



Low temperature preparation of α -tricalcium phosphate and its mechanical properties

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Abstract

In this work, α -tricalcium phosphate (α -TCP) was successfully prepared by the thermal transformation of amorphous calcium phosphate (ACP) precursor. β -cyclodextrin (β -CD) was used for preparation of ACP precursor and played an important role in designing its special structure. The phase composition and microstructures of the obtained α -TCP at different annealing temperature were analysed by X-ray diffraction and scanning electron microscope, and confirmed that α -TCP can be prepared at 650 °C for 3 h using ACP as precursor, which is much lower than the phase transition temperature of α -TCP. Mechanical properties were tested 24 h after mixing the obtained α -TCP with 30 wt.% of deionised water. The compressive strength and the flexural strength were 26.4 MPa and 12.0 MPa, respectively. The flexural strength was higher than that of α -TCP prepared by other methods.

Keywords: α -tricalcium phosphate, thermal transformation, amorphous calcium phosphate, β -cyclodextrin

I. Introduction

The past 40 years have witnessed a wide application of calcium phosphate as bioactive ceramic material in bone substitutes [1–3]. α -tricalcium phosphate (α -TCP), a high-temperature polymorph of tricalcium phosphate, is stable at 1125–1430 °C and can be retained at room temperature by sudden cooling in air [4]. Typically, α -TCP can be converted to hydroxyapatite (HAp) in aqueous solutions at room temperature, which is more active than HAp ceramics [5–8]. Therefore, α -TCP has been widely used in the research of bone cement.

Nowadays, there are only a few commercial products of α -TCP in the market even though it has been studied for a long time. Complex preparation technique is one of important factors that hinders its commercial applications. Solid state reaction is a preferred method to synthesize α -TCP presented in many literature reports [3,9–14]. Solid precursors (mixture with molar ratio Ca/P \approx 1.5) are heated above the transformation temperature and then quenched to room temperature after a period

of dwell time. This method has some risks in quenching process and can cause an adverse impact on the sintering furnace because of high thermal shock. Furthermore, the obtained products are often a mixture of α -TCP and some amounts of β -TCP or HAp [15,16]. As a result, scientists have been searching for new strategies to improve the preparation process and obtain the pure α -TCP. Subsequently, it was found that α -TCP can be synthesized at temperatures much lower than the transition temperature to avoid the reversion of α -phase [17–20]. This synthesis method is often accomplished by thermal transformation of a tailor-made amorphous calcium phosphate (ACP). However, the α -TCP prepared by these methods also had a small amount of β -TCP and the hydrolytic and mechanical properties were not analysed and compared with the α -TCP prepared by traditional methods. Therefore, scientists have to find a new approach for preparing the pure α -TCP with excellent hydrolytic and mechanical properties due to their commercial importance.

β -cyclodextrin (β -CD) can be used as building block of ACP because it can be linked both covalently and noncovalently in a regioselective manner [21]. Therefore, the targeted compounds can be synthesized with

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special structure using β -CD. For example, Li *et al.* [22] synthesized ACP in aqueous solution at room temperature using cyclodextrins. Xiao *et al.* [23] prepared spherical HAp crystals successfully with β -CD as template by biomimetic method. In this paper, the precursor ACP was also prepared in aqueous solution using β -CD as template and optimal heating conditions for preparation of α -TCP were studied. The hydrolysis, compressive strength and flexural strength were used to evaluate the properties of the obtained α -TCP.

II. Experimental procedure

2.1. Preparation of α -TCP

Amorphous calcium phosphate (ACP) was prepared by chemical precipitation method. Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and β -CD were dissolved in deionised water to form 0.2 mol/l calcium nitrate saturated β -CD solution. The solution was kept in water bath at 25 °C for 24 h to ensure complete reaction of Ca^{2+} with β -CD. The same volume of dibasic ammonium phosphate ($(\text{NH}_4)_2\text{HPO}_4$) solution, with the Ca/P molar ratio of 1.5 to $\text{Ca}(\text{NO}_3)_2$, was added to the above solution dropwise. The reaction was kept in water bath at 25 °C for half an hour, meanwhile, the pH value of the solution was adjusted to 10–11 by the addition of ammonia. The precipitates were washed with deionised water and absolute ethanol for several times, then dried at room temperature for 24 h until white loose powders were obtained, which is ACP precursor. This precursor was heated at different temperature (550, 600, 650, 700 and 800 °C) for 2–4 h to form α -TCP.

