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Hydration mechanism of a novel PCCP + DCPA cement system

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Abstract A novel partially crystallized calcium phosphate (PCCP) + dicalcium phosphate anhydrous (DCPA) system bone cement was introduced and the mechanism of the hydration was studied by means of solubility product constant (K_{sp}), XRD, pH value, and BET. Results showed that DCPA was more soluble than PCCP and HA was the most insoluble compound, and DCPA disappeared fast during hydration of the cement. Therefore, the mechanism of the hydration in the PCCP + DCPA system cement was the dissolution and hydrolysis of DCPA and PCCP. And their by-products H_3PO_4 and $Ca(OH)_2$ reacted through a acid-base neutralization reaction, thus the DCPA and PCCP dissolution and hydrolysis process happened until DCPA and/or PCCP was exhausted. As the conserving time prolonged, fine nano-scale pores were formed due to the hydroxyapatite precipitated into the pores, which were occupied by water before.

Introduction

Calcium phosphate cements (CPC) are of great interest for hard tissue repair due to their good biocompatibility, excellent bioactivity, self-setting characteristic, low setting temperature, adequate stiffness and easy shaping for any complicated geometry [1]. Calcium phosphate cements are widely used clinically in cranio- and maxillofacial surgery for filling non-load bearing bone defects [2, 3].

Calcium phosphate cements are constituted of one or more calcium phosphates that, once mixed with a liquid phase, give a moldable paste. In a short time, the paste sets because of the in situ formation of apatite through a dissolution–precipitation mechanism. The setting reaction provokes hardening of the paste through entanglements of the crystals of the precipitate [4]. The product of the setting reaction of CPC is quite often the calcium deficient hydroxyapatite (HA), which resembles the poorly crystalline carbonated apatite of bone and teeth.

Calcium phosphate cements have been developed since 1983 [5]. After that CPC received much attention over the last 15 years [6–8]. The mechanism of cement hydration is based on the pH dependent solubility of calcium phosphates [9]. Previous studies [10, 11] showed that two types of cements are distinguishable: at pH below 4.2, brushite (DCPD, $CaHPO_4 \cdot 2H_2O$) is formed, and at pH above 4.2, hydroxyapatite is formed.

In this study, a novel PCCP + DCPA cement system was introduced. And the mechanism of the hydration was studied by means of K_{sp}, XRD, pH value, and BET.

Experimental

Materials and preparation

The cement was prepared by mixing PCCP and DCPA. PCCP was synthesized from an aqueous solution of $Ca(NO_3)_2 \cdot 4H_2O$ (0.36 mol/L) and $(NH_4)_2HPO_4 \cdot 12H_2O$ (0.15 mol/L) by chemical precipitation method in our

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laboratory. Then the deposit was centrifugally separated, freeze-dried, calcined at 450 °C for 2 h in a furnace. The calcined PCCP powders were milled in a planetary mill using ZrO_2 balls (weight: 3 g each). 100 g of powder were milled with 100 balls at 400 rpm for 2 h. DCPA was commercially obtained from the Shanghai No. 4 Reagent & H.V. Chemical Co. Ltd, China. The cement powders were homogeneously mixed with de-ionized water with a liquid to powder weight ratio of 0.5 and incubated in an incubator at 37 °C and 97% humidity.

Characterization

The solubility product constant K_{sp} of PCCP was determined by the method introduced by Fernández [12]. Changes in pH of the CPC solutions (with the liquid to powder ratio of 10) were measured using a pH meter (Jingke Leici Co., China). The cements were quenched in acetone after incubating for 30 min, 2 h, 4 h and 5 d, respectively, and then preserved at –80 °C. The absorption of the acetone into the porous cement can stop the hydration process by eliminating the remaining water [13]. After having been quenched in acetone for 2 h at –80 °C, the cement samples were freeze-dried in a freeze-dryer for BET test (Tristar 3000, Micrometritics Co., USA), and milled with a mortar for X-ray diffraction test (X'Pert Pro, PANalytical Co., the Netherlands).

Results and discussion

Table 1 shows PCCP, DCPA, HA, and their K_{sp}. K_{sp} indicates the degree to which a compound dissociates in water. The higher the K_{sp}, the more soluble the compound. The $-\log K_{sp}$ value for PCCP, DCPA and HA was 10.7, 7.02, and 58.6, respectively, at 37 °C. So DCPA was more soluble than PCCP, and HA was the most insoluble compound as shown in Table 1.

