

## Synthesys and characterization of nanostructured powders of hidroxiapatite and $\beta$ -calcium phosphate.

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Abstract: Biphasic calcium phosphate (BCP) bioceramics are composed in a general manner from a mixture between hydroxyapatite (HA), and  $\beta$ -calcium phosphate. In the recent years, the BCP bioceramics are pointed out in researches from regeneration and reconstitution in osseous tissue, in reason of their similar mineralogical characteristics of the human bone structure, as great biodegradation, absorption and formation of precocious osseous tissue. The biphasic materials (BCP) are detached for use in medical and dental application, as filling bone cavities, maxillofacial treatment, medicaments discharge for treatment cancerous osteomelit and antibiotics discharge related with orthopedic injuries reparation. The aim of this work focused in synthesys and characterization of hydroxyapatite and  $\beta$ -calcium phosphate. The presented results are related with the mineralogical characterization with X-ray diffraction, thermal behavior with Differential Scanning Calorimetry and Dilatometer. The Scanning Electronic Microscopy (SEM) was used to help in the morphological characterization of the nanostructured powders.

Keywords: Calcium Phosphate, Hydroxyapatite,, Nanostructured, Biomaterials

### INTRODUCTION

The biphasic calcium phosphates (BCP) belong to a biomaterials group available as a bone issue reconstruction. They consist of hidroxiapatite (HA) and tricalcium phosphate-  $\beta$ .<sup>[1-2]</sup> The biphasic nanostructured bioceramics, have been successfully used as bone regeneration and bone issue reconstitution, because this material presents growth superficial area, a equi-axial morphology from its nanoparticles and sizes lower than 100 nm, what allow better wetness and dissolution by biological environment, in this way contributing by bone issue regeneration and reconstruction.<sup>[3-4]</sup> The hidroxiapatite and calcium phosphate-  $\beta$  are bioactive and bioabsorbed ceramics<sup>[5]</sup>. The biphasic ceramics are promising for biomedical application, because they present mineralogical characteristics same as that presented in bone apatite from human skeleton.<sup>[7-11]</sup>

The aim of this work concentrated about synthesis and characterization of hidroxiapatite and calcium phosphate nanocomposites. The results presented in this research are related with morphological and mineralogical characterization research that verify if after synthesis and calcination at 900°C/2h, the hidroxiapatite and the calcium phosphate-  $\beta$  were found.

## EXPERIMENTAL METHOD

In this work were synthesized two compositions of nanostructured powders from calcium phosphate, beginning with a molar relation Ca/P of 1,6 and 1,67 molar, but for composition Ca/P=1,6 a solution with phosphorus pentoxide ( $P_2O_5$ ) was utilized and for composition Ca/P=1,5 a solution with phosphoric acid ( $H_3PO_4$ ) was utilized.

For synthesis of nanostructured powders, was utilized a Becker containing deionized water, with pH around 7. The deionized water was put under mechanical agitation with 420 rpm and added calcium oxide (CaO) powder slowly making an aqueous solution, providing an alkaline colloidal solution. At each 20 minutes for all colloidal solutions a measure from pH were made, controlling in this its value. The solutions were under mechanical agitation for two hours. Later we added the acid phosphoric required to Ca/P= 1,67 composition and phosphorus pentoxide to Ca/P= 1,6 composition. The dribbling velocity for acid solution was 2ml/min. We observed a stabilization from pH value for different colloidal solutions, after 2 hours from acid solution incorporation. The colloid remained under mechanical agitation for 24 hours.

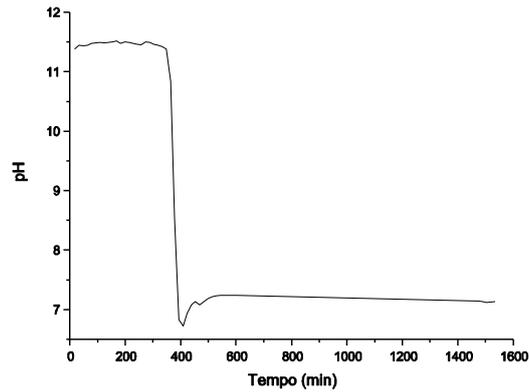
The colloid took from Becker was introduced into a pear balloon to eliminate the solvent. The balloon was fixed into a rotating evaporator, this stayed partly submersed inside a silicon oil bath which were at  $70^\circ C$ , under a rotation of 8 rpm. The ceramic powder recovered from the balloon presented over agglomerates with white color. This material passed for the grind process by hand mortar and sifting in mesh  $100\mu m$ .

