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Thermal and structural characterization of synthetic and natural nanocrystalline hydroxyapatite

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ABSTRACT

The aim of this work was to study the thermal stability on heating and to obtain the processing parameters of synthetic and bone-derived hydroxyapatite over temperatures between room temperature and 1400 °C by thermal analysis (thermogravimetry (TG)/differential scanning calorimetry (DSC) and thermo-mechanical analysis—TMA). Structural and surface modifications related to samples origin and calcination temperature were investigated by Fourier transformed infrared (FTIR) and Raman spectroscopy, X-ray diffraction (XRD) and BET method. FTIR spectra indicated that the organic constituents and carbonate are no longer present in the natural sample calcined at 800 °C. Raman spectra highlighted the decomposition products of the hydroxyapatite. The calcination treatment modifies the processes kinetics of the synthetic samples, being able to isolate lattice water desorption processes of decarbonization and the dehydroxylation processes. Shrinkage of calcined synthetic sample increases by 10% compared to uncalcined synthetic powder. From the TMA correlated with TG analysis and heat capacity data it can be concluded that sintering temperature of the synthetic samples should be chosen in the temperature range of the onset of dehydroxylation and the temperature at which oxyapatite decomposition begins.

1. Introduction

Hydroxyapatite (HAP), ($Ca_{10}(PO_4)_6(OH)_2$), is the main bone mineral component and is known as an implantable ceramic material for bone tissue and teeth reconstitution [1–6]. In addition to various synthetic chemical methods used to produce HAP, there are alternative ways to obtain HAP by its extraction from natural resources. The materials used as sources for the isolation of natural hydroxyapatite bone are varied: bovine [2,7], chicken [8], fish [9], pork [7,8], sheep bones [10], eggshells [11], coral [12] and seashells [13]. Natural HAP characteristics are different depending on the extraction applied method [4]. Various studies on HAP [5,7] indicate that there are considerable differences between synthetic hydroxyapatite and natural ones. Carbonate ions are a common impurity found in HAP and carbonated HAP appears to be an excellent material for bioresorbable bone substitutes [6].

High temperature processing of HAP-based materials is essential for biomedical applications and this implies the need for knowledge and understanding of thermal stability and transitions on heating. Thermal treatment of hydroxyapatite results in a series of physical and chemical processes that depend on the history and obtaining conditions of samples and significantly influence subsequent behavior of the material. The HAP phase transformation on heating consists of following processes: dehydroxylation, which takes place in two stages, according to the following reactions

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow Ca_{10}(PO_4)_6(OH)_{2-2x}O_x\square_x + xH_2O \tag{1}$$

$$Ca_{10}(PO_4)_6(OH)_{2-2x}O_{x}{}_{\ x} \rightarrow Ca_{10}(PO_4)_6O + (1-x)H_2O, \tag{2}$$

where □ denotes hydrogen vacancies, $Ca_{10}(PO_4)_6(OH)_{2-2x}O_{x\ x}$ is oxyhydroxiapatite (OHA), $Ca_{10}(PO_4)_6O$ is oxyapatite (OA), and decomposition of OA (stable in a narrow temperature range around 800–1050 °C [5]) along with HAP in calcium phosphates, according to the following reactions [6]:

$$Ca_{10}(PO_4)_6O \rightarrow 2Ca_3(PO_4)_2 + Ca_4(PO_4)_2O \tag{3}$$

$$Ca_{10}(PO_4)_6(OH)_2 \rightarrow 2Ca_3(PO_4)_2 + Ca_4(PO_4)_2O + H_2O \tag{4}$$

where $Ca_3(PO_4)_2$ is tricalcium phosphate (TCP) and $Ca_4(PO_4)_2O$ is tetracalcium phosphate (TTCP). Another possible decomposition reaction of OA [5] is:

$$Ca_{10}(PO_4)_6O \rightarrow 3Ca_3(PO_4)_2 + CaO \tag{5}$$

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The study of decomposition mechanisms is thus of key importance to optimize the processing of HAP materials. Sintering is one of the most important manufacturing steps that a ceramic body is subject to. It determines, mostly, the final properties of the ceramic, its behavior in service. The achievement of the desired final properties is dependent of the processing parameters. Therefore data are needed at sintering temperatures.

The aim of this work consists of thermal (TG-DSC, TMA), structural (X-ray diffraction, FTIR and Raman spectroscopy) and surface (BET, SEM, dynamic light scattering, DLS) characterization of the synthetic and natural HAP powders, emphasizing the influence of originating of samples and calcination temperature on the thermal stability of HAP samples. Thermal behavior of the HAP samples is discussed in terms of sample porosity and phase composition.

2. Materials and methods

2.1. Materials

The investigated samples were synthetic, namely, commercial hydroxyapatite from Aldrich (HA) and calcined commercial hydroxyapatite at 900 °C, in air (HA900), and natural hydoxyapatite, extracted from bovine bone (HAN).

