Characterizations of the β-TCP Suspensions

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In this work some characterizations of the β-TCP suspension were performed from the stability and homogeneity point of view, starting from β-TCP ultra fine powders synthesized by precipitation from solutions. Preparation of the slurries involved combining of the β-TCP ceramic powders with an aqueous medium and dispersants (inorganic and organic) in different rations. The used powders in this work were evidenced by X-ray diffraction analysis (XRD), thermal analysis (TG/DTA/DGA), and the β-TCP suspensions with the ZetaPlus Brookhaven type. Our research results indicate that it is possible to obtain the β-TCP stable suspensions by control of the properties used dispersing agents and specific operations.

Keywords: tricalcium phosphate powder, ceramic suspensions, deflocculation, zeta potential

Calcium phosphate compounds have importance in the field of biomaterials due to their positive (in vitro and in vivo) responses including bioactivity, biocompatibility and osteoconductivity [1]. Tricalcium phosphate $Ca_3(PO_4)_2$ (β-TCP), an osteoconductive as well as bioresorbable ceramic, has found applications as bone cement and bone implant material, respectively.

Different techniques for elaborations of a ceramic materials used in medical applications require a suspensions containing high volume fraction of fine particles with stabile and homogeny characters [1,6-7]. The suspensions behaviour can be adjusted by modifying different processing parameters, such as the chemical composition of the reagents, the particle size, and the addition of dispersing agents; the function of dispersant/ solvent systems is, first, to wet the surfaces so that attractive forces can be overcome and, second, to modify the surfaces proprieties so that the particles will not recombine, or flocculate.

β -TCP powders used for the preparation of suspensions must be characterized by a small particle size and high chemical purity. This powder affect the functional characteristics of the suspensions in which it is included; the mean particle size of the particles in, as well as the surface area and the particle size distribution of the β-TCP can influence the setting time of the suspension and in case foams the compressive strength.

β-TCP powders can be prepared by different methods [2-5], but the most used is the wet – chemical synthesis. Many researchers focus their studies to clarify the changes in the size and morphology of the crystallites that occurs with increasing calcination temperature [2-4]. A Ca-deficient apatite with Ca/P ratio of 1.5 was prepared and, structural changes observed at temperatures between 500 and 1100°C [3]. Under non-equilibrium conditions, the phase transformation from Ca-deficient apatite to β–TCP occurred over the temperature range of 710 – 740°C. The synthesized pure Hap and TCP powders were found to be stable at 1300°C in air for prolonged heating times [4].

By the nature of aqueous chemistry of calcium phosphate phase system (CaO-P_2O_5-H_2O – ternary system), it is theoretically not possible to form β-TCP powder in a single-step, aqueous chemical precipitation process. Therefore, the only choice is to obtain $Ca_9(HPO_4)(PO_4)_5OH$ powder (precipitate), which is also named ,,apatitic tricalcium phosphate", and then to convert it to TCP by calcinations at different low temperatures.

Low temperature calcinations will not destroy the chemical composition of the precipitates. These calcinations will only cause the evaporation of 1 molecular unit of H_2O from one formula unit of the apatitic tricalcium phosphate, according to the following reaction:

$$Ca_9(HPO_4)(PO_4)_5OH = 3Ca_3(PO_4)_2 + H_2O \quad (1)$$

However, it is important to know and to control the phase evolution during the process for its optimizing in obtaining of pure β - TCP ultra fine powders, also to know the suspension characteristics for better understanding of the ceramic materials behaviour in future studies.

Experimental part

Preparation of the powders

Ceramic nanopowders based on tricalcium phosphate, variation of the low temperature, beta, were synthesized by precipitation chemical synthesis, from salt solutions. The starting raw materials such as $Ca(NO_3)_2\,4H_2O$ and $(NH_4)_2HPO_4$ were of high-purity, being made by Fluka. All samples with a Ca/P ratio of 1.5 were obtained by adding an aqueous solution of $Ca(NO_3)_2\,4H_2O$ to an aqueous solution of $(NH_4)_2HPO_4$ under stirring. Upon addition of calcium nitrate, the solution immediately becomes opaque and precipitates. A certain amount of concentrated (25%) ammonia water (NH_4OH) was added to the reaction mixture to ensure the formation of apatitic tricalcium phosphate ($Ca_9(HPO_4)(PO_4)_5OH$) with continuous stirring. The solution was stirred for 1-2 h and then washed with distilled water, dried at 60 °C /6 h , followed by calcination in air at 800°C for 2 h.

The formation of the TCP and the main temperature transformation of the precursor (apatitic tricalcium phosphate) was evidenced by X-ray diffraction analysis (XRD) and thermal analysis (TG/DTG/DTA).