The studies on morphological and mineral characterization were conducted through a Scanning Electron Microscope, namely ZEISS DSM 940A, 30 Kv by means of a system of secondary electron (SE) and an X ray Diffractometer, namely Shimadzu X ray Diffractometer Lab X XRD-6000, with a copper anti- cathode; the parameter was the diffraction angle  $2\theta$  with goniometric dislocation of  $2^\circ/\text{min}$ . The specimens were prepared for observation in the scanning electron microscope and the microanalysis through EDX. Preparation was done through a sample holder and a carbon double-sided tape, that is, the carbon double-sided tape was attached under the flat surface of the sample holder, then the ceramic powder, were fixed under the surface of the carbon tape. All of the specimens were covered with metallic films through an sputter coater, namely Bal-Tec model SCD 050 Sputter Coater. The parameters of ionic deposition were set up as follows: temperature in the camera of metallization at  $20^\circ C$ , the current was 40 mA, the stress was 2 kV and time of deposition, 120 seconds.

Differential Scanning Calorimetry and Dilatometer using equipment for thermal analysis Netzsch STA 449C did the thermal behavior study. The specimens are prepared in powder form, placed inside of an alumina's pan and after that placed inside of the chamber from the analysis thermal system with argon. The specimens heating velocity was  $5^\circ C/\text{min}$ . until the temperature of  $1400^\circ C$ .

## RESULTS AND DISCUSSION

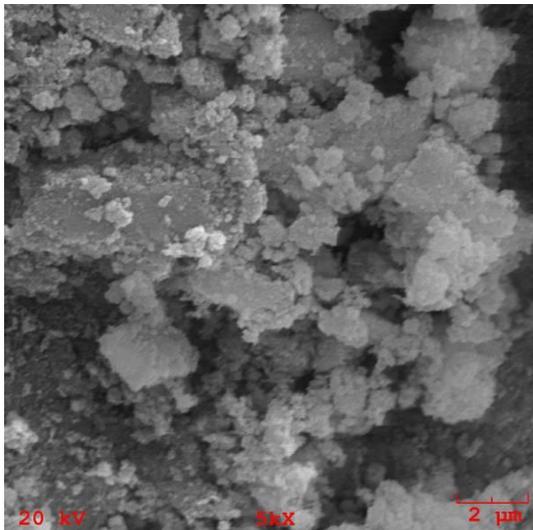
Figure 1 illustrates the pH values referent to pH measure values, it has shown that with the incorporation of calcium oxide powder in the aqueous solution, the pH value increased from  $\approx 7$  until  $\approx 11,5$ . When the acid solution were added the pH value strongly decreased, after 6,5 hours under the mechanical agitation, passing from  $\approx 11$  until  $\approx 6,7$ . The stabilization occur after 8 hours and the value were  $\approx 7,2$ , indicating the process of semi-amorphous hydrated calcium phosphate reckless.



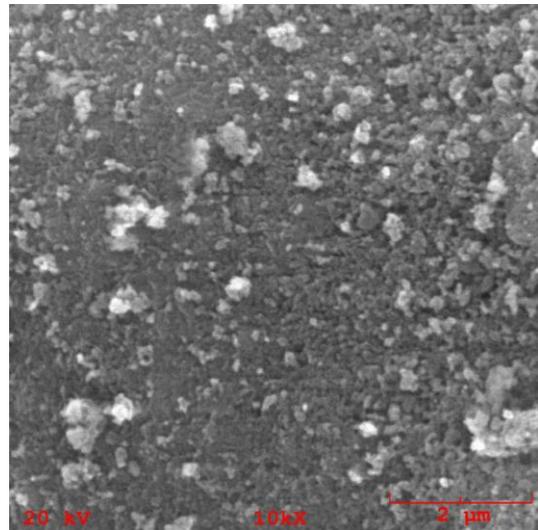
**Figure 1.** shows the curve of pH values from colloidal solution measures during the synthesis process.

