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Synthesis and characterization of nano-sized β-Tricalcium phosphate: Effects of the aging time

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Abstract: *In this study, nanosized powders β -Tricalcium phosphate β -$Ca_3(PO_4)_2$ (β -TCP) were synthesized via aqueous precipitation technique using a diammonium phosphate solution $(NH_4)_2HPO_4$ and a calcium nitrate tetrahydrate solution $Ca(NO_3)_2,4H_2O$ as precursor materials, with a Ca/P molar ratio 1.50 from the initial reagents. The effects of various aging time on the nanocrystalline β –TCP properties was studied during synthesis process. 2, 24, 48, and 72 h aging times were chosen. The crystallinity, composition phases, morphology and particle size of the products were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FT-IR), differential thermogravimetry, thermal analysis (TG–DTA) and inductively coupled plasma ICP AES atomic emission spectroscopy. The influence of various aging time on the Ca/P ratio and composition of TCP phase was also been investigated.*

Keywords**:** *β-Tricalcium phosphate, aging time,chemical precipitation, X-ray diffraction, FTIR.*

I. Introduction

Tricalcium phosphate $Ca_3(PO_4)_2$(TCP) is frequently used as bone graft substitutes in many surgical fields like the orthopedic, dental, plastic surgeries [1]. Its chemical composition, near to the bone, confers to its excellent biocompatibility and osteointegration properties. Moreover, its high resorbability in the human biological environment allows a significant recolonisation of the operational site by advancing bone growth during the progressive degradation of this material.

TCP can exist under three polymorphs, such as: β-TCP stable below 1120°C, α-TCP stable between 1120 and 1470 ◦C and α‘-TCP above 1470◦C. The latter is of no interest because it transforms into the α-form during cooling. β-TCP is stable at room temperature and reconstructively transforms at 1125°C into α-TCP, which is metastably retained until room temperature during the cooling [2]. The ideal Ca/P ratio of β-TCP is 1.5. As reported by Dickens and al. [3, 4], the β -TCP crystallizes in the rhombohedral space group R3c with unit-cell parameters a = 10.4121(3); c = 37.3517(5) Å [5].

TCP is a resorbable temporary bone space filler material. When implanted, TCP will interact with body fluids and form the hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$ or HA). The biocompatibility andsimilarity of calcium phosphates like hydroxyapatite and tricalcium phosphate to the mineral composition of human bone and teeth have made them suitable for substitution ofdamaged segments of human skeleton system [6, 7]. Many methods are used to synthesize of such biomaterials including wet-chemical method [8, 9], solid-state process [10, 11] and microwave irradiation [12, 13]. The most conventional is the precipitation in aqueous medium starting from $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$ as raw materials. However, the synthesis of a pure β -TCP by this method requires a close control of many parameters such as, reaction pH, temperature, stoichiometry of the raw materials, aging time. A light variation of these experimental parameters can generate drastic variations in composition of the final product [14] and reveal the pyrophosphate calcium phase ($Ca_2P_2O_7$ or CPP) or the hydroxyapatite phase $Ca_{10}(PO_4)_6(OH)_2$. Since these properties are affected by synthesis conditions and aging time is the most important factors in the synthesis of TCP. In this work an attempt was made to investigate the influence of aging time on the crystallinity and structural development of TCP.

By the nature aqueous chemistry of calcium phosphate system (i.e, $CaO-P_2O_5-H_2O_2$) ternary system, it is theoretically impossible to form TCP, $Ca_3(PO_4)_2$, powders in a single-step. Aqueous precipitation process therefore is the best thing to doin order to precipitate the $Ca_9(HPO_4)(PO_4)_5OH$, this product named apatitic tricalcium phosphate having a Ca/P ratio of 1.5, and then convert it to TCP by calcination. The evaporation of 1 molecular unit of H_2O from 1 formula unit of the apatitic tricalcium phosphate, according to the below, hypothetical reaction:

$$Ca_9(HPO_4)(PO_4)_5(OH) \rightarrow Ca_9(PO_4)_6H_2O \rightarrow 3Ca_3(PO_4)_2 + H_2O$$

This reaction involves a slight change in the crystal structure of the initial precipitate, therefore, sufficient time must be allowed at the temperature to push the reaction for completion.

