	3.0715	9.7	$Ca_5(PO_4)_3(OH)$	2	1	0	0.686	12.5
31.771	2.8142	100	$Ca_5(PO_4)_3(OH)$	2	1	1	0.723	11.9
32.09	2.7869	83.8	$Ca_5(PO_4)_3(OH)$	1	1	2	0.862	10.0
32.929	2.7178	27.2	$Ca_5(PO_4)_3(OH)$	3	0	0	0.48	18.0
34.007	2.6341	14.8	$Ca_5(PO_4)_3(OH)$	2	0	2	0.42	20.7
39.813	2.2623	13.5	$Ca_5(PO_4)_3(OH)$	3	1	0	0.664	13.3
46.69	1.9438	16.8	$Ca_5(PO_4)_3(OH)$	2	2	2	0.484	18.7
48.011	1.8934	4.6	$Ca_5(PO_4)_3(OH)$	3	1	2	0.424	21.4
49.488	1.8403	14.2	$Ca_5(PO_4)_3(OH)$	2	1	3	0.444	20.6
50.489	1.8061	2.4	$Ca_5(PO_4)_3(OH)$	3	2	1	0.215	42.7
51.296	1.7796	1.9	$Ca_5(PO_4)_3(OH)$	4	1	0	0.322	28.6
53.089	1.7236	11.3	$Ca_5(PO_4)_3(OH)$	0	0	4	0.434	21.4
Average size of the hydroxyapatite crystallites								20

3.2 Chemical analysis of the hydroxyapatite powder revealed by FTIR infrared spectroscopy

In order to obtain information regarding the presence of molecular groups in synthesized hydroxyapatite structure powders heat treated was used a modern method of investigation, Fourier transform infrared spectroscopy (FTIR).

FTIR spectra of hydroxyapatite synthesized in accordance with the technological process and heat treated at 200^{0}C is shown in Figure 2. The bands located at 565 cm^{-1}, 603 cm^{-1}, 962 cm^{-1}, 1038 cm^{-1} and 1095 cm^{-1} are characteristic of the phosphate groups in the structure of hydroxyapatite. The presence of hydroxyl groups in the structure of hydroxyapatite is shown, as a result of thermal treatment carried out at low temperatures (200 ^{0}C) by the presence of peaks located at 3570 cm^{-1} and 630 cm^{-1}.

Also, the presence of carbonate groups is evidenced by the peak located at 1420 cm^{-1}, and the presence of water in apatite structure is highlighted by the presence of bands located at 3550 cm^{-1} and 1650 cm^{-1}.

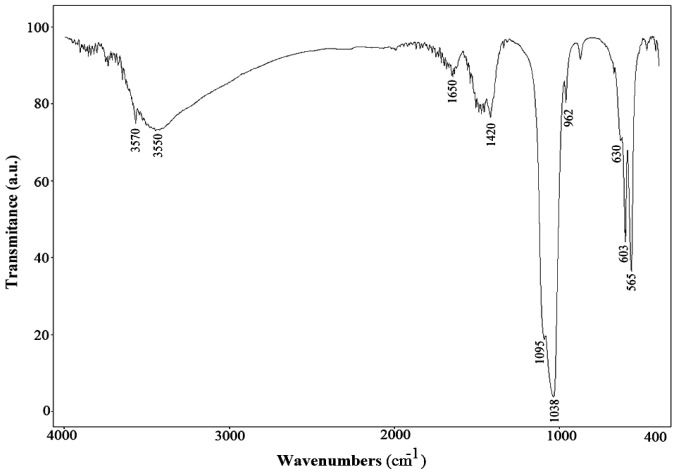

Fig. 2. FTIR spectra of synthesized hydroxyapatite powders heat-treated at 200 ^{0}C

3.3 Particle size distribution of hydroxyapatite powders

This subsection presents the analysis of particle size distribution of nano hydroxyapatite synthesized according to the technological process presented and annealed at 200 ^{0}C.

In Figure 3 there is a unimodal distribution, showing an average particle diameter of 444 nm [10].