Morphological characterization, investigated by scanning electron microscopy (SEM), was performed on the nanostructured powders with Ca/P 1,67 and 1,6 molar ratio obtained after drying in a rotating evaporator and after calcination at 900°C for 2 hours. After drying, the powders showed a morphology formed by agglomerated nanoparticles with size  $d < 20\text{nm}$  (**Figure 2 e 3**).

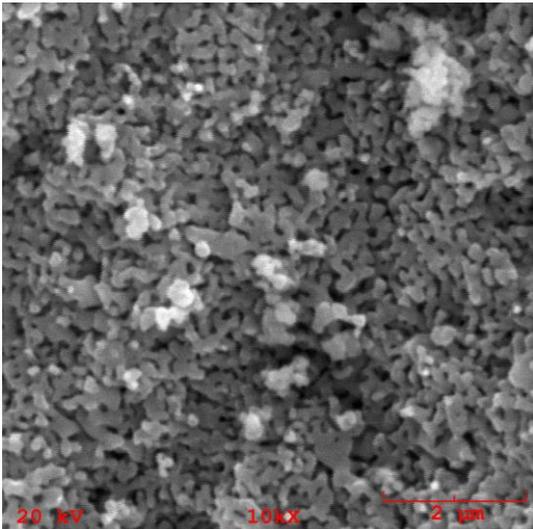
The results obtained with the powders, after treatment at 900°C for 2 hours, indicate the presence of crystallites from hidroxiapatita with Ca/P 1,67 molar ratio and calcium phosphate-  $\beta$  with Ca/P 1,6 molar ratio. Another observation was the equiaxial crystal form with a size below 100 nm (**figure 4 e 5**).



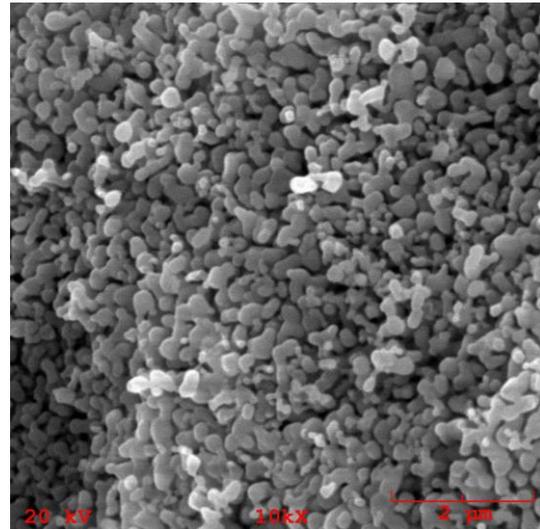
**Figure 2.** shows the morphology of nanostructured power obtained from Ca/P= 1,67 molar ratio after drying.



