

Obtaining and characterization of hydroxyapatite through the modified polymeric precursors method

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ABSTRACT: Extensive attention has been devoted to the development of materials and production methodology for clinical use. Bioceramics are a family of ceramics used to repair and regenerate diseased and damaged parts of the musculoskeletal system and periodontal anomalies. Hydroxyapatite [HAp, Ca₁₀(PO₄)₆(OH)₂] is a bioceramic that holds a lot of interest due to its excellent properties. This study aimed to produce HAp using a modified polymeric precursor method and to evaluate the influence of synthesis parameters on the characteristics of the obtained powders, through different citric acid/metallic cations and citric acid/ethylene glycol ratios. The samples were characterized by X-ray diffraction and scanning electron microscopy. The 5:1 ratio of AC/CM and 50/50 AC/EG was the parameter with the best results, obtaining the highest percentage of the hydroxyapatite phase, with a crystallite size of 47 nm and a degree of crystallinity of 97.6%.

KEYWORDS Hydroxyapatite. Bioceramics. Synthesis.

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I. INTRODUCTION

The technological progress of man has always been linked to the development of materials. Nowadays, much attention has been paid to this area, mainly for the production of biomaterials, both towards the manufacture of innovative devices, and for the improvement of existing ones. This great interest stems from the needs caused by age advancement and changes in the population's lifestyle, as well as the technological advances in bioengineering that promote greater awareness of implants, which ends up driving the bioimplant market [1,2].

Among the materials used for this purpose, Hydroxyapatite (HAp) [Ca₁₀(PO₄)₆(OH)₂] stands out, which is the most recognized member of the calcium phosphate family in biomedical applications. It is the largest inorganic constituent of bones and teeth, constituting about 70% of bone and dental mass [3, 4]. Biocompatibility, bioactivity, osteoconductivity and non-toxicity, in addition to non-inflammatory and non-immunogenic behavior in its synthetic form are notable properties arising from its compositional nature; these attributions, together with the similarity with the chemical and crystallographic structure of human bone tissues, largely direct HAp to bone-related applications, being: traumatology, orthopedics, craniofacial surgery and dental technology some of its fields of activity [5-7]. An important fact about its structure is that it easily allowed the occurrence of cationic and anionic substitutions, enabling the use of HAp in other fields, such as gas sensor, chromatography, drug release and water purification [8-11].

As a result, due to this varied range of employment, there is a lot of interest in obtaining it and many chemical methods carry out obtaining HAp. Among these methods, the polymeric precursor method (Pechini) has become an attractive synthetic technique for the preparation of several inorganic oxides, due to its lower cost and milder processing temperature. In addition, the precise control of the stoichiometric relationships linked to the mixture at the molecular level, results in products of high purity and with homogeneous compositions [12,13]. Basically, it is a modified sol-gel method where the network is based on covalent and coordination bonds formed by polyesterification of the chelated metallic cation and glycol, promoting the opportunity to control the structure, shape, size and chemical, physical and optical properties through control of parameters [14,

15].

However, it is a little discussed process in the literature for obtaining hydroxyapatite [16-19] which opens the way for several questions, mainly regarding the influence of the synthesis parameters. In this context, Pechini processing, since it is a sol-gel process that is highly sensitive to conditions, a good control of the synthesis parameters is necessary, to lead to the optimization of the process in the long term [20].

In this study, a synthetic hydroxyapatite was through the Pechini method, modifying some parameters of its patent [21], such as: the solvent used. In addition, it was studied, studying the influence of the citric acid / metallic cations ratio and the citric acid / ethylene glycol ratio.

II. EXPERIMENTAL PROCEDURES

2.1 Materials and methods:

The materials used for the production of HAp powders were: ethyl alcohol, citric acid monohydrate, calcium nitrate, dibasic ammonium phosphate and ethylene glycol.