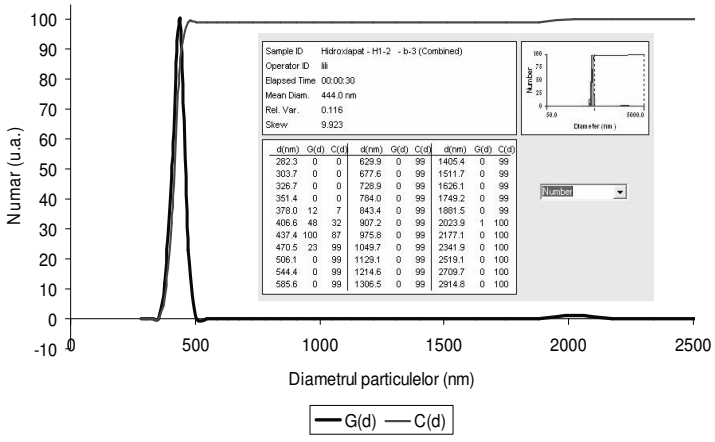

Fig. 3. Particle size distribution of hydroxyapatite powders heat-treated at 200 ^{0}C

3.4 Morphological analysis of hydroxyapatite powders

In order to achieve morphological study the synthesized hydroxyapatite powders have been analyzed by scanning electron microscopy technique.

Figure 4 (a, b) highlights aspects of irregular shape and unevenness dimensional uniformity of the powder particles. These have a rough appearance consisting of several platelet - shaped crystallites, irregularly distributed and overgrown each other.

This shape of hydroxyapatite crystallites are due to synthesis conditions in this case high values for pH and temperature of synthesis reaction. It is known that the temperature influences the morphology of hydroxyapatite powders. Synthesis at a temperature below 60^0C favor formation of crystallites with elongated shape as opposed to the synthesis performed at high temperature, higher than 80^0C, when the particles were spherical.

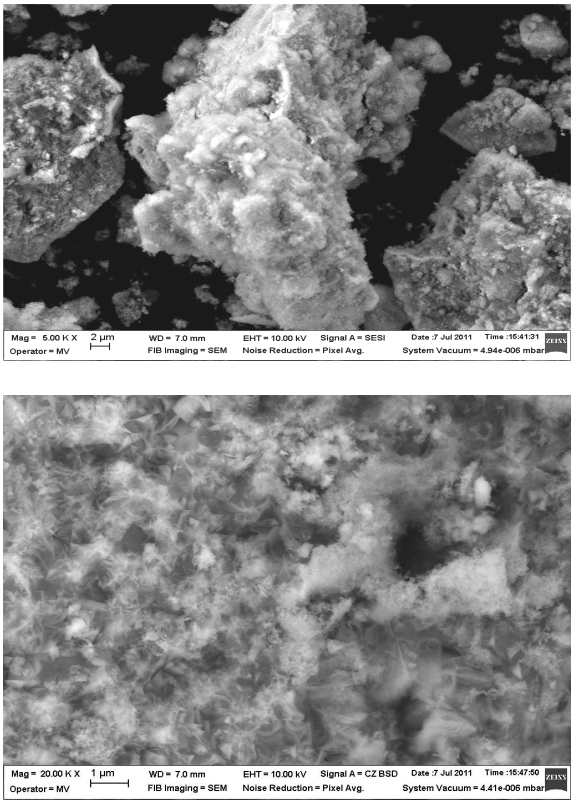

Fig. 4. SEM micrographs for hydroxyapatite powders heat treated at 200^0C

4. CONCLUSIONS

Experimental research has approached the synthesis of hydroxyapatite by chemical co-precipitation method. Hydroxyapatite powders were obtained as a result of chemical reactions in aqueous solution.

As regards the composition of the crystal phases, X-ray diffraction analysis revealed that the hydroxyapatite are the only crystalline phase, in case of powder heat treated at temperature of 200^0C, also the crystallite size was 20 nm.

Fourier transform infrared spectroscopy (FTIR) highlights the presence of carbonate groups (CO_3^{2-}), phosphate (PO_4^{3-}), hydroxyl (OH^-) in the hydroxyapatite structure.

DLS analysis showed the presence of particles with nanoscale dimensions, the average particle diameter was 444 nm.

SEM analysis reveals synthesis of hydroxyapatite characterized by low crystallinity. This aspect was highlighted by the powders morphology, in this case nano-sized particles with platelet shape characterized by heterogeneous distribution.

5. REFERENCES

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