**Figure 3.** shows the morphology of nanostructured power obtained from Ca/P= 1,6 molar ratio after drying.

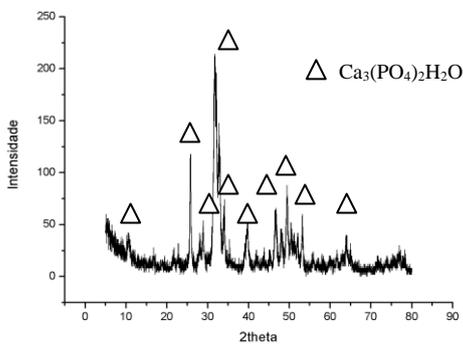


**Figure 4.** shows the morphology of nanostructured power (Ca/P= 1,67) hydroxiapatite after calcination at 900°C/2h.

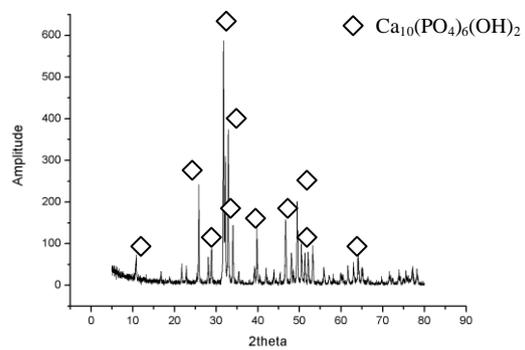


**Figure 4.** shows the morphology of nanostructured power (Ca/P= 1,6) calcium phosphate after calcinations at 900°C/2h.

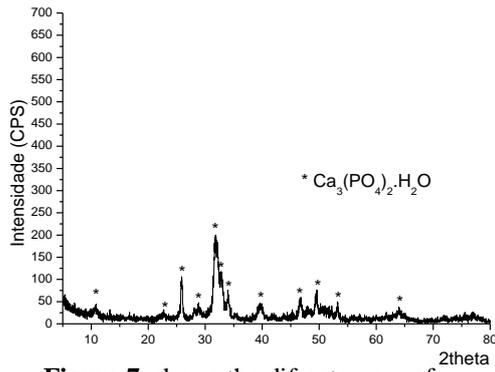
The results from X-ray diffraction (XRD), performed on the powders after drying in the rotating evaporator (figure 5 and 6), have shown at diffractogram for the two compositions with Ca/P 1,67 and 1,6, the presence of hydrated calcium phosphate, by composition ( $\text{Ca}_3(\text{PO}_4)_2\text{H}_2\text{O}$ ). For the powders heat treated at 900°C/2h it was observed for composition with Ca/P 1,67 molar ratio the presence of hydroxiapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) (Figure 8) and for composition with Ca/P 1,6 molar ratio  $\square$  - tri-calcium phosphate, as illustrated in figure 9.



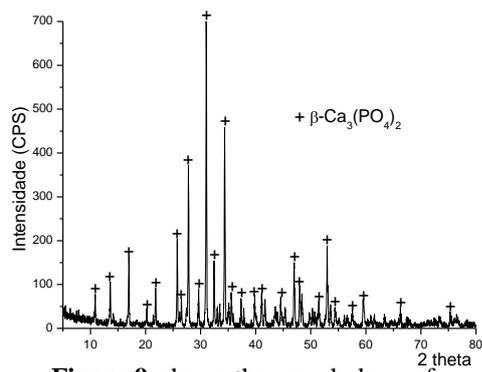
**Figure 6.** shows the diffractogram of nanostructured power obtained from Ca/P= 1,67 molar ratio after drying.



**Figure 8.** shows the diffractogram of nanostructured power (Ca/P= 1,67) hydroxiapatite after calcination at 900°C/2h.

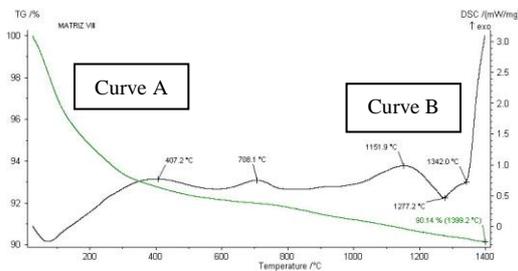


**Figure 7.** shows the diffractogram of nanostructured powder obtained from Ca/P= 1,6 molar ratio after drying.

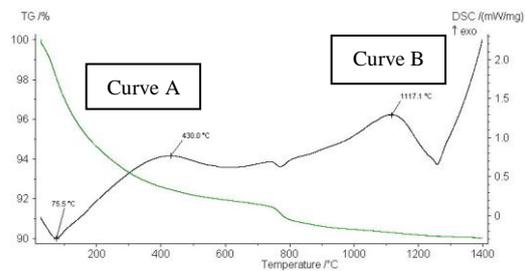


**Figure 9.** shows the morphology of nanostructured powder (Ca/P= 1,6) calcium phosphate after calcination at 900°C/2h.

The results obtained in Differential Scanning Calorimetry (DSC) over the powders compositions Ca/P= 1,67 e 1,6 molar have shown in your curves (A) (Figures 10 e 11) a endothermic peak approximately at 100°C, showing the absorbed water liberation without bioceramic powder structure change, a lengthy endothermic peak with maximum point between 407 a 430°C temperature (figure 11), indicating the desidroxilization. At figure 10, we can observe two endothermic peaks, one approximately at 700°C, indicating the hidroxiapatite formation and another approximately at 1151°C, indicating the calcium phosphate-β-phase formation. For figure 11, we can observe two peaks, one endothermic approximately at 780°C, showing the absorbed water liberation from the powder crystalline structure and another exothermic peak, approximately at 1117,1°C, showing the calcium phosphate-β-phase formation. The dilatometer curves (B) represented by TG (Figures 10 and 11) evidence a significant mass lost from 25°C until 900°C, for the two nanostructured powder compositions.



