Study of the effect of calcination in obtaining nanostructured HAp by combustion reaction

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ABSTRACT

Human bone is made up of 9% water, 20% organic components, and 69% calcium phosphates. These phosphates are also present in the bone composition of different animal species, arousing great biological and medical interest, as it is a highly biocompatible material, that is, it could be compatible with living tissues and organic fluids without toxic effects or even immunological reactions. One of the most widely used representatives of the group of bioactive materials of calcium phosphate of synthetic origin is hydroxyapatite - HAp, Ca10(PO4)6(OH)2, due to its high osteinduction, which enables bone regeneration, structure and composition similar to that of phosphate present in skeletal tissue, also known as biological apatite, and its excellent biocompatibility. This research work proposed to study the influence of different calcination temperatures, within a predetermined range, combined with the use of two distinct fuels, glycine and urea, through the method of synthesis by combustion, in obtaining HAp formed by nanometric grains, so that its structure would be as similar as possible to biological apatite. For this investigation, the following techniques were used as methods of structural and morphological characterization: X-ray diffraction (XRD), energy dispersive spectroscopy (EDX), scanning electron microscopy (SEM) and thermogravimetry (TG). The results of the characterizations showed that using the two fuels it was possible to obtain the HAp phase, with grains of nanometric size forming heterogeneous clusters of easy deagglomeration, being the most efficient and with a higher degree of purity when using glycine, and calcined at 1200°C.

Keywords: Hydroxyapatite, Combustion reaction, Biomaterial, Calcination.

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INTRODUCTION

Approximately 70% of human bone is composed of calcium phosphates, and this inorganic part consists of an amorphous phase and a crystalline phase, formed by biological apatite (TORKITTIKUL and CHAIPANICH, 2012). Ceramic materials based on this phosphate have been attracting more and more attention in the medical-dental area due to their similarity with the biological material, and the main examples of this are hydroxyapatite (HAp) [$Ca_{10}(PO_4)_6(OH)_2$] and β-phosphate tricalcium [$Ca_3(PO_4)_2$], due to their high biocompatibility, excellent osteoinduction, in addition to structure and composition very close to those of bioskeletal material (EPPLE and TADIC, 2003). HAP is also widely used in dental implants, reconstructive surgeries and orthopedic surgeries, replacing bone grafts, as described in the medical literature.

The uses of the most diverse reagents and methods to synthesize HAP in the laboratory are reported in the literature, as examples of the latter are: gravitational (NATHANAEL et al, 2011), hydrothermal (SIMOMUKAY, 2013), microwave (KALITA and VERMA, 2009), precipitation (ARAÚJO et al, 2012), combustion reaction (GHOSH et al, 2010) and sol-gel (RODRIGUES, 2008). The choice of the synthesis method used is made considering the particle size that can be obtained, which is an extremely important characteristic with regard to its application.

The characterization of the powders obtained can be carried out through the X-ray diffraction technique (XRD), as to its structure, scanning electron microscopy (SEM), as to its morphology and for chemical analysis it can be used to the technique of energy dispersive spectroscopy (EDX), among others.

This work proposed to obtain hydroxyapatite formed by nanometric grains, through the method of synthesis by combustion, studying the influence of different calcination temperatures, within a predetermined range, combined with the use of two distinct fuels, glycine and urea, on the structure of the HAp obtained. The combustion reaction synthesis method was chosen due to its easy execution and low cost, and it can be used to produce HAp powders on a large scale.

Synthesis by combustion reaction is further described by ALVES, BERGMANN and BERUTTI (2013) as:

> A method based on the principle that once a reaction under heat is initiated, an exothermic reaction occurs and becomes self-sustaining for a certain period of time, resulting in a powder as the final product. The exothermic reaction starts at the ignition temperature and generates a certain amount of heat which is called maximum temperature or combustion temperature. Solution by combustion synthesis has the advantage of quickly producing fine and homogeneous powders. Because it is an exothermic and self-sustaining process, and with a high rate of heat release, it can be explosive and must be carried out with extra care.