All used chemicals were analytical grade. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$, ammonia and absolute ethanol were purchased from Sinopharm Chemical Reagent CO., LTD (Shanghai, China) and β -CD was purchased from Kemiou Chemical Reagent Co., LTD (Tianjin, China).

2.2. Hydrolysis of α -TCP

α -TCP was ground for 5 h at 400 r/min in a ball mill and passed through 300 mesh screen to form calcium phosphate cement (CPC) powder. The CPC powder was mixed with 30 wt.% of deionised water to form CPC paste. This CPC paste was quickly injected in a mould and air bubbles were eliminated by oscillation. After that, the paste was kept at 37 °C and 100% humidity environment for 24 h.

2.3. Mechanical test

The CPC specimens after hydrolysis were made to $\varnothing 6 \text{ mm} \times 12 \text{ mm}$ cylinder for compressive strength testing and $3 \text{ mm} \times 4 \text{ mm} \times 25 \text{ mm}$ cuboid for flexural strength testing. Compressive strength was calculated by the following equation:

$$\sigma_c = \frac{4P_m}{\pi \cdot d^2} \quad (1)$$

where P_m is the maximum load and d is the diameter of the cylinder specimen. A three-point test was employed for flexural strength which was calculated by equation (2):

$$\sigma_f = \frac{3 \cdot P \cdot L}{2 \cdot b \cdot h^2} \quad (2)$$

where P is the fracturing load, L is the span, b is the width of sample and h is the height of the sample. At least 5 samples for flexural strength and compressive strength were tested to get the average values.

2.4. Characterization

Differential scanning calorimetry (DSC) was used to analyse the ACP precursor in the temperature range from room temperature to 800 °C with the heating rate of 5 °C/min to confirm the phase-transition temperature. The polymorphism of specimens was determined by X-ray diffraction (XRD) patterns which were conducted on a Rigaku Dmax-rc diffractometer with Ni-filtered $\text{Cu K}\alpha$ radiation ($V = 50 \text{ kV}$, $I = 80 \text{ mA}$). Step scan (2°/min) was used for calculation of the crystallite sizes by Debye-Scherrer equation:

$$D = \frac{K \cdot \gamma}{B \cos \theta} \quad (3)$$

where D is the average thickness of crystalline grain in vertical direction of lattice plane, K is the Scherrer constant, γ is the X-ray wavelength, B is the full width at half maximum (FWHM) of diffraction peaks and θ is the X-ray diffraction angle. Fourier transform infrared spectroscopy (FTIR) was conducted on a Bruker Vertex 70 spectrometer over the range of 400–4000 cm^{-1} with resolution of 4 cm^{-1} . The morphologies of α -TCP and hydrolysis products were analysed on a Hitachi SU-70 scanning electron microscope (SEM).

III. Results and discussion

3.1. Heating conditions for α -TCP formation

Figure 1 shows the DSC curve of ACP precursor. A crystallization peak starts to form at 650.8 °C and reaches its maximum at 657.1 °C, which indicates that