For the synthesis of nano HAp by the Pechini method, 100 ml of ethyl alcohol was added to a beaker, which was placed on a heating plate with constant stirring with the temperature maintained at around 70°C with the aid of a thermometer. Citric acid was added to the solution in fractional form, just after 15 minutes the precursors, calcium nitrate and ammonium phosphate. The amount of reagents was calculated according to the proportion for the synthesis, the AC/CM ratio varied between 1:1, 3:1 and 5:1. After 15 minutes of stirring, ethylene glycol was placed in the solution. Ethylene glycol was measured according to the 50/50 and 40/60 AC/EG ratios, for each of the citric acid/metal cation ratios. After the disposal of ethylene glycol, the temperature was increased and maintained between 100 to 120°C for the performance of the polyesterification reactions and the consequent formation of the gel. Pyrolysis was performed on the gel at 400°C/1h, with a heating rate of 10°C/min, for the elimination of organic matter. The material obtained was de-agglomerated with the aid of a mortar and pestle, and then immediately passed through an ABNT sieve No. 200 (0.074mm), and calcined at a temperature of 1000°C, for 1 hour, with a heating rate of 10°C/min, to obtain the desired phase. The samples obtained were named as follows, Sample AEXY, where: X = 1, 3 and 5, when the AC/CM ratio is 1:1, 3:1 and 5:1, respectively. Y = 5 or 4, when the AC/EG ratio is 50/50 or 40/60, respectively.

2.2 Characterizations:

The synthesized samples were characterized by X-ray diffraction (XRD), to identify the formed phases, quantify the phases, crystallinity and crystallite size. The equipment used for this analysis was the X-ray diffractometer model XRD-6000 from Shimadzu with α radiation from copper and scanning from 20 to 60°. The quantification of the phases was performed using the HighScore Plus program. The size of the crystallite was calculated from the Scherrer equation. Crystallinity was determined from the ratio between the integrated peak area for the crystalline phase and the area for the amorphous fraction. The morphological aspects of the samples obtained were analyzed by scanning electron microscopy (SEM), using a Hitachi scanning electron microscope, model TM3000.

III. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffractograms of the samples obtained with AC/CM ratios of 1:1, 3:1 and 5:1, with the AC/EG ratio of 40/60.

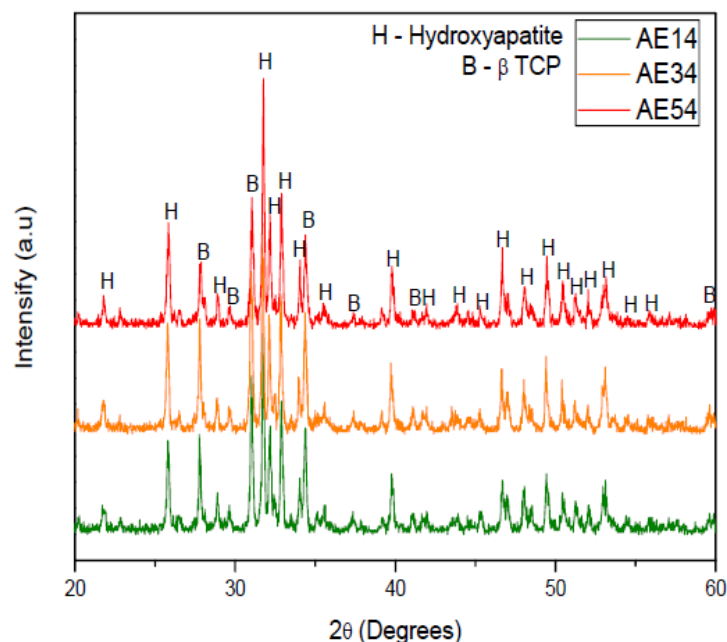


Figure 1: X-ray diffractograms of the samples obtained with AC/CM ratios of 1:1, 3:1 and 5:1, with the AC/EG ratio of 40/60.