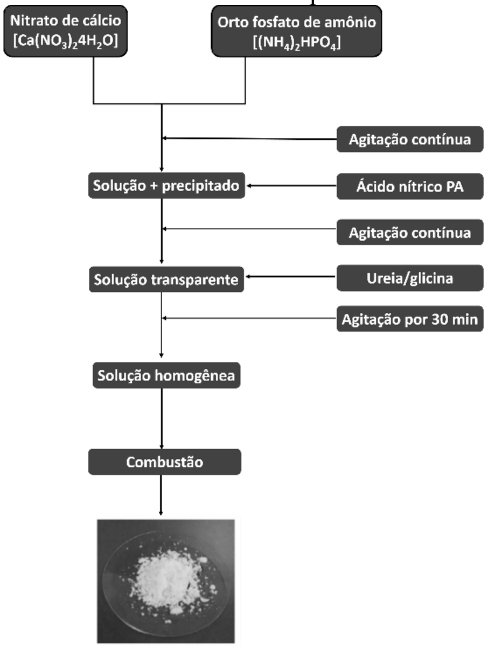
MATERIALS AND METHODS

For study purposes, hydroxyapatite powders were synthesized and analyzed as described in the following subsections.

EXPERIMENTAL PROCEDURE

Fig. 1 illustrates the procedure for obtaining HAP.

Figure 1 – Schematic representation of the combustion process of solution for HAp synthesis [10].



To carry out the syntheses in this work, the methodology and proportions of reagents proposed by Ghoshet al (2010) were followed. Calcium and phosphorus precursors were calcium nitrate tetrahydrate (Vetec – Química Fina, Brazil) and di-basic ammonium phosphate (Vetec – Química Fina, Brazil). The mixture was then placed under magnetic stirring, and nitric acid (Vetec – Química Fina, Brazil, 69%) was added in small quantities until the precipitate was completely diluted.

Subsequently, the resulting solution was removed from the agitator and added to the fuel, being placed under agitation again. The solution was then transferred to a crucible and placed in an electrical resistor for combustion.

The product obtained was left to cool until it reached room temperature, being macerated Three of the samples were placed to calcine in a muffle furnace, with an initial temperature of 25ºC until they reached 600ºC, 900ºC and 1200ºC, respectively, at a rate of 10ºC/min and remaining at these temperatures for 12 hours.

The steps for obtaining HAP powders by combustion reaction are illustrated in Fig. 2 and 3, for glycine and urea fuels, respectively.

Figure 2 – Stages of obtaining HAP by combustion reaction, using glycine as fuel. (a) Heating of the reactant mixture in the resistance, (b) release of gases from combustion and (c) HAp powders obtained after complete combustion.

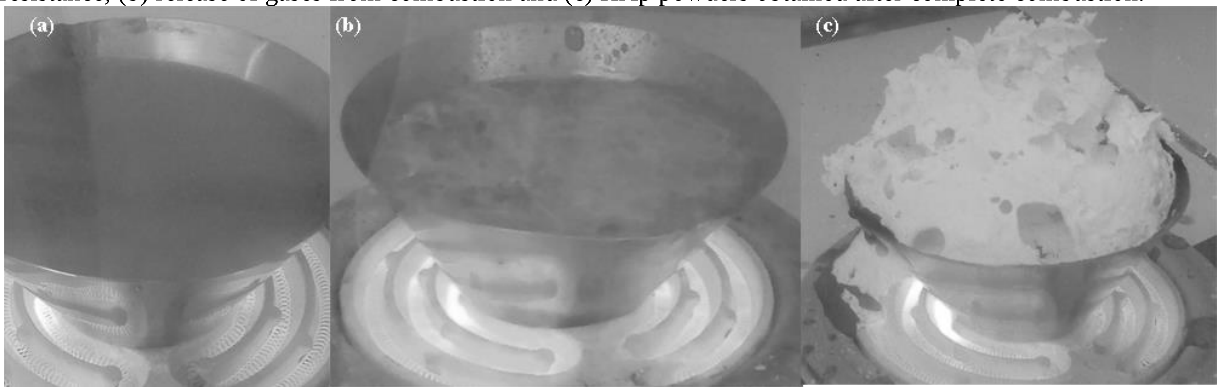


Figure 3 – Stages of obtaining HAP by combustion reaction, using urea as fuel. (a) Heating of the reactant mixture at the resistance, (b) release of gases from combustion, and (c) HAP powders obtained after complete combustion.