**Figure 10 –** Curves showing (a) DSC and (b) TG both obtained for nanostructured powder with Ca/P 1,67 molar ratio after rotating evaporator.



**Figure 11 –** Curves showing (a) DSC and (b) TG both obtained for nanostructured powder with Ca/P 1,6 molar ratio after rotating evaporator.

## CONCLUSION

The nanostructured biomaterials of biphasic calcium phosphate are fortunate for biomedical applications in orthopedics, traumatology and orthodontia. At orthopedics, as a matrix element in bone issue regeneration and reconstitution, trough preventive methods, at traumatology in lost or traumatized bone issue recuperation and reconstitution, at orthodontia in cavity treatment, direct restoration, coating, filling and bone reconstitution.

The obtained results in this work put in evidence, that the powder synthesis allow to obtain fine nanometric agglomerated particles of hidrated calcium phosphate, that posteriorly by heat treatment can be transformed into biphasic bioceramic powders.

1. LEGEROS, R.Z., LIN, S., ROHANIZADEH, R., MIJARES, D. LEGEROS, J.P. Biphasic calcium phosphate bioceramics: preparation, properties and applications. *Journal of Materials Science: Materials in Medicine*, p. 201-209, 2003.
2. DACULSI, G., LABOUX, O., MALARD, O., WEISS, P., Current state of the art of biphasic calcium phosphate bioceramics. *Journal of Materials Science: Materials in Medicine*, p. 195-200, 2003.
3. NURIT, J., MARGERIT, J., TEROL, A., BOUDEVILLE, P. pH-metric study of the setting reaction of monocalcium phosphate monohydrate/calcium oxide-based cements. *Journal of Materials Science: Materials in Medicine*, v. 13, p. 1007-1014, 2002.
4. DELIMA, S.A., SOUZA, J.C.P., AGUIAR, J.F., CAMARGO, N.H.A., GEMELLI, E. Efeito da sinterabilidade sobre a micro e a nanoestrutura de uma matriz óssea de fosfato de cálcio e nanocompósitos alumina-a sol-gel, 52º Congresso Brasileiro de Cerâmica, Florianópolis, SC, p. 1-12, 2008.
5. CAMARGO, N.H.A., CHELLAT, F., FERNANDES, J., FOLGUERAS, M.V., GEMELLI, E., YAHIA, L.H., “Estudo do Comportamento de Culturas de Osteoblastos Numa Matriz Cerâmica de Fosfato de Cálcio pela Técnica de Microscopia Eletrônica de Varredura”, In: anais do VII Congresso Brasileiro de Física Médica, pp. 568-576, Porto Alegre RS, 2003.
- 6.
7. BUCHOLZ, R.W., CARLTON, A., HOLMES, R.E., *Orthop. Clin. N. Am.* 18 (1987) 323.
8. DRIESSENS, F.C.M. *Bioceramic of Calcium Phosphate*, CRC Press, Boca Raton, FL, 1983.
9. LEGEROS, R. Z., *Adv. Dent. Res.* 2 (1988) 164.
10. DENISSEN, H., MANGANO, C., VENINI, G. *Hidroxyapatite implants*, Piccin, Padua, 1985.
11. SHIKINAMI, Y., OKUNO, M., *Bioresorbable devices made of forged composites of hydroxyapatite (HA) particles and poly-L-lactide (PLLA)*, *Biomaterials* 20 (1998) 859.
12. TENHUISEN, K. S., MARTIN, R.I. KLIMKIEWICZ, M., BROWN, P.W., *Formation and properties of sintetic bone composite: hidroxy-apatite collagen*, *Journal of biomedical materials research* , 29: 7, 1995 Jul, 803-10.
13. TENHUISEN, K. S., BROWN, P.W., *The formation of hydroxyapatite-gelatin composites at 38 degrees C*, *Journal of biomedical materials research* 1994;28(1):27-33
14. HUTMACHER, D.W. *Scaffolds in tissue engineering bone and cartilage*, *Biomaterials*. 2529-2543 (2000) 21.
15. LI, S. H., DEGROOT, K., LAYROLLE, P., J.P. *Preparation and characterization of porous titanium*. *Key Eng Mater* 218–220 (2002) 35.