The diffractograms in Figure 1 show the formation of a biphasic ceramic, with peaks characteristic of the hydroxyapatite (HAp) and beta tricalcium phosphate (β -TCP) phases. The phase referring to hydroxyapatite was identified through the standard form JCPDS 9-432 and the β -TCP phase through the standard form JCPDS 9-169. It is noted that there was a growth of certain peaks of hydroxyapatite; to the detriment of the reduction of some beta peaks, showing an increase of the Hap phase to the detriment of a decrease of the beta phase, according to the increase in the variation of the AC/CM molar ratio from 1:1 to 5:1. With the increase in citric acid, there was a greater possibility of capture of metal ions, as there was a greater number of carboxyls and hydroxyls that allowed such action, thus the desired phase tended to increase because the ions that formed it were present in greater numbers, obeying the reason for the formation of HAp [22].

However, the growth trend occurs in a non-linear manner, with a drop in the 3:1 ratio, growing again in the 5:1 ratio. This may have occurred due to small variations in the conditions of the synthesis, such as time of dissolution of the reagents and heat distribution in a given format of the plate for calcination. Thus, these variations in the synthesis conditions had a stronger influence on the crystallization kinetics of hydroxyapatite, in this case, than the AC/CM ratio. Other authors who studied the synthesis of other materials by Pechini, analyzing the content of AC/CM, also observed a greater influence of some parameters of the synthesis in the formation of the phases [23, 24].

The presence of the second phase β -TCP may have occurred due to a poor complexation of the PO_4^{3-} group, which caused an insufficient homogeneity in the ion distribution of the complex with consequent segregation and formation of phosphate phases [16]. However, the presence of β -TCP in Hap can be beneficial, the Ca deficient apatite has better bioresorbable properties than stoichiometric HAp, because the compound promotes a strong and fast connection to natural bones by rapid resorption. Since HAp is considered not to be soluble in the physiological environment. Therefore, it was believed that the presence of a low intensity of β -TCP can optimize the reabsorption of Hap [25].

Table 1 presents the quantification of the phases, crystallinity and crystallite size of the samples synthesized in the proportions AC/CM 1:1, 3:1 and 5:1 and in the ratio 40/60 of AC/EG.

Table 1 - Quantification of the phases, crystallinity and crystallite size of the samples synthesized in the proportions AC/CM 1:1, 3:1 and 5:1 and in the ratio 40/60 of AC/EG.

QUANTIFICATION OF PHASES (%)				
SAMPLE	HYDROXYAPATITE PHASE	BETA PHASE	CRYSTALLITE SIZE (nm)	DEGREE OF CRYSTALLINITY (%)
AE14	63	37	45	93,7
AE34	58	42	52	96
AE54	73	27	54	96,3

According to Table 1, it is noticed that the crystallinity values are high for all samples and both crystallinity and crystallite sizes show an increase as the stoichiometric ratio between AC/CM increased. This occurred because the greater amount of citric acid provides more carboxylic groups, these are available to chelate more cations, resulting in greater uniformity of the metallic elements in the ester, and thus, greater crystallinity [22]. Possibly, the higher citric acid content also provided a greater tendency for aggregate formation during the calcination process, increasing the size of the crystallite [26]. The sample in the 5: 1 ratio was the one with the highest crystallinity value, which was 96.3% and the largest crystallite size was 54 nm. These values show the nanometric character of the particles and are in accordance with the literature for the synthesis of Hap by other sol-gel routes [27, 28], enabling better properties to the produced hydroxyapatite.

Figure 2 shows the X-ray diffractograms of the samples obtained with AC/CM ratios of 1:1, 3:1 and 5:1, with the AC/EG ratio of 50/50.

