

Studies Concerning the Synthesis and Characterization of Hydroxyapatite Powder

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Introduction: Recently, a special attention was given to the growth of some biomaterials with the goal of renewal and/or reconstruction of bone tissue. Of these biomaterials, hydroxyapatite (HA) presents a series of properties such as biocompatibility and bioactivity, being frequently used for bone grafts realization and to cover some metallic components of some prosthesis used in orthopedics. Although HA is available on the market as synthetic material for more than 15 years, being used for ceramic implants for more than 10 years, new solutions are looked for the inclusion in its structure of some anionic or cationic substitutes in order to bring its composition closer to the biologic apatite.

Aim: The aim of this study was to synthesize and characterize hydroxyapatite powder.

Method: Of the synthesis methods of HA, we used the wet-precipitation method. The obtained compound using this method was characterized by X-ray diffraction (XRD), FTIR microspectroscopy and laser diffractometry.

Results: The XRD spectra showed that the obtained material is HA and we managed to establish the optimum parameters for obtaining HA uncontaminated by impurities and crystalline.

Conclusions: Using a method of chemical synthesis through precipitation, we obtained a HA powder, crystalline and stoichiometric.

Keywords: hydroxyapatite, biocompatibility, bioactivity

Introduction

Lately, the development of biomaterials in order to restore and/or to reconstruct the bone texture is the topic of many research laboratories. Among these biomaterials, a special attention is paid to the development of some special ceramic called bioceramics [1].

This bioceramics are obtained as powders. They are used to fill the empty spaces that can occur in the bones and also to cover the metal components of prostheses used in orthopedics [2–4].

Among the calcium phosphate based bioceramics it has been noticed that crystalline hydroxyapatite (HA) is the most stable phase in contact with body fluids.

Although HA is available on the market as synthetic material, new solutions are searched to include in its structure some anionic (i.e. F⁻, Cl⁻, SiO₄⁴⁻, CO₃²⁻) or cationic substitutes (i.e., Na⁺, Mg²⁺, Sr²⁺) in order to make HA more similar to biological apatite [5–7].

Considering the fact that the most commonly used medicines to treat diseases that are based on bone resorption augmentation (e.g. osteoporosis), are part of bisphosphonates (BP) class, solutions are being seeked for including these drugs on the surface of the metal parts of the prostheses used in orthopedics [8–11]. Another approach is to produce a HA-BP type composite and to deposit it directly to the metal component of the prosthesis [12–14].

There are also studies concerning the use of HA microparticles and nanoparticles as drug release systems [15–17].

This paper presents experimental results on the possibility of chemical synthesis of nano- sized HA particles,

which would eventually allow us to include in its structure some anionic or cationic substitutes or to realize a HA-BP type composite. In the specialty literature, there are several methods of chemical synthesis such as sol-gel method [18], hydrothermal synthesis [19], solid-state reaction [20], and wet methods [21].

Among these methods, we have chosen the wet chemical precipitation, being an easy method to implement [22].

The powder obtained through this method was characterized by X-ray diffraction and FTIR microspectroscopy. At the same time, by using dynamic light scattering (DLS), there was determined the mean particle size and particle size distribution.

Material and method

The synthesis of hydroxyapatite was carried out in N₂ atmosphere, using 50 ml of 1.08M Ca(NO₃)₂•4H₂O solution at pH adjusted to 10 with NH₄OH 28% aqueous solution. To this solution, heated at 80°C, 50 ml of 0.65M (NH₄)₂HPO₄ solution at pH adjusted to 10 with NH₄OH were added drop-wise under stirring. A white precipitate appeared that was maintained in contact with the reaction solution for 3h at 80°C under stirring. The pH of the reaction mixture was maintained at approximately 10 by regular additions of small amounts of NH₄OH solution. Afterwards, the precipitate was centrifuged at 6,000 rpm for 10 min and washed 3 times with distilled water. The product was dried at 100°C (for 24 hours), then calcined at 400°C for 4 h in order to eliminate all water traces and to improve its crystallinity.

in the temperature interval 500–800 °C the weight loss is around 0.5%, and the rest of 1% is lost until 1200 °C.

Discussions

Concerning the chemical synthesis using the precipitation method, there are two main directions: the first one is based on the reaction of orthofosforic acid with calcium hydroxide [24] while the second one is based on the reaction between diammonium hydrogen phosphate and calcium nitrate [25].