The crystal structure analysis and mineralogical composition were determined by a X-ray powder diffractometer, Bruker-AXS, D8 ADVANCE with CuK_α

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radiation. The particles sizes of the calcined samples were evidenced with ZetaPlus Brookhaven type device.

The transformation temperature from apatitic tricalcium phosphate to β-TCP was determined by a thermal analysis (TG/DTG/DTA), using a Derivatograph MOM Budapest at a heating rate of 10 K/min.

Preparation of the suspension

In order to obtain stable and homogenous suspensions with an initial solid content of 60wt%, two dispersant were tested: sodium polyacrylic acid and di-sodium pyrophosphate made by Merk.

The slurries were prepared by first mixing deionized water and dispersants (0-2 wt% based on dry solid mass) ultrasonic and mechanical. Then powders were progressively added for a period of 20 min and agitation for a 30 min to prepare a fluid system enable to all further utilizations (like sponge techniques).

The dispersibility of β-TCP powder in deionized water was evaluated firstly by simple sedimentation experiments, using 10 wt% solid-loaded suspensions (2 g powder in 10 cm^3 deionized water) in the *p*H range 6-12, and as a function of the quantities of the two dispersing agents added (0-2 wt%, with respect to the β-TCP powder). The zeta potential of the samples was determined with a ZetaPlus Brookhaven type device.

Results and discussion

Characterization of the powder

Firstly, from this method (precipitation synthesis, from salt solutions), intermediary precursor was obtained; characteristics peaks are apatitic tricalcium phosphate, in accordance with ASTM 46-0905 files (fig. 1.).

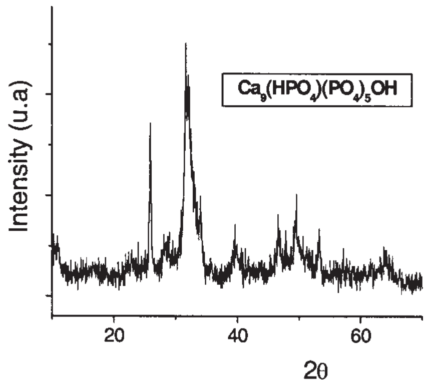

Fig. 1. Curve profile of the X-ray diffraction for the formed precursor

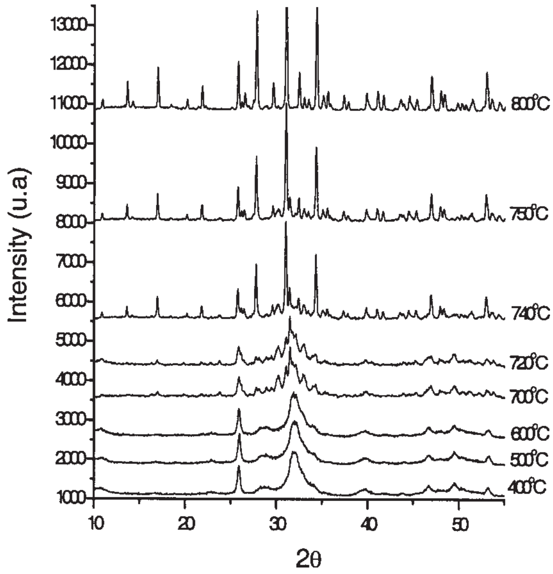

Fig. 2. XRD patterns showing the transformation of apatitic tricalcium phosphate to crystalline β -TCP that occurs at a temperature between 700 – 800 °C

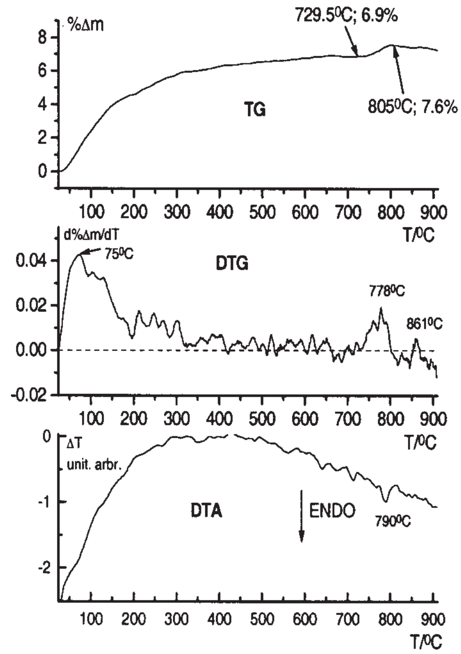

Fig. 3. Curves of TG/DTG/DTA for formation of the β -TCP compound

XRD analysis of the calcined samples indicated that the transformation from apatitic tricalcium phosphate to β-TCP, like unique phase, was realized at ~ 800°C (fig. 2).