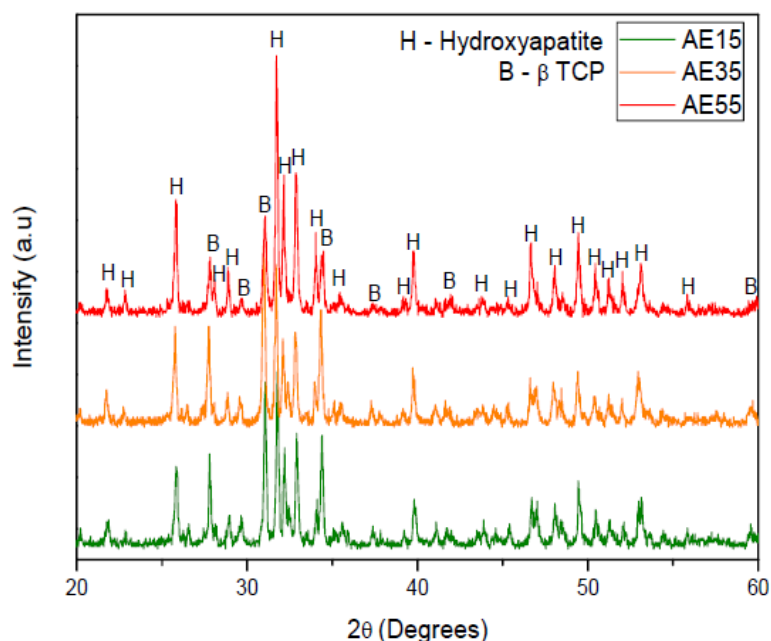


Figure 2: X-ray diffractograms of samples obtained with different AC / CM ratios of 1:1, 3:1 and 5:1, with an AC/EG ratio of 50/50

Evaluating Figure 2, also observe the formation of biphasic ceramics composed of Hap and β -TCP. It is also noticed that with the increase in the ratio 1:1 to 5:1 of AC/CM, there was an increase in the formation of the Hap phase from 62 to 75%. In the 3:1 ratio, the growth profile of the phase of Hap was non-linear. These results are similar to those in Figure 1, and occurred for the same reasons as previously reported. It is noted that the increase in the ratio between the AC/EG from 40/60 (Figure 1) to 50/50 (Figure 2) did not influence the results. Table 2 shows the quantification of the phases, crystallinity and crystallite size of the samples synthesized in the AC/CM 1:1, 3:1 and 5:1 ratios and in the 50/50 AC/EG ratio.

Table 2 - Quantification of the phases, crystallinity and crystallite size of the samples synthesized in the proportions AC/CM 1:1, 3:1 and 5:1 and in the ratio 50/50 of AC/EG.

QUANTIFICATION OF PHASES (%)				
SAMPLE	HYDROXYAPATITE PHASE	BETA PHASE	CRYSTALLITE SIZE (nm)	DEGREE OF CRYSTALLINITY (%)
AE15	62	38	50	94,2
AE35	48	52	52	94,7
AE55	75	25	47	97,6

Analyzing Table 2, high crystallinity values are perceived for all samples, with a maximum value of 97.5% for the sample with a 5:1 ratio. The size of the crystallite varied from 47 to 52 nm. Comparing Tables 1 and 2, it can be noted that there were no significant changes in the crystallite and crystallinity values, in view of

the increase in the AC/EG ratio. Regarding the size of the crystallite, the samples generally presented a small increase as the stoichiometric ratio between citric acid / metallic cations increased, obtaining a maximum crystallite size of 52 nm for the sample with a 3:1 ratio.

Comparing the AC/EG molar ratio, by means of Tables 1 and 2, it is noted that very little variation occurred regarding the phase formation or crystallinity of the samples. For all synthesized samples, the crystallite tends to decrease as the concentration of EG increases, as a result of the increase in nucleation sites under high concentrations of ethylene glycol [29, 30]. However, this fact does not apply to samples AE55 (Table 2), probably this may have occurred due to the superfluous citric acid, which promoted points of overheating in some small areas, generating agglomeration of the particles, due to the excessive heat produced during the process calcination [31].

According to the X-ray diffractograms of all samples obtained by Pechini, the samples of ratio 5:1 of citric acid/metallic cations, in both citric acid / ethylene glycol ratios, presented a higher percentage of Hap, therefore, only these samples the other characterizations continued.

Figures 3 and 4 show the morphology of samples AE54 and AE55, respectively.