II. Experimental

1. Preparation of the apatitic tricalcium phosphate (Ap-TCP)

The apatitic tricalcium phosphate $Ca_9(HPO_4)(PO_4)_5(OH)$ powders were prepared by aqueous precipitation technique using a diammonium phosphate solution $(NH_4)_2HPO_4$ (DAP) and a calcium nitrate tetrahydrate solution $Ca(NO_3)_2,4H_2O$ (CNT) as precursor materials. CNT and DAP solutions were prepared by dissolving the crystals in distilled water. In all the reactions, the ratio of calcium to phosphorous was Ca/P = 1.5 (mole ratio). All reactions occur at CTN and DAP concentrations of 0.15M and 0.1M, respectively, at room temperature, and at a pH of about 10. CNT solution was added to the DAP solution in constant stirring. 2 ml of 25 vol.% ammonium hydroxide NH_4OH solution was added to regularize the pH value following the addition of calcium phosphate. This precipitated solution was stirred for 2 h and aged at room temperature for different times ranging from 2h to 72h. The precipitate was filtered and washed repeatedly using distilled water to remove NH_4^+ and NO_3^- ions. The resultant precipitate was dried at 60° C for 24 h in a dry oven.

2. Production of β -$Ca_3(PO_4)_2$.

These fine powders produced are calcined at 800°C (with a heating rate of 10°/mn) in electrically heated chamber furnace into alumina crucible and soaked at this temperature for 12 hours. Samples were cooled to room temperature with a cooling rate of 5° C/mn.

III. Investigations methods

1. XRD patterns

Crystalline phases were identified by means of a XPERT-PROPW3050/60 (Theta/Theta) X-ray diffractometer (XRD) using CuKα radiation and operating at 45 kV and 40 mA. XRD patterns were collected over the 2θ range of 3-90° at a step size of 0.06°. Crystalline phases detected in the patterns were identified by comparison to the standard patterns from the ICDD-PDF (International Center for Diffraction Data-Powder Diffraction Files).

The mean crystallite size (D) was calculated from the XRD line broadening measurement from the Scherrer equation [15] Eq (1):

$$D = 0.89\,\lambda / \beta \cos\theta \quad (1)$$

Where λ is the wavelength of the used Cu Kα radiation, β is the full width at the half maximum of the β-TCP line and θ is the diffraction angle.

The fraction of crystalline phase (Xc) of the β-TCP powders was evaluated by the following Eq. (2) [16]:

$$Xc = 1 - \nu/I \quad (2)$$

Where I is the intensity of highest diffraction peak and ν is the intensity of the hollow between two considered diffraction peaks of β-TCP.

2. FTIR spectra

The functional groups present in the prepared powder were recorded on FTIR spectrophotometer, VERTEX 70, Genesis Series (400–4000 cm-1, resolution 4, scans 20). For this 1% of the powder was mixed and ground with 99% KBr and the spectrum was taken in the range of 400 to 4000 cm^{-1}.

3. Thermogravimetric analysis

Thermogravimetric analysis TG/DTA (Model Lapsys DSC-DTA/TG SETARAM) were performed in an air atmosphere only on the starting chemicals of our powder synthesis route over the range of 30°–1000°C, with a scan rate of 20°C/min.

4. Chemicalanalyzes by ICP-AES

The Ca/P ratio of the dried powder was measured by inductively coupled plasma ICP-AES atomic emission spectroscopy (modela2- JobinYvon). No differences were observed in the Ca/P values between the as-dried and calcined powders.

5. Transmission electron microscopy

The size and morphology of fine powders were observed on a transmission electron microscope (Philips CM10, Eindhoven, The Netherlands) that operated at the acceleration voltage of 100 kV.

IV. Results and discussion

The XRD patterns of the samples aged for different aging periods and sintered at 800°C are given in Figure 1.

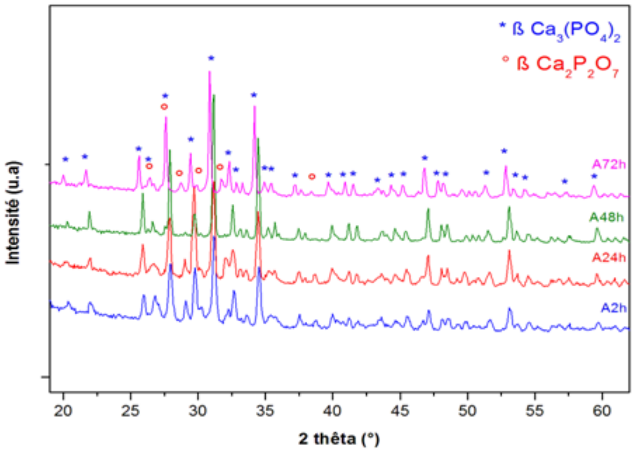

Figure 1: XRD spectra of the samples calcined at 800°C and aged at differents times.

All the diffraction peaks positions match well with the standard XRD pattern of β -TCP (JCPDS NO.9-169). The diffraction peaks are high and narrow, implying that the β -TCP crystallizes well, this being the main crystalline phase present. In addition, a minor amount of pyrophosphate (CPP) β-$Ca_2P_2O_7$ (JCPDF 9-346) was also found. The XRD patterns of the powder with aging time 48h showed that a presence of pure β -TCP with only a trace amount of β-$Ca_2P_2O_7$ undetectable by XRD.