2.1.1. Bovine bone-derived hydroxyapatite

A bovine tibia was obtained from a slaughterhouse and washed in water to remove visible tissues on the bone surface. A piece of cleaned bone of around 100 g was cut and ground to transform it into a fine powder (HANb). To remove the internal fats and proteins the bone powder was washed with deionized water until the pH of the washing water had the same value with the initial deionized water. This washed bone powder was treated with hydrogen peroxide 3% and then again rinsed with deionized water following the same previous protocol. The resulting powder was then dried in the oven under ambient conditions, at 100 °C, with 2 h holding time. Natural HAP was obtained after calcinations of the dried powder (HAN100) in an electric furnace under ambient conditions. Three calcination temperatures were tested, namely 700 °C, 800 °C and 900 °C, with one hour holding time [7]. The calcined powders of HAN100 were ground again and characterized by FTIR and TG-DSC techniques to find the optimal calcination temperature.

All HAP powders were stored in air atmosphere without humidity/carbon dioxide control.

2.2. X-ray diffraction

Powder X-ray diffraction (XRD) patterns were recorded using a Panalytical XPERT-PRO diffractometer with Bragg–Brentano configuration, operating with a PIXcel detector using Cu Kα radiation. Data were acquired in the range 10–70° (2θ) using a step size of 0.0263° (2θ). The sample was rotated on a monocrystalline silicon support. XRD analysis was carried out to identify different phases present in the starting powders as well as the formation of any thermal decomposition product of HAP. To measure the instrumental line broadening a known silicon powder standard was used.

The mean crystallite size (d) was calculated using Scherrer equation:

$$d = \frac{K * \lambda}{\left(\beta_{\text{sample}} - \beta_{\text{standard}}\right) * \cos\theta} \tag{6}$$

where shape factor, K was taken 0.9, assuming that the crystallites were spherical particles, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM), and θ is the Bragg angle.

2.3. Thermal analysis

For the thermal characterization a simultaneous high temperature thermogravimetry (TG) and differential scanning calorimetry (DSC) were employed. Thermal properties (temperature of transformations and mass change) of the HAP samples were measured by a TG-DSC Setaram Setsys Evolution 17 analyzer, in the temperature range from 40 to 1400 °C, with a scanning rate of 10 °C/min, in alumina crucibles, using Ar flow. Sample mass for simultaneous TG-DSC measurements was about 20 mg. The thermoanalyzer calibration was previously reported [14]. The error of TG measurement is $\pm 0.154\%$.

Heat capacities were determined in the temperature range of 400–1450 °C, using a sample mass of about 100 mg, the same gas flow, Ar, at a rate of 16 ml/min, in Pt crucibles. The protocol of heat capacity running is similar to that used in paper [14]. To determine peak temperatures and heat capacities, instrument software (Calisto-AKTS) was used. Peak deconvolution was done using modified Gaussian function (CALISTO software).

Linear expansion behavior of samples was measured from 40 to 1400 °C at a heating rate of 5 °C/min, in an Ar flow, using a thermomechanical analyzer (TMA) Setaram Setsys Evolution 17. Load is 0.049 N. By TMA technique the sample deformation under non-oscillating stress in function of a temperature program was measured. Powders were previously compacted at a pressure of 200 MPa in a 5 mm cylinder die. For each analyzed sample a blank curve obtained under the same conditions as those employed to test the samples was subtracted.

2.4. Surface and morphology characterization

Specific surface area (S, $m^2\ g^{-1}$) of HAP samples was measured by the Brunauer–Emmett–Teller (BET) nitrogen adsorption method in a Nova 2200e Quantachrome surface area analyzer. The samples were dried and degassed at 150 °C for 3 hours, and analyzed using a multipoint N_2 adsorption/desorption method. The pore volume and average pore radius were calculated using Barrett–Joyner–Halanda (BJH) model. The primary particle size (D_{BET}) was calculated by assuming the primary particles to be spherical [15]:

$$D_{\text{BET}} = \frac{6}{S\rho} \tag{7}$$

where ρ is the theoretical density of stoichiometric HAP (3.156 g/cm^3) and S is the specific surface area (S).

Size distribution and polydispersity index (PDI) of the powders were determined by dynamic lighting scattering (DLS, Malvern Nano ZS ZEN3600). PDI represents a dimensionless measure of the broadness of the size distribution calculated from the cumulants analysis (obtained by Zetasizer software). Surface characterization and size distribution of the sintered samples at 910 °C, 950 °C and 800 °C, 2 hours, in air, for HA, HA900 and respective HAN800 samples were also undertaken.

Powder morphology was examined by scanning electron microscopy (SEM) using a high-resolution FEI Quanta 3D FEG (Dual Beam) microscope.

2.5. Spectroscopic analysis

2.5.1. FTIR spectroscopy

Fourier Transform Infrared Analysis (FTIR) spectra were performed using the NICOLET IS10 equipment in the attenuated total reflection (ATR) mode, in the wavelength range of 525–4000 cm^{-1}, using 32 scans and a spectral resolution of 4 cm^{-1} to obtain information about the various chemical bonds. The peak locations and intensities were determined with the Omnic software (Nicolet Instrumentations Inc., Madison, WI, USA).