

Combining particle size distribution and isothermal calorimetry data to determine the reaction kinetics of α -tricalcium phosphate–water mixtures

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Received 7 September 2005; received in revised form 11 January 2006; accepted 12 January 2006

Abstract

Many calcium phosphate bone substitutes are based on the use of α -tricalcium phosphate (α -TCP) powder. This compound has been intensively studied, but some aspects of α -TCP reactivity are still controversial. The goal of this study was to determine the setting kinetics of α -TCP based on a new approach that compared particle size distribution data to isothermal calorimetry data. Results indicated that α -TCP conversion is mostly controlled by surface reactions, with at later stages a diffusion-controlled mechanism. The presence of an X-ray amorphous α -TCP fraction in the crystalline α -TCP powder increased the dissolution rate threefold, without modifying the reaction mechanism.

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Keywords: Calcium phosphate; Cement; Kinetics; Particle size distribution; Bone substitute

1. Introduction

Many formulations of hydraulic calcium phosphate cements contain α -tricalcium phosphate (α -TCP) powder as the main component. As a result, the hydraulic properties of α -TCP have been analyzed by several authors. In 1996 and 1997, respectively, Fernandez and Ginebra et al. [1,2] observed that the compressive strength and extent of reaction increased linearly with time, subsequently reaching a saturation level. In 1999, the latter authors refined their analysis based on the particle size distribution of α -TCP powder [3]. It was concluded that the reaction was initially controlled by α -TCP surface area, and then by the diffusion of reactants through the hydrated layer around α -TCP particles. Similar results were obtained by Sarda et al. [4]. Durucan and Brown [5] proposed a slightly different interpretation of the hydrolysis reaction of α -TCP: α -TCP hydrolysis reaction was believed to be

initially controlled by a surface-controlled mechanism, and later on by the rate of apatite formation according to a nucleation and growth mechanism.

Despite in-depth studies there is still little known about the effect of the synthesis conditions of α -TCP powders on their reactivity. Ginebra et al. [6] and Ducuran and Brown [7] showed that the setting reaction was accelerated when α -TCP powder was exposed to longer milling times. Recently, Gbureck et al. [8] demonstrated that prolonged milling of α -TCP led to the formation of an X-ray amorphous α -TCP which had a solubility three times that of standard α -TCP. Camiré et al. [9] related milling time and reactivity as measured by isothermal calorimetry. It was found that the total heat released during the conversion of α -TCP into calcium-deficient hydroxyapatite (CDHA) was increased two- to threefold when α -TCP was milled for a prolonged time. However, no kinetics data were presented. Therefore, the aim of the present study was to analyze the reaction kinetics of the α -TCP transformation into CDHA with respect to the milling conditions of the α -TCP powder.

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2. Materials and methods

The α -TCP powders used in the present study were the same as those used in a previous study [9]. An in depth description of materials and methods can be found in the latter document, and only a brief description is given here. Two α -TCP batches were produced from 2:1 molar mixtures of calcium carbonate (Merck, Germany, Art 102076) and dicalcium phosphate (first batch: Merck Art No 112076; second batch: Aldrich, Switzerland, Art 23475). The first powder (batch 1) was produced by Synthes Biomaterials (Bettlach, Switzerland), whereas the second powder was produced at the Robert Mathys Foundation. Both powders underwent a heating cycle characterized by a calcination at 900 °C (1 h), followed by a de-agglomeration step (with a pestle and a mortar until all particles passed a 0.5 mm sieve), and a final calcination at 1350 °C for 4 h. As α -TCP is a high-temperature phase metastable at room temperature, the powder was removed from the furnace at 1200 °C and quenched in air. Both batches were then milled according to two different routes. The powder of batch 1 was crushed by hand until all particles passed through a 2 mm sieve, and then milled by ball milling at 60 revolutions per minute (rpm) in ethanol (300 g ethanol, 370 g α -TCP powder, and 2.3 kg ZrO₂ beads; 2 L polyethylene containers—diameter 11 cm). The ethanol had a relatively low purity (96.2% ethanol, 3.6% methanol) for cost reasons. The powder–alcohol mixture was then sieved through a 0.5 mm sieve to remove the beads, and dried in a well-ventilated oven at 60 °C. Even though the latter powder is normally used as such, the powder was milled in a planetary mill (Pulverisette 5, Fritsch, Germany) using ZrO₂ spheres (weight: 3 g each) for 3, 7, 15, 30 and 45 min (100 g powder, 100 ZrO₂ beads, rotation speed: 400 rpm). The powder of batch 2 was milled with a jaw crusher (Pulverisette 1, Fritsch, Germany), and then by hand with a pestle and a mortar until all particles passed through a 2 mm sieve. The latter powder could not be used as such, and had to be milled additionally with the planetary mill for 15, 30, 75, 150 and 225 min with the same parameters as for batch 1.

