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Structural stability of calcium phosphate cement during aging in water

Hsiu-Ching Hsu [a], Chin-Yi Chiu [a], Wei-Hsing Tuan [a,*], Hsin-Yi Lee [b]

[a] Department of Materials Science and Engineering, National Taiwan University, Taipei 106, Taiwan
[b] National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan

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Abstract

A calcium phosphate cement (CPC) has been prepared by mixing dicalcium phosphate anhydrate (DCPA, $CaHPO_4$) and calcium hydroxide ($Ca(OH)_2$) with a sodium phosphate (Na_2HPO_4) solution. After setting and hardening, the cement is aged in water. High resolution structural and microstructure analyses are carried out to evaluate the stability of the CPC in water over a period of 150 days. The lattice parameters of the apatite crystal remain the same throughout the aging process. The size of apatite crystallites is not changed either; nevertheless, the shape of the particles changes from equiaxed to rod-like.

Keywords: Bone cement; Hydroxyapatite; Crystal structure; Morphology

1. Introduction

Calcium phosphate cement (CPC) has received wide interest for its potential use as bone cement [1–3]. Apart from the processing of the CPC, its biological affinity has been systematically investigated. Some CPCs have been proven to be bioactive and can be used as the fixation of the artificial joints (hip joints or knee joints) to bone stock.

The most attractive property of CPC is its ability to transform into an apatite structure at room temperature or human body temperature through a dissolution–precipitation mechanism [4–8]. Though the reaction takes place at room temperature; the reaction is very fast in the beginning 10 to 60 min [9–13]. After setting, the hardened CPC is inserted into a biological environment. The long-term stability of the CPC during aging in water is essential for its applications. Since the structure and morphology of the apatite particles affect the mechanical properties of CPC [8,14,15], the long-term structure and microstructure stability during aging in water is thus of interest.

Dicalcium phosphate anhydrous (DCPA; $CaHPO_4$) is frequently used as the starting material for bone cement. As a cement liquid is added into the powder mixtures of DCPA and $Ca(OH)_2$, a bone cement is formed [4,9,11,13,16,17]. Hydroxyapatite (HAp; $Ca_{10}(PO_4)_6(OH)_2$) is the major product of the reaction. The resulting HAp particles are in nanometer size range, it thus imposes challenges on the phase and morphology analyses. Though the structure and morphology of HAp particles have been characterized carefully by many groups [13–17], the long-term structure stability of HAp crystals has received relatively little attention. In the present study, the structure and morphology stabilities of the bone cement in water over a period of 150 days are investigated through high resolution XRD and SEM analyses.

2. Experimental

In the present study, dicalcium phosphate anhydrous (DCPA; $CaHPO_4$, 15–20 μm, Acros Organics Co., USA) and calcium hydroxide ($Ca(OH)_2$, 5–7 μm, Acros Organics Co., USA) were used as the starting materials. These two powders were mixed thoroughly in an attritor (Union Process Co., Ohio, USA) in alcohol (purity 99.5%) at a rotation speed of 500 rpm for 6 h. The ratio of the starting materials was adjusted to yield a Ca/P ratio of 1.67, the ratio for the stoichiometric hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$). The slurry was dried at 100 °C and screened to pass through a plastic sieve of #150. The final particle size of the powder mixtures was 1–3 μm.

Bone cement was prepared by mixing the powder mixtures with a cement liquid, 1.0 M Na_2HPO_4 solution, in a mortar and pestle. The liquid/powder weight ratio was 0.5. The cement was then squeezed into a stainless mold to form cylindrical discs under an external pressure of 3 MPa. The discs were left at room

* Corresponding author. Tel.: +886 2 23659800; fax: +886 2 23634562.
E-mail address: tuan@ccms.ntu.edu.tw (W.-H. Tuan).

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temperature for 24 h, then soaked in distilled water at 37 °C for various soaking times from 0.5 h to 3600 h. The pH value of the water bath was also monitored.

