

Preparation and characterization of a novel strontium-containing calcium phosphate cement with the two-step hydration process

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Abstract

A novel Sr-containing calcium phosphate cement (CPC) with excellent compressive strength, good radiopacity and suitable setting time was developed in this work. The two-step hydration reaction resulted in a high compressive strength, with a maximum of up to 74.9 MPa. Sr was doped into the calcium-deficient hydroxyapatite as a hydrated product during the hydration reaction of the CPC. Because of the existence of Sr element and the compact microstructure after hydration, the Sr-containing CPC shows good radiopacity. It is expected to be used in orthopedic and maxillofacial surgery for bone defects repairing.
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1. Introduction

Since first being presented by Brown and Chow [1,2] in 1986, calcium phosphate cement (CPC), a mixture comprising several different kinds of calcium phosphates, has been developed as a successful material for bone defect repair. With its self-setting, easy plasticity and good biocompatibility, CPC has been the focus of increasing attention. The hardening process of CPC is usually based on acid–base reactions between different calcium phosphates, which have different solubilities under different pH values. In terms of the difference in hydration products, two types of CPCs are distinguishable: the brushite cement and the apatite cement [3]. The brushite cement sets at $\text{pH} < 4.2$, and is more degradable than the apatite cement and thus absorbed much more quickly in vivo [4]; for apatite cement, the reactants are weakly basic crystalline calcium phosphates, such as tetracalcium phosphate [5–7] and α/β -tricalcium phosphate [8–11], and weakly acidic compounds, such as dicalcium phosphate anhydride (DCPA)

and monocalcium phosphate monohydrate, and the cement sets at $\text{pH} > 7$. In recent years, amorphous calcium phosphate (ACP) and partially crystallized calcium phosphate have been used to prepare bone cement, especially injectable calcium phosphate bone cement [12,13]. However, the low compressive strength of the aforementioned CPCs limits their clinical application.

ACP is often encountered as a transient phase during the formation of calcium orthophosphates in aqueous phase [14], and the structure Ca/P ratio of ACP are uncertain. Infrared spectra of ACP show broad, featureless phosphate absorption bands and X-ray diffraction (XRD) patterns showed ACP is non-crystalline. Biologically, ACP is also found in soft-tissue pathological calcifications [15].

Recently, the beneficial effect of strontium on bone regeneration has been recognized in the treatment of osteoporosis. In human bone minerals, ionic strontium (Sr^{2+}) shares the same physiological pathway as calcium [16], and the substitution of calcium (Ca) by strontium (Sr) will cause lattice expansion due to the larger atomic radius of Sr than of Ca, which alters the solubility of the mineral [17,18]. Chen et al. [19] suggested that the incorporation of low-dose strontium introduces more lattice distortions

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into the structure of hydroxyapatite and increases its solubility. Moreover, it has been reported that the strontium element enhances the replication of preosteoblastic cells, and simulates bone formation in calvarial cultures in vitro [29].

Some authors have reported that the biocompatibility of the biomaterial is improved by a mechanochemical method [4,20]. Through mechanochemical activation, hydroxyapatite (HA) and its derivatives are obtained [21–28]. From the standpoint of classical (thermal) chemistry, low-temperature solid-phase mechanochemical synthesis $A(\text{solid}) + B(\text{solid}) = AB(\text{solid})$ is only possible in the absence of diffusion [22]. Dispersion of the powder in grinding mills leads to radical changes of its microstructure. Not only does grinding increase the surface area of particles, it also changes the state of the surface layers. In addition, defects (vacancies, dislocations and disclinations) accumulate in the volume, and different reaction centers are formed at the site of bond rupture [24].

Herein, the Sr-containing amorphous calcium phosphate (Sr-ACP) was obtained by a mechanochemical method for the first time. Also, a novel Sr-containing CPC composed of as-prepared ACP and DCPA was prepared and characterized in the present study.