Table 1 Compounds and their K_{sp}

Compound	Molecular formula	Ca/P	$-\log K_{sp}$ (37 °C)
DCPA	$CaHPO_4$	1.0	7.02 [14]
HA	$Ca_{10}(PO_4)_6(OH)_2$	1.67	58.6 [14]
PCCP	$Ca_3(PO_4)_2$ (partially crystallized)	1.5	10.7

Chemical reactions controlling the hydration of the cement involve dissolution of the main reactants and precipitation of new mineral phases from a supersaturated solution. Solubility for calcium phosphates allows prediction of the thermodynamic behavior of mixtures of calcium phosphates [14, 15], including the order of dissolution of the reactants in the liquid phase and the precipitating phases. That means, from the point of thermodynamics, DCPA and PCCP can dissolve in water and convert into HA in this study. However, theoretical conclusions may not actually agree with the observed setting and hardening behavior of the cement [4, 12]. Thus there is a need for kinetic studies of the chemical reactions during the cement setting, which involves arresting the chemical reactions at fixed times and identifying the phases present [13, 16–18]. XRD was used to investigate the phase evolution of the cement during hydration in this study.

The XRD patterns for the as-prepared cement powder and hydrated cement are shown in Fig. 1. The results were compared to standard files (DCPA: JCPDS 01-077-0128; HA: 01-074-0566). For the as-prepared cement powder (Fig. 1: cement powder), the diffraction peaks corresponding to DCPA were narrow and intense. And the unmarked weak peaks were corresponding to PCCP. As the cement hydrated, DCPA disappeared and HA appeared gradually (Fig. 1: 30 min, 2 h, 4 h, 5 d). For the cement hydrated for 5 d, only the diffraction peaks of HA presented. DCPA and PCCP disappeared, as they had converted into HA.

Figure 2 gives the changes of pH value of PCCP, DCPA, and cement solutions for various time periods. It can be seen that PCCP and DCPA quickly reached their balance pH values of 12.6 and 6.2 within 30 min, respectively. As for the cement, the pH value was first increased to 11.7 within 30 min, then decreased to 7.6 at 70 h, and remained almost constant till 120 h. After that the pH value began to increase and kept constant at 8.7 in 360 h. The first increase of the pH value of the cement was due to the dissolution of the residual basic impurities in PCCP, which

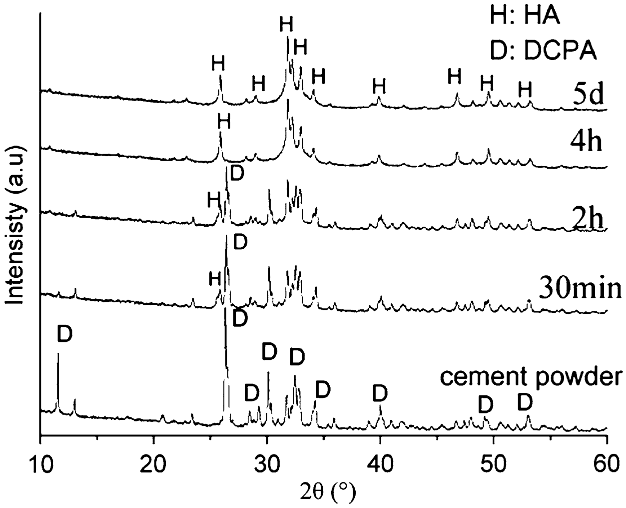

Fig. 1 XRD patterns of the hydrated CPC with different conserving time

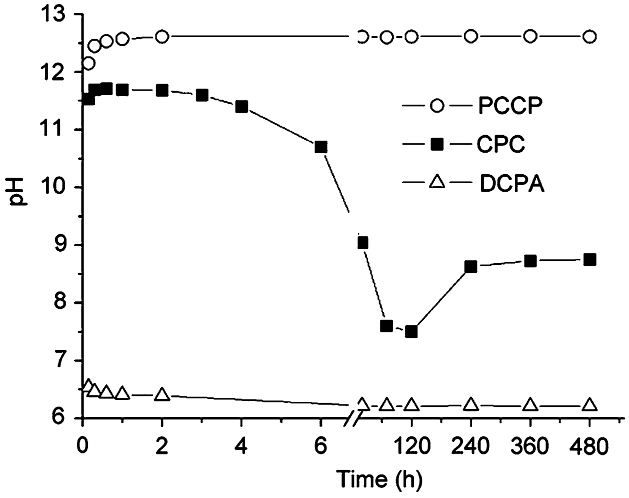

Fig. 2 pH value of PCCP, DCPA, and the cement solutions for various periods of time

were formed during the synthesis of PCCP. Then the pH value decreased since dicalcium phosphate anhydrous was gradually dissolved in the liquid. The K_{sp}, XRD, and pH tests (Table 1, Figs. 1 and 2) proved that during the cement hydration, DCPA dissolved faster than PCCP. The dissolution of PCCP accounted for the succedent increase of the pH value.

