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Alpha-tricalcium phosphate synthesized by two different routes: Structural and spectroscopic characterization

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Abstract

In the present study two alpha-tricalcium phosphate powders (αTCP-1 and αTCP-2) were synthesized by slightly different routes. For structural comparison, commercial pure α-TCP (αTCP-st) was used. The influence of the preparation method on physicochemical properties of α-TCP was investigated using scanning electron microscopy (SEM) and powder X-ray diffraction (PXRD). The chemical structure of the samples was determined using spectroscopic methods: mid-infrared spectroscopy (FT-IR), Raman spectroscopy and solid-state nuclear magnetic resonance (ssNMR). Specific surface area of the synthesized αTCP-1, αTCP-2 and standard αTCP-st powders was measured using the BET method with nitrogen adsorption. The studies have shown differences in morphology of the samples. αTCP-1 is characterized by small grains forming agglomerates below 2 μm while the αTCP-2 powder has a tendency to form compact clusters with micropores below 5 μm. Its specific surface area is about 5 times lower than αTCP-1 and close to the reference material. PXRD demonstrated that αTCP-1 is significantly less crystalline. In addition, the crystallinity of αTCP-2 was comparable to that of the standard sample. FT-IR and ssNMR experiments have indicated that αTCP-1 is not homogenous but contains beside alpha-tricalcium phosphate amorphous calcium phosphate (ACP). We suggest that ACP may be found in the interior of agglomerates and therefore it is not converted to a highly crystalline form at higher temperature. Different ways of grinding and heat treatment strongly influence characteristic properties (crystallinity, Ca/P molar ratio, phase composition, specific surface area) of the obtained αTCP.

Keywords: B. Electron microscopy; Alpha-tricalcium phosphate; Infrared spectroscopy; Nuclear magnetic resonance

1. Introduction

Calcium phosphates play a key role in reconstructive and reparative surgery, and in dentistry due to their considerable similarity to the mineralized fraction of bone tissue and the hard tissues of the teeth [1–3].

The compound most frequently used for the production of bioceramics is hydroxyapatite (HA) with the molecular formula $Ca_{10}(PO_4)_6(OH)_2$ and with a Ca/P molar ratio of approximately 1.67. Hydroxyapatite exhibits the greatest similarity to biological apatite, which is the main component of mineralized tissues (bones, enamel, dentine, and cementum), but is characterized by poor resorbability [1,4]. Therefore, in practice hydroxyapatite is often mixed with beta-tricalcium phosphate (βTCP) at varying HA/βTCP ratios, to form the so-called biphasic calcium phosphates in order to increase the bioreactivity of the ceramic material [5–8].

Another phosphate material that has been recently gaining popularity is alpha-tricalcium phosphate (αTCP). Thanks to its relatively high solubility, it has been applied as a component of bone cements and other bone substitutes [8–13]. αTCP with the liquid phase forms a very hard material that can be used for filling bone defects as well as for joining another (e.g., metallic) biomaterial with bone tissue. Moreover, according to Eq. (1), αTCP reacting with water leads to calcium deficient

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apatite, which imparts high biocompatibility to the cement [14–17].

$$3Ca_3(PO_4)_2 + H_2O \rightarrow Ca_9(PO_4)_5(HPO_4)OH \quad (1)$$

A major problem with the application of αTCP as an implantation material is its instability at ambient temperature. It should be noted that this calcium phosphate is thermodynamically stable in the temperature range of 1140–1470 °C [18]. Therefore, its synthesis is quite difficult as the material produced at high temperature must be rapidly cooled to stabilize its structure. However, it has recently been observed that some ions (such as silicates) improve the stability of the material at lower temperatures [19].

Despite the difficulties linked to obtaining αTCP, researchers continue to seek new areas of its application and new methods of its synthesis [20–24]. Ref. [25] offers a review of current findings in this bioceramic domain.

The objective of our work was to synthesize alpha-tricalcium phosphate by two slightly different routes and to examine the effect of the synthesis method on the structure and physicochemical properties of the obtained material. The analytical methods used included powder X-ray diffraction (PXRD), transmission (TEM) and scanning electron microscopy with energy-dispersive spectroscopy (SEM/EDS). Furthermore, the chemical structure of the obtained materials was determined by vibrational spectroscopy (mid-infrared FT-IR and Raman spectroscopies) and solid-state nuclear magnetic resonance (ssNMR) studies.