The Ca/P molar ratios were carried out by ICP and summarized in Table 1.

Table 1: Characteristics of the synthetic powders aged at different aging times and calcined at 800°C.

Aging time (h)	Ca/P ratio	crystallite size D (nm)	fraction of crystalline phase (Xc)
2	1.30	32	83
24	1.32	42	86
48	1.35	42	95
72	1.37	42	94

The values of Ca/P molar ratio vary between 1.30 and 1.37, this parameter increases slightly with the rise of times of aging. The Ca/P ratio of the precipitate did not depend directly on the Ca/P value of the initial reagents. Some powders were synthesized using a Ca/P ratio of 1.667 for the initial reagents, but this ratio had to be decreased down to 1.50 in order to synthesize powders with a Ca/P ratio close to 1.50 [17].

We note the Ca/P modification of the initial reagent. The difference between initial and final Ca/P ratio can be explained by a slight variation of manufacturing process parameters, as working temperature, reaction pH, slurry stirring, weighing, etc [18].

This second phase ($Ca_2P_2O_7$) occurs when the Ca/P ratio is less than 1.5. When we heated to 800°C, $CaHPO_4$ and Ap-TCP are transformed into β-$Ca_2P_2O_7$ and β-TCP as shown in the following equation:

$$Ca_9(HPO_4)(PO_4)_5(OH) + 2CaHPO_4 \rightarrow 3Ca_3(PO_4)_2 + Ca_2P_2O_7 + 2H_2O$$

The determined amounts of crystallinity and crystallite size (determined by Scherrer equation) of calcined β-TCP are given in Table 1. The crystallite size and the degree of crystallinity increase with aging time and become stable after 48h for both.

In order to identify the molecular arrangement of the precipitated powders, FT-IR analysis was performed. The figure 2 illustrates the representative FT-IR spectra of the calcined powders.

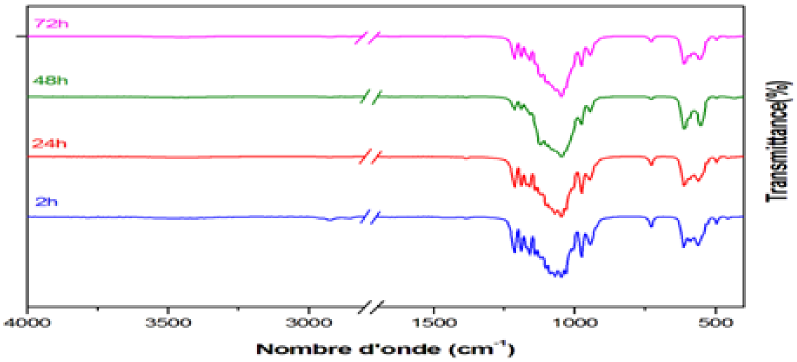

Figure 2: FT-IR spectra of the samples calcined at 800°C and aged at different aging time.

It has been found that [19–22] the functional groups generally observed in the FT-IR spectra of calcium phosphate-based materials are PO_4^{3-}, OH^-, CO_3^{2-}, and HPO_4^{2-} groups in the range 4000–400 cm^{-1}. These spectrumsare similar to that of β–TCP, it clearly shows the characteristic bands of phosphate groups appeared for all the samples: ν2 PO_4 at 456 cm^{-1}, ν4 PO_4 bands at 561–613 cm^{-1}, and ν3 PO_4 band in the rangeof 1100–1000 cm^{-1} in all the cases. The presence of bands at 1120, 1100, 1006 and 945 cm^{-1} can be assigned to PO_4 groups of β–TCP. Hydroxyl groups were also discerned at 1640 and 3400 cm^{-1} (weak intensity). In addition, at 727, 1190 and 1213 cm^{-1}, we can observe the presence of $P_2O_7^{4-}$ group, which is characteristic to the calcium pyrophosphate phase $Ca_2P_2O_7$ in agreement with the previous XRD results. It should be noted that the characteristic peaks of $Ca_2P_2O_7$ were not found in XRD profiles of the powder with aging time 48h.

The DTA/TG data are shown in figure 3. Two endothermic peaks at ~100º C and ~460º C are associated to the removal of absorbed and crystalline water respectively. The third at ~800° C correspond to the transformation from precursor to β-TCP.