CHARACTERIZATIONS

The structural characterization of the HAP powders obtained was performed by the X-ray diffraction (XRD) technique. A BRUKER D2 PHASER diffractometer was used to record the data at 2θ in the range of 3° to 70°. The data obtained were analyzed using the Origin 9.4 software and the peaks classified according to the JCPDS chart for HAp. The chemical analysis was performed through Energy Dispersive Spectroscopy (EDS) using a Bruker XFlash 430 H detector. Morphological characterization was performed by Scanning Electron Microscopy (SEM) using a Hitachi tabletop electron microscope model TM-3000. To perform the thermogravimetric (TG) analyses, the TG 209F1 thermobalance model NETZSCH was used, in the range of 0 to 1000°C at a rate of 50/20.0 (K/min).

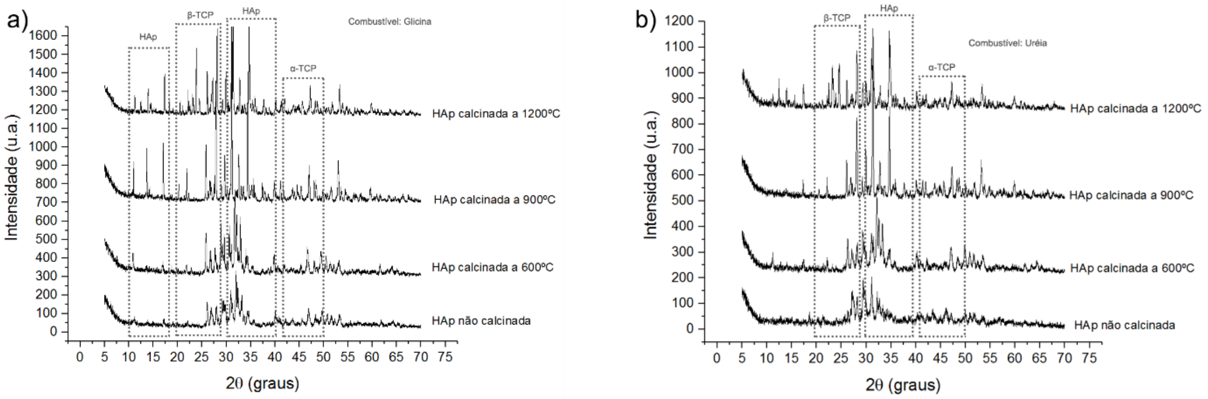
RESULTS AND DISCUSSION

X-RAY DIFFRACTION (XRD)

From the analysis of the crystallographic peaks present in the diffractograms and their comparison with the standard HAp sheet of the JCPDS and results presented by Bezzi et al (2002), Ghosh et al (2009) and Kalita and Verma (2010), it was possible to prove the formation of HAp as the main phase for the two fuels used. However, there was also the formation of two other phases: β-phosphate tricalcium (β-TCP), which occurs between 20 and 30°, this phase being similar to that of HAp in urea samples, and α-phosphate tricalcium (α-TCP), which occurs between 40-50°. In the glycine samples, the predominant phase was HAP, which occurs in the intervals between 10 and 20° and between 30 and 40°, as illustrated in Fig. 4.

Thus, it is possible to verify, through the diffractograms, that the material obtained in the synthesis by combustion reaction was not the pure hydroxyapatite phase as desired, but a mixture of three phases of calcium phosphate.

Figure 4 – HAp synthesized using (a) glycine and (b) urea as fuel



SCANNING ELECTRON MICROSCOPY (SEM)

The results of the morphological analysis showed that the increase in the calcination temperature and the type of fuel used had a direct influence on the morphology of the grains, with the HAp grains synthesized using glycine as fuel being smaller, more irregularly shaped and their agglomerates more porous, as shown in Fig.5 and 6.

Figure 5 - Micrographs of the HAp samples synthesized with glycine fuel, with 200X magnification. (a) Non-calcined, (b) Calcined at 600°C, (c) Calcined at 900°C, (d) Calcined at 1200°C.