The crystal structure of CPC was characterized with a synchrotron X-ray source; these synchrotron experiments were performed at wiggler beamline BL-17B1 in the National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan. Incident X-rays were focused vertically with a mirror and made monochromatic to an energy of 8 keV with a Si (111) double-crystal monochromator; the sagittal bend of the second crystal focused the X-rays in the horizontal direction. With two pairs of slits between the sample and the detector, the typical scattering vector resolution in the vertical scattering plane was set to $\sim 5\times10^{-3}$ nm^{-1} in these experiments. The scattering angle (2θ) varied from 25 to 45°. The lattice spacing, d, of each plane was determined by using the following equation [13,18]:

$$d = \frac{1}{\sqrt{\frac{4}{3a^2}(h^2+k^2+hk)+\frac{l^2}{c^2}}} \quad (1)$$

The crystal size was determined by measuring the width at half the maximum intensity and calculated with the Scherrer's equation [16,18] as

$$G = \frac{K\lambda}{B\cos\theta} \quad (2)$$

In the above equation, G is the average diameter of crystallites, K the shape factor (a value of 0.9 was used), B the width of the

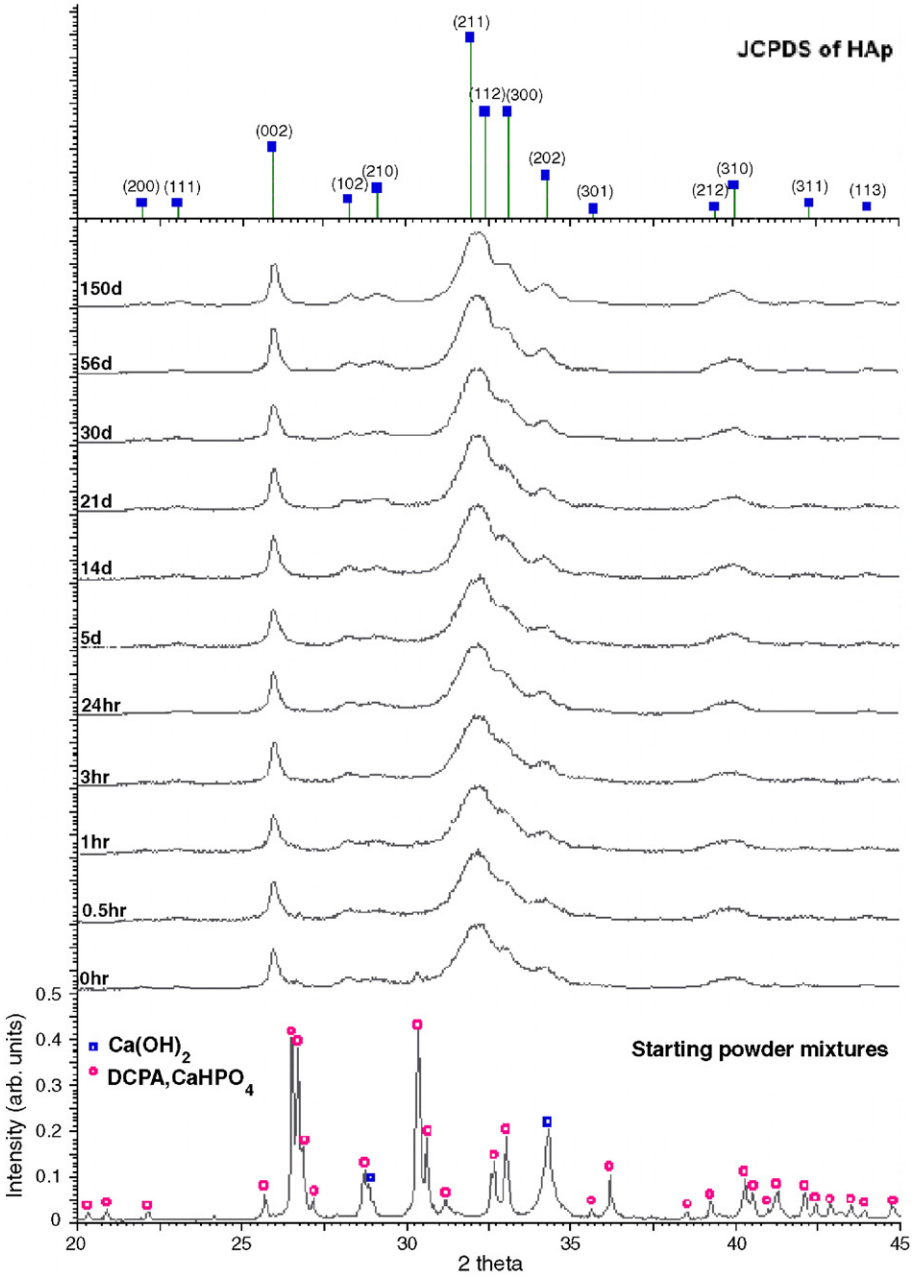

Fig. 1. XRD patterns of CPC after incubation in water for various times. The pattern for the starting DCPA/$Ca(OH)_2$ powder mixture is also shown.