Differential thermal analysis (DTA) data shown in figure 3, indicate an endothermic peak at 790°C, corresponding to the transformation from precursor to β-TCP, in correlation with X-ray diffraction measurements.

The particles sizes of the β -TCP powders used, evidenced with ZetaPlus Brookhaven type device was very fine in the range of nanometric values with particles size under 210 nm (fig.4.).

Characterization of the suspensions

The particle-settling characteristics of a 10wt% slip left undisturbed for sediment in a glass cylinders were studies by measuring sedimentation heights as a function of *p*H. The sedimentation heights after 24 h, shown in figure 5, reveal that the β-TCP powder was highly flocculated in deionized water. The lowest sedimentation volume which indicates the highest stabilization was obtained at condition where *p*H level was 10-11 for samples made with dispersing agents.

The suspensions containing 0.01wt% particles without and with two dispersants (sodium polyacrylic acid and di-sodium pyrophosphate made by Merk) was characterized with ZetaPlus Brookhaven type device. Figure 6 shows the zeta potential curves of the β-TCP powders as a function of *p*H, without and with dispersing agents (2% sodium polyacrylat acid and di-sodium pyrophosphate). The iso-electric point (IEP), in absence of dispersants, was found at *p*H 7.52. The addition of the different dispersants increases the negative zeta potential values leading to an increase of the repulsive force among particles.

The β -TCP powders synthesized by precipitation, from salt solutions were highly flocculated when dispersed in

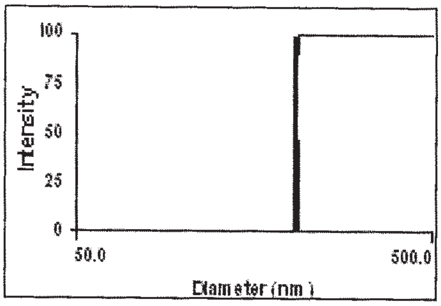

Fig.4. Particles size of the β-TCP powders

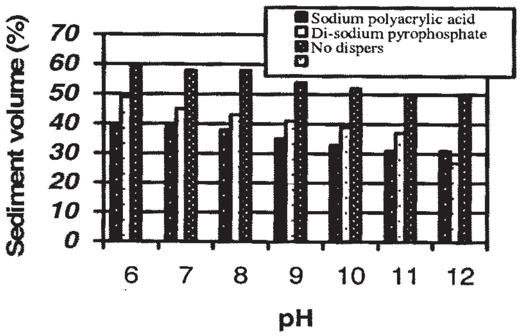

Fig.5. Variation of sediment volume with *p*H level

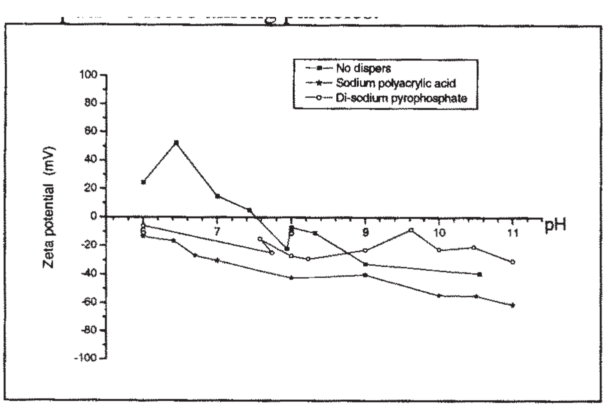

Fig.6. Zeta potential curves of β-TCP particles in the absence and presence of dispersing agents

aqueous medium; the iso-electric point (IEP), was found at *p*H =7.52. The type and amount of dispersing agent added revealed to be an important factor that determines the behavior of the β-TCP suspensions. Two dispersing agents (sodium polyacrylic acid and di-sodium pyrophosphate made by Merk) were studied for their influence on the deagglomeration and dispersion of β-TCP powders in aqueous media.

The most efficient dispersant used in this work was sodium polyacrylic acid enables to prepare a stable suspensions containing 60 wt% solid. It was determined that a 2 wt% dispersing agents with respect to the ceramic powders at a *p*H level between 10-11 was sufficient for deflocculating of β -TCP powders.

Conclusions

The pure β-TCP powders used in this work obtained by precipitation chemical synthesis, from salt solutions was very fine in the range of nanometric values with particles size under 210 nm.

Sodium polyacrylic acid is dispersant that produce the higher negative zeta potential values and it is recommended for further applications, because it is the most promising electrostatic stabilizers, and would enable to achieve high solids loading.

The main results are in concordance with the data from specialty literatures.

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