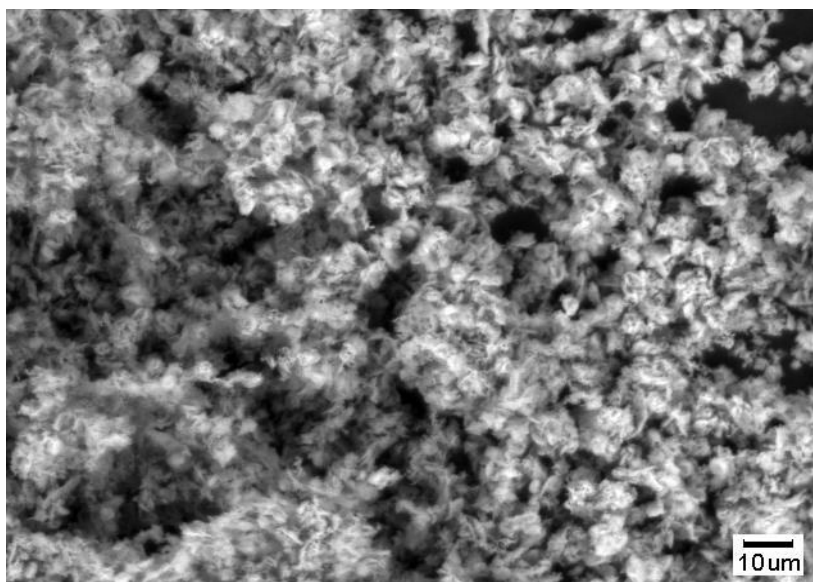


Figure 3: Scanning electron microscopy of the AE54 sample at magnitudes of x1000

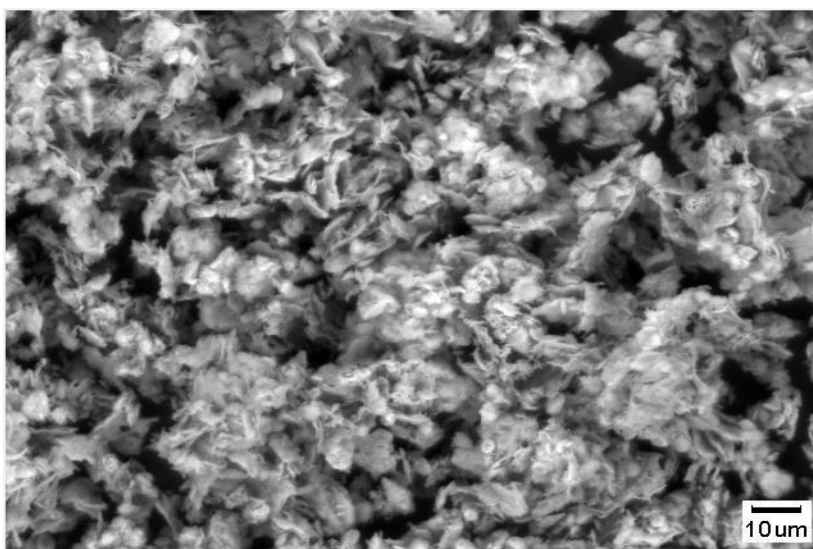


Figure 4: Scanning electron microscopy of the AE55 sample at magnitudes of x1000

Through scanning electron micrographs, it is noted that the morphologies are presented in a very similar way, where the particles are quite grouped generating irregularly shaped aggregates. The high degree of agglomeration of the powder induces a high reactivity of the same. According to the literature, calcium nitrate,

which was the precursor of Ca used in the synthesis, may have potentiated the formation of these aggregates [32]. It was also observed the presence of a certain degree of porosity in the material, which is quite beneficial for biological applications, as it allows to develop the growth of osteoblast cells in the bone-implant application [33].

IV. CONCLUSION

The Pechini method was efficient for the production of hydroxyapatite nanoparticles, however the formation of a secondary phase of beta tricalcium phosphate occurred. The synthesis parameters analyzed influenced the formation of the phases, where the 5: 1 ratio of AC / CM and 50/50 AC / EG was the parameter with the best results, providing the obtaining of the samples with the highest percentage of the hydroxyapatite phase.

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