It was known that the hydration process of CPC is controlled by the dissolution and precipitation of the starting calcium phosphates [4] and the dissolution and precipitation of a compound is related to the degree of its supersaturation or undersaturation of the corresponding solutions. The dissolution ability of different calcium phosphate determines the direction of the chemical reaction in cement systems. Calcium phosphate cements sets because of the in situ formation of less soluble phase, usually HA, through a dissolution–precipitation mechanism [9–11].

Dicalcium phosphate anhydrous was more soluble than PCCP as shown hereinbefore. Then it can be concluded that during the hydration reaction, firstly, the faster dissolution and hydrolysis of DCPA leads to the formation of $Ca_5(PO_4)_3OH$ and H_3PO_4.

$$5CaHPO_4 + H_2O \rightarrow Ca_5(PO_4)_3OH + 2H_3PO_4 \quad (1)$$

The faster dissolution and hydrolysis of DCPA decreased the pH value of the solution due to the formation of H_3PO_4, and thus accelerated the dissolution and hydrolysis of basic PCCP. The dissolution and hydrolysis of PCCP leads to the formation of $Ca_5(PO_4)_3OH$ and $Ca(OH)_2$.

$$PCCP + H_2O \rightarrow Ca_5(PO_4)_3OH + Ca(OH)_2 \quad (2)$$

Then $Ca(OH)_2$ reacted with H_3PO_4 through a acid-base neutralization reaction as follows:

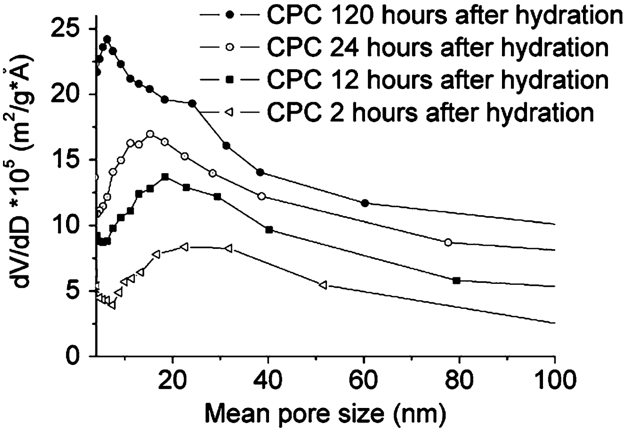

Fig. 3 Pore size distribution curve determined by BET

$$3H_3PO_4 + 5Ca(OH)_2 \rightarrow Ca_5(PO_4)_3OH + 9H_2O \quad (3)$$

All of the above mentioned reactions led to the formation of HA. The reaction (3) made the reactions (1) and (2) happen until DCPA and/or PCCP exhausted.

Pore size distribution also proved the above mentioned hydration mechanism. The small pore size distribution measured by BET is detailed in Fig. 3. There was an obvious distribution at the range of 5–100 Å, which might belong to the nano-scale pores. As the conserving time prolonged, the pore volume of the pores between 5 and 100 Å increased (Fig. 3). During the hydration of the CPC, DCPA, and PCCP dissolved and HA precipitated in the pores, which were occupied by water before. Thus fine nano-scale pores were formed as the cement hydrated.

Conclusions

The mechanism of the novel PCCP + DCPA system cement hydration was studied by means of K_{sp}, XRD, pH value, and BET in this work. K_{sp} test showed that DCPA was more soluble than PCCP, and HA was the most insoluble compound. XRD test showed DCPA disappeared fast. The pH test showed a decrease of pH value at first and then increased. Therefore, the mechanism of the hydration in the PCCP + DCPA system cement was the due to the dissolution and hydrolysis of DCPA and PCCP. And their by-products H_3PO_4 and $Ca(OH)_2$ reacted through a acid-base neutralization reaction, thus the DCPA and PCCP dissolution and hydrolysis process happened until DCPA and/or PCCP was exhausted. As the conserving time prolonged, HA precipitated into the original pores and thus the fine nano-scale pores formed.

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