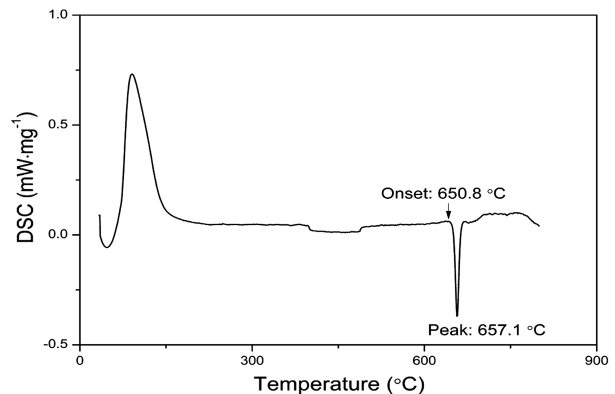


Figure 1. DSC curve of ACP precursor

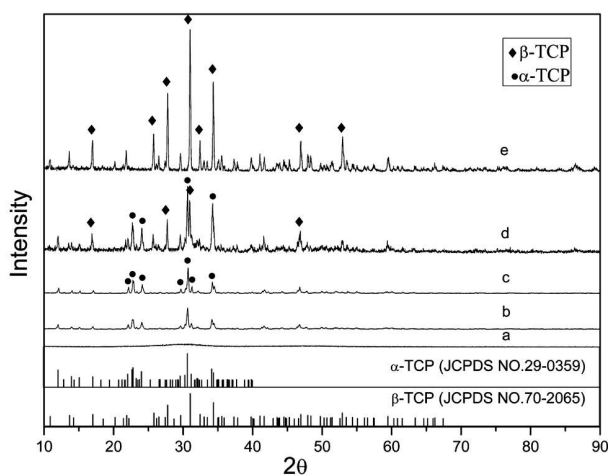


Figure 2. XRD patterns of ACP precursors heated at different temperature: a) 550 °C, b) 600 °C, c) 650 °C, d) 700 °C and e) 800 °C for 3 h

the transition temperature of α -TCP is around 650 °C.

The XRD patterns of ACP precursor heated at different temperature for 3 h are shown in Fig. 2. All the diffraction peaks in Figs. 2b and 2c match well with α -TCP (JCPDS NO.29-0359). However, when the temperature was increased to 700 °C, the peaks of β -TCP appeared. After being heated at 800 °C, the products are typical β -TCP (JCPDS NO.70-2065) without any other diffraction peaks. Therefore, the phase transition temperature of α -TCP was 600–650 °C, and α -TCP would be transformed to β -TCP when the temperature reached 700 °C.

To better recognize differences, SEM analyses of α -TCP heated at 600 °C and 650 °C were done, (Figs. 3a and 3c). The particles heated at 600 °C 3 h (Fig. 3a) are partially crystallized and exhibit irregular shape. However, short rod-like α -TCP particles, fully crystallized, can be clearly observed in Fig. 3c. Therefore, 650 °C is the optimal heating temperature for preparation of α -TCP.

The influence of annealing time on the formation of α -TCP at 650 °C was also studied. The XRD patterns of ACP precursors annealed at 650 °C for 2 h and 4 h were the same (Fig. 2c), which means that the pure α -TCP can be prepared by the ACP precursors heated at 650 °C for period from 2 to 4 h. The crystallite sizes (average

thickness of crystalline grain in vertical direction of different lattice planes) of α -TCP were calculated according to Debye-Scherrer equation (3), and the results were shown in Fig. 4. It can be concluded that the crystalline size of α -TCP increased with the extension of annealing time. Accordingly, the SEM images of α -TCP in Figs. 3b and 3c showed the same changing trend in particle sizes. According to literature data [24] it is better to get α -TCP with smaller particle size, because it can produce a substantial decrease of setting time and accelerates the hardening of cement without significantly affecting the final strength attained, and thus, it will be more suitable for clinical application. Besides, the body colour of α -TCP powders appears gray when the annealing time was less than 3 h, which may be caused by the incomplete combustion of β -CD. The suitable heating conditions for the preparation of the pure α -TCP using ACP as precursor are 650 °C for 3 h.

