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Biomaterials 26 (2005) 2787–2794

Biomaterials

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Correlating crystallinity and reactivity in an α-tricalcium phosphate

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Received 10 May 2004; accepted 4 August 2004
Available online 11 September 2004

Abstract

In this study, the effect of how variant milling time affects material characteristics of alpha phase tricalcium phosphate powder (α-TCP) was studied. Two α-TCP batches were separated in small lots and milled for various times for up to 4 h. The resulting milled lots were characterized by measuring their crystallinity, particle size, specific surface area, thermal stability, and heat released during hydration. Mechanical treatment was seen to greatly increase the α-TCP X-ray amorphous fraction and heat release during hydration, almost independently of α-TCP particle size and specific surface area. Therefore, the results suggest that the formation and presence of an X-ray amorphous phase in the α-TCP powder greatly contribute to its reactivity. The exotherm of the powders increases from 103 to 238 kJ/mol after milling.

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Keywords: Bone; Bone cement; Bone graft; Calcium phosphate; Calcium phosphate cement; Hydroxyapatite

1. Introduction

Hydraulic cements based on calcium phosphates [1–6] offer the advantage of being freely moldable and adaptable to bone defects. Additionally, they have an excellent biocompatibility and their low temperature formation enables incorporation of organic molecules and even living cells [7–11]. Brown and Chow [2,3] first reported the formation of an apatitic cement consisting of a mixture of tetracalcium phosphate (TTCP) and dicalcium phosphate anhydride (DCPA); other cement systems are based on the hydrolysis of alpha-tricalcium phosphate (α-TCP) to calcium-deficient hydroxyapatite (CDHA) according to Eq. 1 [4,5]:

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

Emphasis was placed on producing cements that would undergo a setting reaction, given proper conditions, resulting in hardened bone substitute. Although Monma and Kanazawa first described the setting reaction of α-TCP [4,5], the reaction was deemed too slow for clinical situations [12] leading to the addition of phosphates and or salts in solution to improve reaction kinetics and provide for faster setting harder materials [13–16]. The mechanism of α-TCP hydrolysis was modeled taking into account the particle size distribution of the starting material, the rate of dissolution at the particle surface and diffusion of ions through the precipitated HA-layer on the particles [14–18]. The model indicated that setting was initially controlled by the surface area of the reactants, such that the only ceramic variables thought to influence reaction rate was particle size and degree of agglomeration.

The particle size and hence the specific surface area of cement reactants is commonly altered by milling the solid phase in wet or dry conditions. By prolonged milling, crystalline salts can become amorphous [19], hence increasing both the kinetic and thermodynamic solubility of the material rendering the powder more reactive [19–21]. This concept has recently been applied

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0142-9612/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biomaterials.2004.08.001

to crystalline water-free calcium phosphates [22] such as ß-tricalcium phosphate [23] and tetracalcium phosphate [24]. Besides an increase of the solubility of the compounds, the formation of amorphous CaP by mechanical activation should increase the formation enthalpy of the materials and hence of the exothermic behavior of the cement setting reaction [19]. This work aimed to investigate the influence of prolonged milling of α-TCP on these enthalpy changes by means of differential scanning calorimetry (DSC) of the milled powders as well as by isothermal calorimetry during cement setting with a 2.5% Na_2HPO_4 solution.

2. Materials and methods

2.1. Powders

Two α-TCP batches were produced from mixtures of calcium carbonate (Merck, Germany, Art 102076) and dicalcium phosphate (First batch: Merck Art No 112076; Second batch: Aldrich, Switzerland, Art 23475) theoretically at a 2:1 molar ratio. The material then underwent a heating cycle ending at 1350 °C for 4 h. These batches were milled in a planetary mill (Pulverisette 5, Fritsch, Germany) using ZrO_2 spheres (weight: 3 g each). 100 g of powder were milled with 100 spheres at 400 rpm. The milling times were 3, 7, 15, 30, and 45 min for the first batch, and 15, 30, 75, 150, and 225 min for the second batch, in turn resulting in α-TCP powders of distinctly different characteristics from the same sources of α-TCP.

2.2. Characterization

The specific surface area of the powders was determined using nitrogen adsorption and applying the BET theory (Gemini 2360, Micromeritics, USA). The particle size distribution was determined using a laser particle size analysis (L300, Horiba, Kyoto, Japan). 100 mg of the powder particles was suspended in 200 ml isopropanol and dispersed by applying ultrasound for 15 min prior to measurement. The crystalline composition of the powders was determined by X-ray diffraction (powder method). The powder was packed in a cavity in an aluminum sample holder. The measurements were done on a Philips PW1800 X-ray powder diffractometer (XRD) using Ni-filtered Cu-Ka radiation (40 kV, 30 mA) and an automatic divergence slit. The investigation range was from 4° to 40° (2θ) with 1 s per step (0.02° 2θ). The results were compared to standard files (α-TCP: JCPDS 9-348; CDHA: 9-432; β-TCP: 9-169). The (semi-quantitative) fraction of each phase was estimated with the ratio of the 100% peaks of α-TCP, β-TCP and HA. No β-TCP could be detected in any of the powders. Negligible amounts of HA were detected in the first α-TCP batch. The crystal size of the α-TCP powders was estimated from the XRD spectra using the peak-breadth at half-maximum (FWHM) and the Scherrer equation:

$$d \approx \frac{0.9 \bullet \lambda}{\beta \bullet \cos(\theta)} \tag{2}$$

where d is the crystal diameter, λ is the wavelength, θ is the diffraction angle (in radians) and β is the FWHM. The FWHM of two neighboring peaks was determined: (i) at $d = 2.619$ (43% peak according to JCPDS file 23–359) and (ii) at $d = 2.600$ (29% peak) using the program "MacDiff", version 4.0.6 (Petschick R.: MacDiff 4.0.6. Software Manual, Johann Wolfgang Goethe-Universität Frankfurt am Main, 1999). The following assumptions were made for the fit: (i) all peaks were assumed to be Lorentzian; (ii) all peaks were assumed to be symetrical; (iii) iterations were made until the change from one iteration to the next one led to a variation smaller than 0.001%; (iv) the background noise was removed by assuming a linear pattern between 20° and 37.5° (2θ); (v) the position of the peak was variable. The crystal size of the α-TCP powder was assumed to be the average of the crystal size measured for both diffraction peaks.

Thermal behavior of the milled α-TCP powders up to 500 °C was determined via differential scanning calorimetry (Mettler TA 4000 with measuring cell DSC-20; Switzerland). Various amounts of powders (10–100 mg), various heating rates (1 °C/min or 10 °C/min), and various atmosphere (air or nitrogen) were chosen. 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 one-gram samples with a liquid to powder ratio of 1:3 with a 2.5% Na_2HPO_4 solution. Calorimetry measurements were recorded in millivolts utilizing PICO software (www.pico.com) every 10 s until the reaction reached zero and maintained a stable baseline. The curves were then analyzed and integrated with Microcal Origin v. 5 yielding exotherm results representing heat generation. These samples were removed and set in acetone for further analysis. Samples were dried thoroughly and phase composition of set α-TCP cements was checked after 24 h setting at 37 °C by X-ray diffraction analysis as described above. The patterns were quantified by means of Rietveld refinement analysis using the TOPAS software (Bruker AXS, Karlsruhe, Germany). As references the systems internal database structures of α-TCP and CDHA were used together with a *Chebychev* forth order background model and a Cu K_α emission profile.

The microstructure of set cements was observed by scanning electron microscopy (SEM). Powder samples were covered with a thin gold layer by sputtering.

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