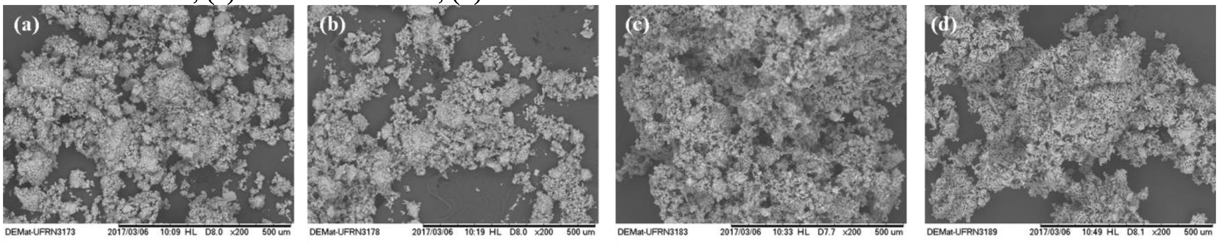
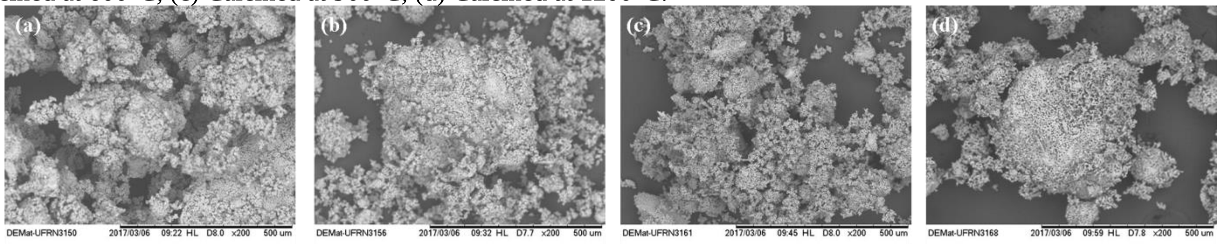


Figure 6 - Micrographs of the HAp samples synthesized with urea fuel, with 200X magnification. (a) Uncalcined, (b) Calcined at 600°C, (c) Calcined at 900°C, (d) Calcined at 1200°C.



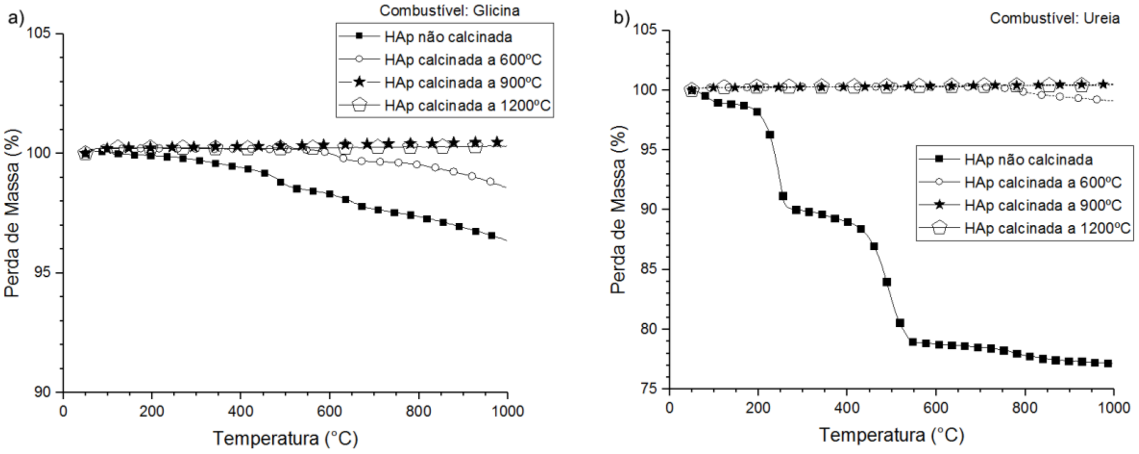
THERMOGRAVIMETRIC ANALYSIS (TG)

It was possible to prove, through the thermogravimetric analyses, illustrated in Fig. 7, that the increase in the calcination temperature has a direct influence on the loss of mass of the powders obtained. The non-calcined samples showed a higher percentage of mass reduction for both fuels.