3.2. Characteristics of ACP precursors

Figure 5 shows the FTIR spectra of β -CD and ACP precursor. In Fig. 5a, the absorption band around 3402 cm^{-1} corresponded to the stretching vibration of O–H bond. The absorption bands around 1420, 1368 and 1336 cm^{-1} were bending vibrations of O–H bond. The peaks located at 1357, 1080 and 1028 cm^{-1} corresponded to the stretching vibrations of C–O [25]. The absorption bands around 1038, 602 and 563 cm^{-1} in Fig. 5b were assigned to PO_4^{3-} group [23]. The stretching vibrations of O–H around 3404 cm^{-1} and bending vibrations of O–H around 1425 cm^{-1} in Fig. 5b confirmed that ACP precursors contained a small amount of β -CD. Figure 6a shows XRD pattern of products obtained from ACP precursors without β -CD heated at 650 °C for 3 h. The product was typical β -TCP. Therefore, β -CD was indispensable to the preparation of usable ACP precursor for synthesis of α -TCP.

In the process of ACP precursor preparation, the reaction temperature and the thickness of filter cake also affected the final products. Figures 6b and 6c show the XRD patterns of products heated at 650 °C for 3 h using ACP precursors prepared at 18 °C and 30 °C. The characteristic diffraction peaks of α -TCP and β -TCP appear in the Figs. 6b and 6c, respectively, and some diffraction peaks of HAP (JCPDS NO.74-0566) were also observed

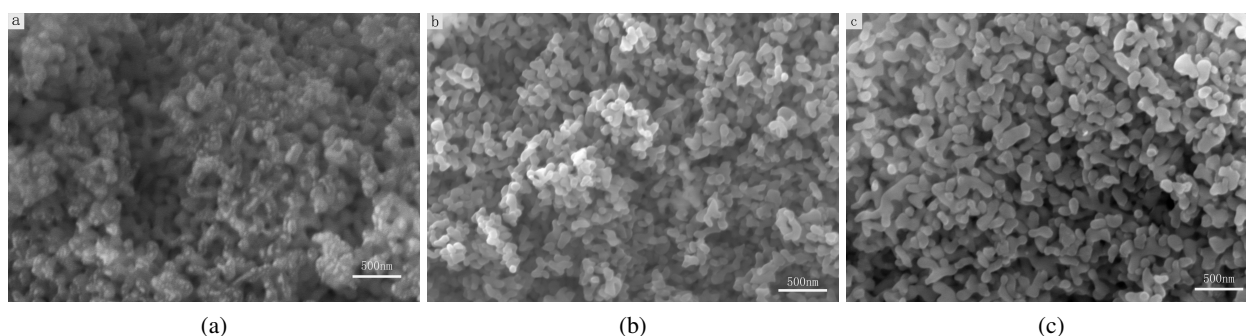


Figure 3. SEM images of α -TCP heated at different conditions: a) 600 °C, 3 h; b) 650 °C, 2 h and c) 650 °C, 3 h

in Fig. 6b. So the pure α -TCP was not prepared by these two ACP precursors. The study result indicated that the

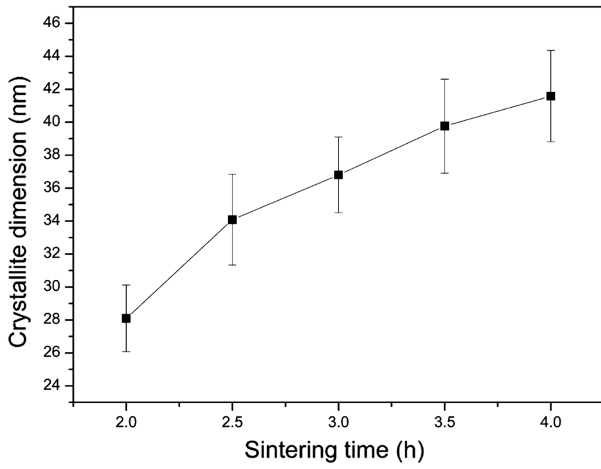


Figure 4. Crystallite sizes of α -TCP prepared at 650 °C with different annealing time