2. Materials and methods

2.1. Materials and preparation

Sr-CPC was prepared by mixing ACP with Sr addition and DCPA with the weight ratio being 2:1. The Sr-containing ACP was obtained by a dry-mechanochemical method with dicalcium phosphate dihydrate (DCPD), calcium hydroxide and strontium carbonate (Shanghai No. 4 Reagent & H.V. Chemicals, Shanghai, China) as the initial materials, weighted with the desired Ca/P ratio (1.67) as reactants. The different Sr/(Sr + Ca) ratios for Sr-ACP were controlled by the content of strontium carbonate in Sr-ACP (30, 15, 7.5 and 3.5%, named Sr-ACP-1, Sr-ACP-2, Sr-ACP-3 and Sr-ACP-4, respectively). The powder was ground using a planet mill at a rotation speed of 500 rpm. Yttria-stabilized tetragonal zirconia balls with a diameter ranging from 5 to 15 mm and polyamide vessels were used to reduce the contamination. Into each pot were loaded 50 g of the powder and 500 g of balls, in a balls to powder mass ratio of 10:1.

Four CPC groups (Sr-CPC-1, Sr-CPC-2, Sr-CPC-3 and Sr-CPC-4), with the different Sr content, were prepared in our work. The solid phase was composed of the as-prepared Sr-ACP (Sr-ACP-1, Sr-ACP-2, Sr-ACP-3 and Sr-ACP-4) and DCPA with the weight ratio of 2:1, and deionized water was used as the liquid phase. The liquid phase and the cement powders were mixed in a mortar to obtain a paste with workable consistency, using a liquid/powder ratio of 0.4 ml g^{-1} and the paste was molded at 24–26 °C and 40–50% humidity. The cement specimens were stored in an incubator at 37 °C and 97% humidity.

2.2. Phase and microstructure characterization

The as-prepared ACP and hydrated Sr-CPC samples were milled into powder and analyzed using XRD (X'Pert Pro, PANalytical, Netherlands). Microstructure of the precipitates was observed by scanning electron microscopy (SEM; H-800, Hitachi, Japan) on gold-coated samples at a magnification of 10,000. The samples were coated with gold and tested at an accelerating voltage of 20 kV. Infrared absorption spectra were recorded by Fourier transform infrared spectroscopy (FTIR; AVATAR 360, Nicolet Co, USA) in the $4000\text{--}400 \text{ cm}^{-1}$ range. Samples were mixed (1 wt.%) in vacuum-dried KBr (spectroscopic grade, Aldrich) and pressed into pellets using a hand presser under 10 kN cm^{-2} pressure. The pore distribution of cement was characterized by mercury intrusion porosimetry (Quantachrome 33/60). The total porosity of cement was calculated by using the following equation: $P_{\text{cpc}} = (d_{\text{HA}} - d_{\text{measured}})/d_{\text{HA}}$ where d_{HA} is the theoretical density of HA (3.14 g cm^{-3}) and d_{measured} is the density of the CPC. The d_{measured} data were determined by measuring the gross weight and volume of specimens. The volume was calculated by the specimen dimensions, as measured with a micrometer, and each linear dimension was the average of the values obtained at three different locations along the specimens.

2.3. Setting time measurements

The setting times of the cements were measured according to the international standard ISO 9917 for dental water-based cement. Ninety seconds after the end of mixing the CPC powders with liquid, the indenter (300 + 5 g in mass, 1 + 0.05 mm in diameter of the needle) was carefully lowered vertically onto the surface of the cement and allowed to remain there for 5 s. Initial setting occurs when a 1 mm needle penetrates 25 mm into cement paste. Final set occurs when there is no visible penetration. Each test was repeated five times and the average value was calculated.

2.4. Compressive strength tests

Steel cylindrical molds with an inner diameter of 6 mm and a height of 12 mm were used to prepare the cement columns for compressive tests. After pouring the cement into steel molds, the cement was pressed with a steel column with a diameter of 5.6 mm under a stress of about 700 kPa for 5 s to eliminate the big air bubbles formed in the paste-filling process. The big bubbles would significantly decrease the final mechanical properties, depending on their size and location.

The cement specimens were stored in an incubator at 37 °C and 97% humidity. Then the samples were ready for mechanical tests. The compressive strength of the columns were measured using a universal material testing machine (INSTRON 5567, INSTRON, Britain) at a cross-head speed of 0.5 mm min^{-1} . Each measurement was repeated six times and the average value was calculated.

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