In the non-calcined sample of HAp synthesized using urea as fuel, as reported in the literature, the mass loss was due to the thermal decomposition of urea into complex compounds and the evaporation of water. While the sample synthesized with glycine and not calcined, there was a mass loss of approximately 3%, Fig. 7a, contrary to the results found by Ghosh et al (2009).

For the samples calcined at 600°C, the percentage of mass variation was lower when urea fuel was used, with an increase of approximately 0.16% at 760.2ºC and a reduction of 0.89% at 997.5ºC, against an increase of 0.27% at 568.7ºC and a reduction of 1.42% at 997.5ºC, for glycine fuel. For the samples calcined at 900 and 1200ºC, with both fuels, no significant changes were observed in the mass percentage, indicating that for this temperature range, the HAp obtained is stable.

Figure 7 - Thermogravimetric analyses of the HAp samples synthesized using the fuels (a) glycine and (b) urea.



ENERGY DISPERSIVE SPECTROSCOPY (EDX)

Through chemical analysis, observing the spectra obtained and the percentages of elements estimated for each sample, it was found that the composition of the eight samples corresponds to the composition of HAp, as expected. However, the quantitative analysis revealed that the Ca/P molar ratio varied according to the fuel and calcination temperature, Fig. 8 and Fig. 9, with the samples calcined at 600ºC, for both fuels, presenting values closer to the expected molar ratio, of 1.67.

Figure 8 - Energy dispersive spectroscopies of HAp samples synthesized with glycine fuel and their Ca/P molar ratios (a) Uncalcined, (b) Calcined at 600°C, (c) Calcined at 900°C, (d) Calcined at 1200°C.