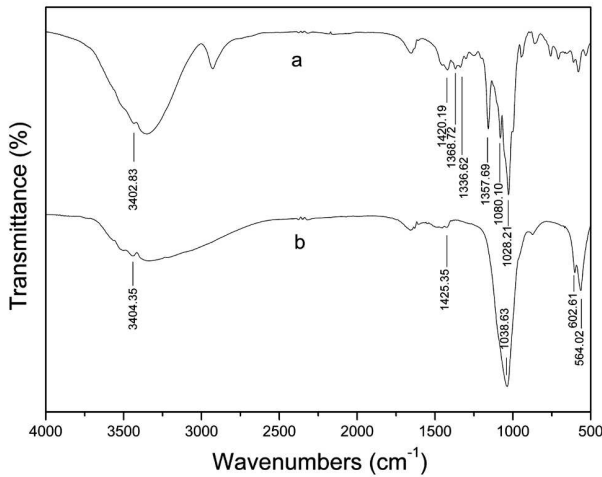


Figure 5. FT-IR spectra of: a) β -CD and b) ACP precursor

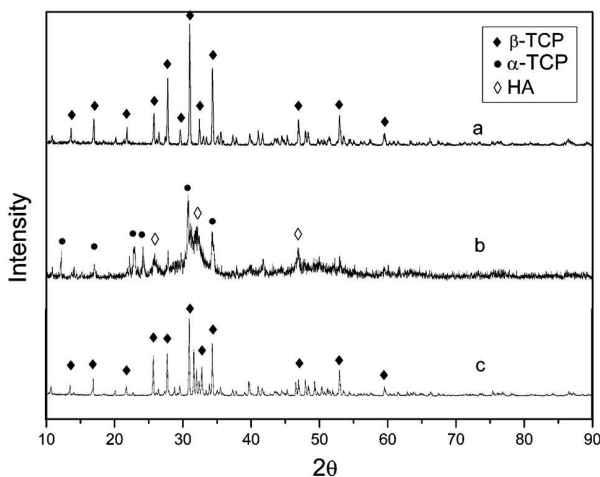
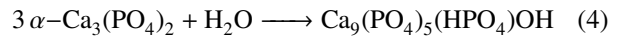


Figure 6. XRD patterns of products (heated at 650 °C for 3 h) prepared using different precursors: a) ACP without β -CD, b) ACP prepared with β -CD at 18 °C and c) ACP prepared with β -CD at 30 °C

best reaction temperature to prepare ACP precursor was 25 ± 3 °C, and it is not possible to get α -TCP if the temperature was outside this range.

3.3. Hydrolysis and mechanical properties of α -TCP

Figure 7 shows the XRD pattern of the hydrolysate of α -TCP. All the diffraction peaks are indexed to calcium-deficient hydroxyapatite (CDHA). The solubility of HAp is the minimal among all calcium orthophosphates under the conditions of hydrolysis [26,27], so it should precipitate during the α -TCP dissolution process. The hydrolysis of α -TCP to CDHA can be expressed with the following equation [28,29]:



The hydrolysis of α -TCP generated a large number of spherical CDHA particles. These particles interconnected and accumulated, as shown in Fig. 8, giving rise to a certain degree of mechanical strength of the cement. Table 1 shows the mechanical properties of CDHA. As commonly reported in literature, the flexural strength of the pure α -TCP is about 5 MPa, and the compressive strength is about 10 to 30 MPa [30–33]. However, the α -TCP particles prepared in this work had smaller particle size and higher activity than with other preparation methods and they could form denser CDHA through hydrolysis, and thus showed a much higher flexural strength.

3.4. Formation mechanism of α -TCP

Compared with other preparation methods of ACP precursors, the difference in this paper is the special structure of ACP due to the introduction of β -CD. The

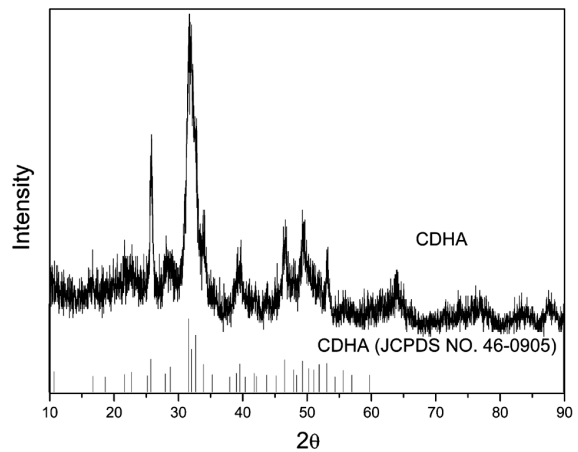


Figure 7. XRD pattern of the hydrolysate of α -TCP

Table 1. Cycle details used for CS and TSS and relative densities of sintered samples