2. Materials and methods

2.1. Synthesis

α-Tricalcium phosphate powders (αTCP-1, αTCP-2) were synthesized by the wet chemical method, applying chemically grade $Ca(OH)_2$ (POCH, Poland) and 85 wt% solution of H_3PO_4 (POCH, Poland) as reagents. The Ca/P molar ratio of reagents was in the range of 1.42–1.50. The pH of the reaction environment varied from 4.0 to 5.5. The suspension of gelatinous amorphous calcium phosphate was subjected to aging and sedimentation processes, after which the solution was decanted and concentrated to a precipitate containing 70–80% of water.

After drying, the filter cake of αTCP-1 material was crushed into fractions below 0.6 mm, subjected to mechanical treatment in an agate mortar followed by calcination at 1300 °C and grinding by attrition to the grain size below 0.06 mm.

In the case of αTCP-2, after drying, the filter cake was crushed in a rotary–vibratory mill to a grain size below 0.06 mm and then followed by two-stage heat treatment at 800 °C and 1300 °C.

2.2. Analytical methods

Specific surface areas of the αTCP-1, αTCP-2 and αTCP-st powders were calculated using the Brunauer–Emmett–Teller (BET) method with nitrogen adsorption (ASAP 2010 Micromeritics). Apatite crystals were observed using transmission electron microscopy (TEM; JEOL JEM 1220). A drop of a sample suspension in ethanol was placed on a Cu grid covered with a formvar film, allowed to dry and analyzed under an accelerating voltage of 80 kV. The microstructure of the powders was examined by scanning electron microscopy (SEM, Nova NanoSem 200). In order to avoid a charging effect, all samples were sputtered with carbon prior to measurements. The Ca/P ratio of studied samples was analyzed using wavelength dispersive X-ray fluorescence (WD-XRF, Thermo ARL). The samples were dissolved in HNO_3. The calibration curve method was employed and each analysis was repeated six times.

The composition of the crystalline phase of the studied samples (including purity and stoichiometry) was examined by powder X-ray diffraction (PXRD, Philips X'pert Pro diffractometer).

Raman spectra were obtained in the backscattering configuration using a Labram HR800 (Horiba Jobin-Yvon) confocal microscope system equipped with a Peltier-cooled CCD detector (1024 × 256 pixel). Diode pumped, frequency doubled Nd:YAG laser (532 nm) was used as an excitation source. The confocal pinhole size was set to 200 μm and the holographic gratings with 600 grooves mm^{-1} were used. Spectra were obtained employing a 50× magnification Olympus objective. The spectrometer was calibrated using the Raman band of a silicon wafer observed at 520 cm^{-1}.

Mid-infrared spectra were recorded using KBr pellets in the region 4000–400 cm^{-1} with a Perkin Elmer Spectrum 1000 spectrometer. The resolution was about 2 cm^{-1} and the number of scans was 30. Photoacoustic spectra (PAS) were collected using an infrared photoacoustic cell (MTEC Photoacoustic, Inc.). For each experiment, resolution and number of scans were set to 8 cm^{-1} and 30, respectively. All FT-IR spectra were then processed using the GRAMS/AI 8.0 software (Thermo Scientific).

Solid-state nuclear magnetic resonance spectra (ssNMR) were recorded at room temperature using a 400 WB Bruker Avance spectrometer at proton and ^{31}P resonance frequencies of 400 and 160 MHz, respectively. For all experiments, a Bruker magic-angle spinning (MAS) probe and ZrO_2 rotors (7 mm in diameter) were used. Spectra were recorded under MAS at 7 kHz.

Both conventional one-pulse-acquire (Bloch-decay, BD) and cross-polarization (CP) ^{31}P spectra were recorded. Recycle delays of 10 s and 30 s were used for ^{31}P CP and BD NMR spectra, respectively. For both the techniques, 32 transients were recorded. Variable contact time $^{1}H \rightarrow {}^{31}P$ CP MAS experiments were done for 64 arrayed contact time values in the range from 25 μs to 20 ms. CP kinetic functions were fitted using Kaleida Graph software (version 3.5 for PC, Synergy, Software, 2000).

3. Results and discussion

Specific surface areas (SSA) measured by the conventional BET method for αTCP-1, αTCP-2 and αTCP-st powders were equal to 5.74 ± 0.03, 1.43 ± 0.17 and 1.15 ± 0.12 $m^2\,g^{-1}$, respectively. The high value of the specific surface area of the αTCP-1 powder may suggest better physicochemical and biological reactivity of this material. The results of SSA measurements and knowledge of the theoretical density of αTCP allowed it to calculate the average grain diameter (D_{BET}) of the investigated powders. An average