The morphologies of the β-TCP calcined powders aged 2h (TCP 2h) and 72h (TCP 72h) were shown in Figure 4a and 4b respectively. It was observed that β-TCP comprised of nanosized particles were almost spherical and highly agglomerated, a slight increase in particle size was observed by increasing the time Ripening, the observed particle size was ~300 nm and ~ 400 nm for (TCP 2h) and (TCP 72h) respectively. It has been found that nanoparticles with sphericalmorphology are better than other irregular morphologies due to the well space fillings and the low percentage of voids in the final product [23].

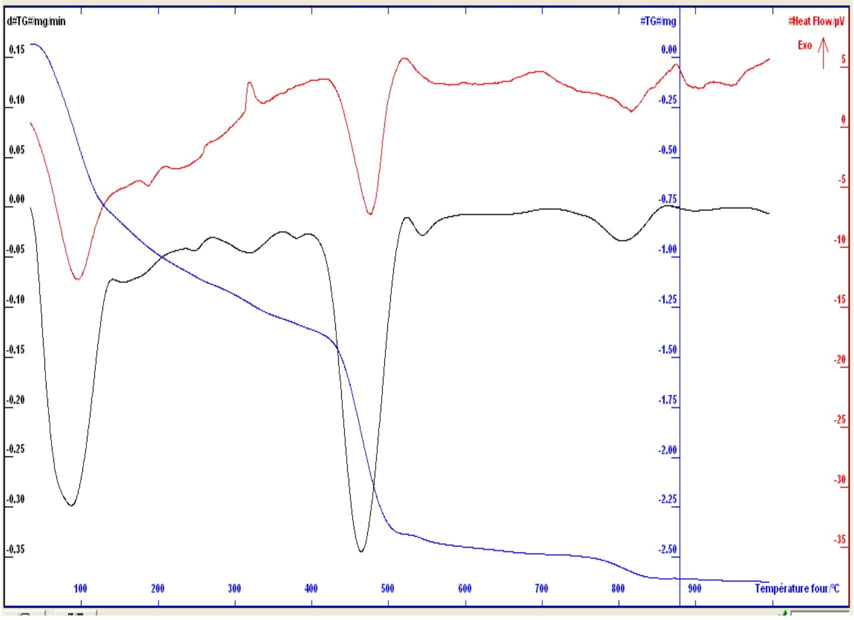

Figure3 : Thermal analysis of the as-dried sample for 2 h of aging

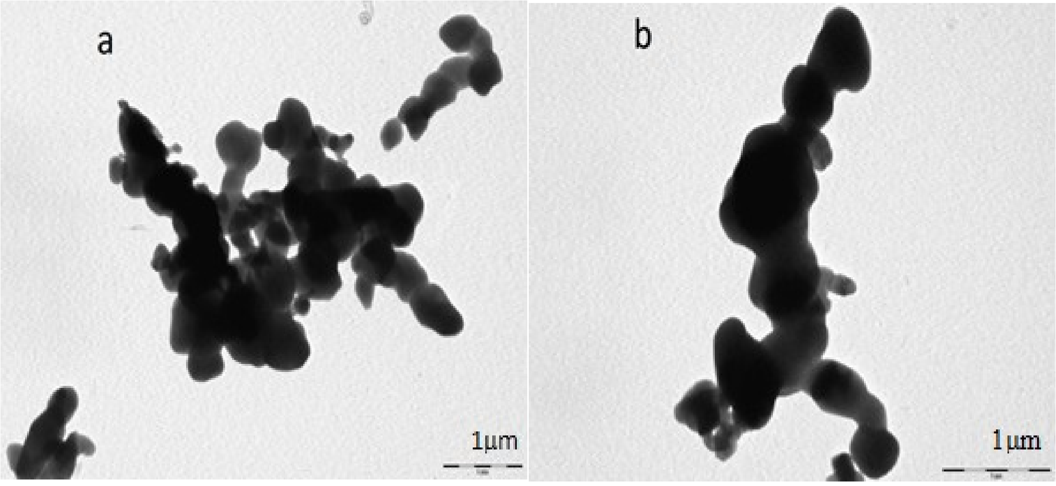

Figure 4: TEM micrograph of calcined powders at 800°C. (a) with 2h aging, (b) with 72h aging.

V. Conclusion

The aim of this study is to present the effects of aging time of the Ca/P molar ratio, microstructure and composition phases of tricalcium phosphate. The TCP is precipitated from aqueous media with the experimental synthesis conditions. The ICP, XRD and FTIR results indicated that for all compounds, the Ca/P ratio is less than 1.5 and this parameter increases slightly with the rise of times of aging. The calcined powders show the presence of two distinguishable crystalline phases β-TCP and a second phase identified as pyrophosphate β-CPP. It could be observed that both the crystallite size and crystallinity increase with the aging time. They become stable after 24h and 48h respectively. According to the MET results, the synthesized nano-powders of β–TCP particles were easy to aggregate and the particle morphology are spherical.

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