Flexural strength [MPa]	Compressive strength [MPa]	Density [g/cm ³]	Porosity [%]
12.0	26.4	1.665	24.4

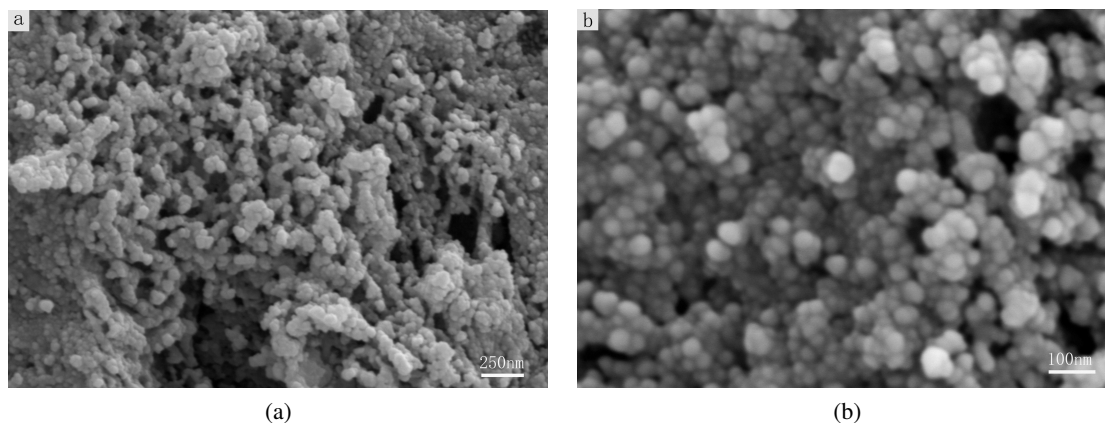


Figure 8. SEM images of the fracture after flexural strength test

molecular structure of β -CD is a hollow frustum of a cone [23,34]. The inside and the upper (one end with smaller diameter) walls of the cavity are hydrophobic, the outside and the bottom (one end with larger diameter) walls are hydrophilic [25,35]. The $-\text{OH}$ groups at the hydrophilic part of β -CD molecule were combined with Ca^{2+} [25], therefore, Ca^{2+} ions distributed on the outside of the β -CD cavity. The complex crystallizes in the space group $P2_12_12_1$, and the β -CD molecules are arranged in a zigzag mode along a 2-fold screw axis [35]. The ACP precursors with special structure were obtained by the complex reacting with PO_4^{3-} . α -TCP belongs to the space group $P2_1/a$. On the other hand, β -TCP belongs to the space group $R3C$ [36,37]. As a result, the short-range crystal structure of ACP precursors is much closer to the α -TCP than β -TCP crystal structure. We can infer that the activation energy for ACP precursor transformation to α -TCP was less than for β -TCP at 650°C . Therefore, α -TCP can be prepared under the conditions far below the phase transition temperature.

IV. Conclusions

α -TCP samples have been successfully prepared by the thermal transformation of ACP precursors with special structure that was shaped by β -CD. Reaction temperature plays an important role in the preparation of ACP. Similarly, heating temperature and time also affect the formation of α -TCP. In summary, the ACP precursors can be synthesized at $25\pm 3^\circ\text{C}$. α -TCP can be obtained by annealing the ACP precursors at 650°C for 3 h. The flexural strength and the compressive strength of the hydrolysate of pure α -TCP were 12.0 MPa and 26.4 MPa, and the flexural strength is higher than that obtained by other methods. In addition to lower heating temperature, this method does not need rapid cooling, which could have promising applications in the market.

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