Although the first one is simpler and is suitable for the industrial scale synthesis, it is generally leading to some non-stoichiometrical HA compounds. This is the reason why we have chosen the second method, which although is more expensive, it leads to stoichiometrical compounds. In both cases, the properties of the synthesized compound significantly depend on the reactants concentrations, pH, stirring speed, reaction temperature and the conditions of the atmosphere where the reaction takes place.

A frequently observed characteristic in the methods of precipitation synthesis is the possibility that a part of PO_4^{3-} and/or OH^- to be replaced with CO_3^{2-} . Even though the carbonate is naturally found in bones, its presence in synthetic HA should be avoided, because it can influence its biological reactivity and the solubility of the implanted material. Moreover, the replacement of PO_4^{3-} group would also lead to an increase of the molar Ca/P ratio, obtaining a non-stoichiometrical compound, which is generally more thermally unstable.

Although the reaction was carried out in nitrogen atmosphere, the presence of slight carbonate traces has been noticed in the IR spectrum, which could appear in HA structure because of subsequent sample handling steps [26]. It can be observed that by heating the sample at 400 °C, these impurities start to disappear from HA structure. After heating at 400 °C, the intensity of the bands characteristic for carbonate group in the IR spectrum decreases, proving the beginning of the decarboxylation process. Concerning the presence of water, it is well known that hydroxyapatite contains two kinds of water in its structure: adsorbed and lattice water [27]. As noticed after analyzing the IR spectrum, the heating process at 100 °C did not eliminate all the water. This treatment could probably eliminate only the adsorbed water. In the spectrum, a broad band can be observed between 2500–3700 cm^{-1} , due probably to lattice water that disappears after the calcinations process at 400 °C. As indicated by literature data [27], lattice water is irreversibly eliminated in the temperature interval 200–400 °C.

These results are in agreement with experimental data obtained by TG analysis, which show that in the temperature interval rt–1200 °C, the mass loss is 6.5%. A pronounced mass loss takes place until around the value of 500 °C, when the elimination of adsorbed and lattice water takes place and when the decarboxylation process of the sample starts to be more intense. The decarboxylation process starts at 400 °C (as confirmed by the IR spectrum) and

probably continues until 900 °C, with a more pronounced mass loss at 800 °C, in agreement with the TG curve. After the temperature of 800 °C, the mass loss is under 1% and is assigned to dehydroxylation of the sample [28].

Concerning the XRD analysis, the spectra of both the as-prepared and calcined specimens overlap on the HA spectrum existent in the JCPDS database [29]. Because there are no displacements of diffraction peaks, this means that the obtained powder is HA and it does not contain other phases. Moreover, the obtained HA powder is stoichiometrical (Ca/P=1.67). The synthesis of non-stoichiometrical HA would also lead to the presence of other phases, like CaO (if Ca/P is more than 1.67) or tricalcium phosphate, TCP (if Ca/P is under 1.67). In addition, the thermal treatment does not induce the apparition of other phases.

Laser diffractometry size analysis shows that the particles of the as-prepared powder have the dimensions in the granulometric interval of [749.9–4217] nm. It can be observed in fig 3, that the biggest volume of particles is situated in the [749.9–1778.3] nm interval. The presence of particles with dimension in the [2371.4–4217] nm interval is due to the fact that these are agglomerates. In fact, most of the reactions of HA synthesis produce heterogenic agglomerates both during the chemical synthesis and afterwards, during the applied thermal processes. These agglomerates must generally be avoided, because agglomerates trap impurities within their interstices [30].

The calcinations process lead to an increase of medium particle size and to a decrease of agglomeration degree. Thus, in this case, the particles dimensions are found in the granulometric interval of [1531.1–2016.9] nm, most of the particles being situated around the value of 1664.3 nm.

Literature data show that particle dimensions and their morphology depend a lot on the reaction temperature. Thus, an increase of the precipitation temperature in the 20–100 °C interval leads to an increase of particle dimension and to a decrease of HA agglomerates size [31].

Conclusions

Using a method of chemical synthesis through precipitation, we obtained a HA powder, crystalline and stoichiometric. Even though the synthesized compound contains slight traces of carbonate, they start to decompose at 400 °C, temperature at which the lattice water that appears during the chemical synthesis was also eliminated. After calcinations, a decrease of HA agglomerates size was also obtained.

References

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