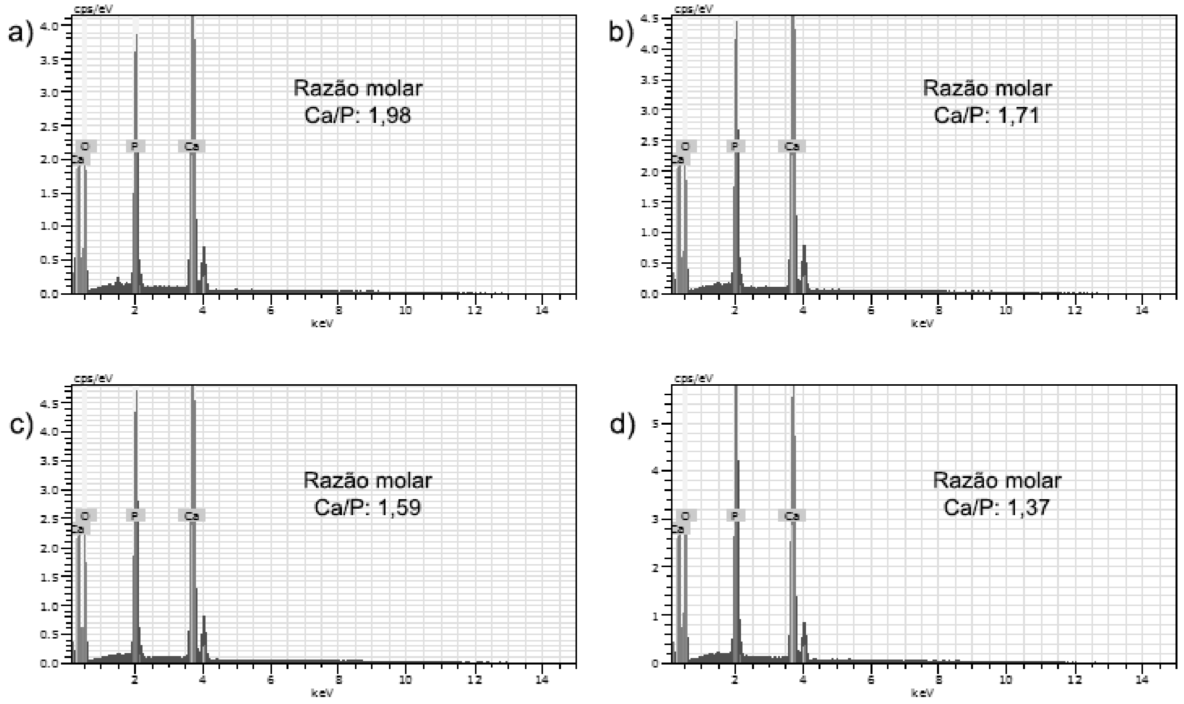
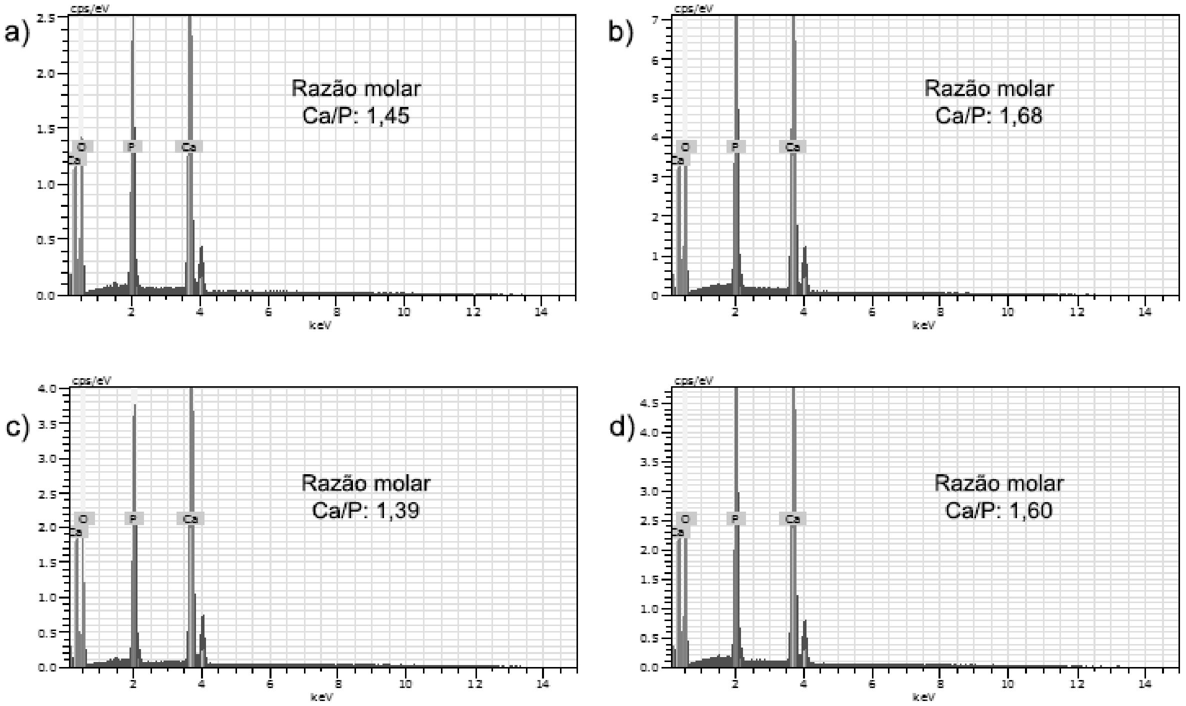


Figure 9 - Energy dispersive spectroscopies of HAp samples synthesized with urea fuel and their Ca/P molar ratios (a) Uncalcined, (b) Calcined at 600°C, (c) Calcined at 900°C, (d) Calcined at 1200°C.



Thus, the HAp sample synthesized with urea and calcined at a temperature of 600ºC was the one that came closest to the Ca/P molar ratio of 1.67 that refers to pure HAP (Brunette et al, 2012)

CONCLUSIONS

Differently from the initial interest, the samples synthesized in this work were not composed only of the hydroxyapatite phase (HAp) but a mixture of three phases of calcium phosphates (HAp + β-TCP + α-TCP). Through the morphological characterization it was possible to classify the powders of the samples as porous agglomerates, with urea samples sizes between 2 and 10μm and glycine samples between 2.5 and 12μm. Through the analysis of the results of the characterizations, it was concluded that the most favorable fuel for the synthesis of hydroxyapatite, although presenting the highest percentage of mass reduction and molar ratio of Ca/P different from that desired for pure HAP, was glycine, since the predominant phase obtained was that of HAP. However, there is a need to improve the synthesis conditions to obtain 100% pure HAP.

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