In this paper, the milling time is arbitrarily defined as the duration of milling in the planetary mill. Therefore, the powder of batch 1 milled for 15 min had sustained a longer total milling time than the powder of batch 2 milled for 15 min. Nevertheless, the first study [9] demonstrated that the powders of batch 1 and batch 2 milled for the same duration in the planetary mill behaved very similarly.

Materials were characterized in a number of ways. The specific surface area (SSA) of the powders was determined using nitrogen adsorption and applying the Brunauer–Emmett–Teller theory (Gemini 2360, Micromeritics, USA). Particle size distribution (PSD) was determined using a laser particle size analysis (L300, Horiba, Kyoto, Japan). Three measurements were performed per powder. The average of these three measurements was subsequently used for the determination of the setting kinetics. No

β -TCP could be detected in any of the powders and only negligible amounts of HA were detected in the first α -TCP batch. The crystal size of the α -TCP powders was estimated from the X-ray diffraction (XRD) spectra using the peak breadth at half maximum (FWHM) of two neighboring peaks ((i) at $d = 2.619$ (43% peak according to JCPDS file 23–359) and (ii) at $d = 2.600$ (29% peak)) and the Scherrer equation. The crystal size decreased from about 60 nm at 3 min milling down to 25 nm at 225 min milling. Thermal behavior of milled α -TCP powders up to 500 °C was determined via differential scanning calorimetry (Mettler TA 4000 with measuring cell DSC-20; Switzerland). Differential scanning calorimetry up to 1500 °C was performed at a heating rate of 10 °C/min (Model STA 409, Netsch, Germany). Isothermal calorimetry tests were performed at physiological temperature by hydrating 1 g samples with a liquid to powder ratio of 1:3 with a 2.5% Na₂HPO₄ solution. The crystalline composition of the milled powders and the degree of conversion of set cements was measured for three powders (batch 1: 3 min milling, and batch 2: 15 min and 150 min milling times, respectively; there was too little powder left for most samples to allow such an analysis for all powders) using X-ray diffraction analysis (Siemens D5005, Karlsruhe, Germany) using CuK α radiation. 1.5 g of powder was mixed with 530 μ l of a 2.5% Na₂HPO₄ solution on a glass slab and the paste was afterwards hardened at 37 °C and 100% relative humidity for defined time periods of 30 min, 1, 2, 4, 8, 16 and 24 h. The hardened cement was then ground in acetone to stop the setting reaction and dried in air following XRD analysis. The phase composition of the set cements was calculated using Rietveld refinement analysis (TOPAS2, Bruker AXS, Karlsruhe, Germany). As references the system internal database structures of α -TCP (PDF No. 09-0348) and CDHA (PDF No. 09-0432) were used together with a Chebychev fourth order background model and a CuK α emission profile.

In the previous publication [9], the PSD and calorimetric data were not fully explored. In that case, only mean particle size and exotherm were considered. Here, the goal was to relate the PSD to the calorimetric data in order to determine the reaction kinetics. For that purpose, two main assumptions were made: (i) the dissolution rate of each particle was independent of its size and (ii) the degree of reaction, α , was proportional to the amount of heat released during the hydraulic reaction. To relate the reacted layer thickness to the reaction time, the same method as that presented by Ginebra et al. [3] was used. To simplify, two functions were used

$$\alpha = f_1(t), \quad (1)$$

where α is the degree of reaction at a time t during the calorimetry experiment, and $f_1(t)$ is a function of t . The second function, f_2 , relates the dissolution depth, δ , of α -TCP particles to the degree of reaction

$$\delta = f_2(\alpha). \quad (2)$$

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