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Reactivity of α-tricalcium phosphate

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The reactivity of α-tricalcium phosphate (α-TCP) in forming hydroxyapatite (HAp) at 37°C was investigated. The effects of synthesis route, HAp seeding and the presence of calcium salts on the mechanism and extent of HAp formation were examined by pH measurements and/or isothermal calorimetric analyses. A synthesis temperature at the lower end in the temperature range of 1100–1300°C and the reaction of α-TCP with a high specific surface area greatly improved rate and extent of HAp formation. The time for complete reaction decreased from 18 h to 14 h, when the reaction was carried out in the presence of 1 wt% of HAp seeds; the hydrolysis mechanism did not change. At HAp seeds proportion of 5 wt% and 10 wt%, transformation occurred without a nucleation period. The calcium salt additives studied were anhydrous and dihydrate form of dicalcium phosphate ($CaHPO_4$ and $CaHPO_4 \cdot 2H_2O$), calcium carbonate ($CaCO_3$), and calcium sulfate hemihydrate ($CaSO_4 \cdot 1/2H_2O$). All the additives delayed HAp formation as determined by the isothermal calorimetric analyses. Their retarding effects in decreasing order are $CaCO_3$, $CaSO_4 \cdot 1/2H_2O$, DCPD, DCP. $CaCO_3$ almost completely retarded HAp formation. After 24 h, hydrolysis was complete only for pure α-TCP and for the α-TCP-DCP blend. Reaction was complete in other formulations before 48 h except for the $CaCO_3$-containing blend. In all mixtures conversion to HAp occurred without forming any intermediates. However gypsum formed in the mixture containing $CaSO_4 \cdot 1/2H_2O$. All the α-TCP-additive mixtures, excluding α-TCP-$CaCO_3$, reached nominally the same strength value after 24 h of reaction as governed by the transformation of α-TCP to HAp. For phase-pure α-TCP, the average tensile strength changed from 0.36 ± 0.03 MPa to 7.26 ± 0.6 MPa. Upon hydrolysis only the $CaSO_4 \cdot 1/2H_2O$-containing mixture exhibited slightly higher strength averaging 8.36 ± 0.9 MPa.

1. Introduction

Bioactive calcium phosphate contents are potentially attractive as artificial hard tissues. Characteristically, they convert to monolithic form by means of low temperature cement-type reactions in aqueous solutions. Typically, hydroxyapatite (HAp) is the reaction product. In situ formation of HAp in this way is advantageous in eliminating the need for performed shapes for *in vivo* biomedical applications. HAp formed by cement reactions is microstructurally and chemically similar to natural apatite, making it biologically more active than ceramic HAp [1, 2].

A large number of formulations of calcium phosphate compounds have been reported to produce HAp near physiological conditions. One group of formulations involve reactions in the aqueous phase between acidic and basic calcium phosphate reactants. Depending on the proportions of the reactant precursors, it has been shown that HAp of variable composition $[Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}]$ can be formed by reaction between $Ca_4(PO_4)_2$ (tetracalcium phosphate or TetCP) and $CaHPO_4 \cdot 2H_2O$ (dicalcium phosphate dihydrate or DCPD) [3].

Alternatively α-$Ca_3(PO_4)_2$ (α-tricalcium phosphate or α-TCP) can hydrolyze by a cement-type reaction with water. Monma and Kanazawa first showed that the α polymorph of TCP formed CDHAp (calcium-deficient HAp) in water at 60°–80°C [4]. The hydration rate was observed to decrease at lower temperatures and hydration proceeded minimally at room temperature. The hardened product formed at elevated temperature had a tensile strength of 20–30 kg/cm^2 (1.96–2.9 MPa) and a bulk density of 0.9–1.2 g/cm^3. Moderate hydration rates were reported in the presence of additives at 37°–40°C [5]. A variety of reaction products were formed. DCPD was the reaction product below pH 5.5, octacalcium phosphate ($Ca_8(HPO_4)_2(PO_4)_4 \cdot 5H_2O$ or OCP) formed at pH 5.5–7.5, and HAp above pH 7.5. The extent of conversion was retarded in the presence divalent inorganic salts, whereas monovalent inorganic or organic salts favored hydration.

In an effort to optimize hydration and reduce the setting times for HAp formed from α-TCP a variety of cements have been formulated based on these early findings. Monma *et al.* reported better mechanical properties and accelerated reaction rates in NaCl solution for α-TCP to OCP with DCPD also forming [6]. After 24 h of reaction at 37°C the wet compressive strength of the product was 14 to 19 MPa and the tensile strength was 3 MPa.

It has been also shown that seeding with the intended product improves the overall reactivity of the cement systems and accelerates the reaction rate. Brown and Chow showed that increasing the proportion of HAp seeds in the DCPD-TetCP system favored HAp formation [7]. They reported the original setting time to be reduced by 50% with the addition 25 wt% of HAp seeds. Mirtchi *et al.* reported accelerated hardening for β-TCP-DCPD-calcite cement in the presence of HAp [8]. Similar findings were reported for α-TCP, where HAp was used as nucleating agent. An increase of HAp content from 2 wt% to 6 wt% reduced the swelling period due to setting from >300 min to 135 min [9].

More recently, cement compositions involving mixtures of α-TCP with $CaHPO_4$ (dicalcium phosphate or DCP) [10, 11] or $CaCO_3$ [12] and in combination of these two precursors have been investigated [13]. In these studies, hydration behavior was investigated according to their initial setting times as measured using Gillmore needles and/or XRD.

We previously investigated the hydration of α-TCP by means of isothermal calorimetry to establish the rates and extents of reactions at different temperatures [14–16]. In the present work, synthesis history and the effects of various calcium salt additives and HAp seeding on reactivity of α-TCP is reported. Hydrolysis behavior of α-TCP synthesized from different calcium and phosphate sources at various sintering temperatures was examined at 37°C. The additives studied are DCP, DCPD, $CaCO_3$ and $CaSO_4 \cdot 1/2H_2O$ (calcium sulphate hemi-hydrate) at 10 wt% addition. The reactivities of the α-TCP-additive blends were also correlated with their physical properties and reported as comparative analyses of the tensile strengths of hydrated products.

2. Materials and methods

2.1. α-TCP synthesis

α-TCP was formed by three routes according to following solid state reactions:

$$2NH_4H_2PO_4 + 3CaCO_3 = Ca_3(PO_4)_2 + 3H_2O + 3CO_2 + 2NH_3 \quad (1)$$

$$2CaHPO_4 + CaCO_3 = Ca_3(PO_4)_2 + H_2O + CO_2 \quad (2)$$

$$Ca_2P_2O_7 + CaCO_3 = Ca_3(PO_4)_2 + CO_2 \quad (3)$$

Reagent grade $NH_4H_2PO_4$ (Fisher Scientific, Pittsburgh, PA) was used. The other precursor $CaHPO_4$ was synthesized from ultra pure $CaCO_3$ ($Mg < 0.01\%$, Osram Sylvania, Towanda, PA) and H_3PO_4 according to a previous a study [17]. $CaHPO_4$ was formed by adding a stoichiometric amount of H_3PO_4 to $Ca(OH)_2$ slurry, obtained from $CaCO_3$ derived CaO. $Ca_2P_2O_7$ was thermally formed by firing $CaHPO_4$ at 500°C for 1.5 h.

In all cases stoichiometric mixtures of the starting powders were first milled in anhydrous ethanol for 5 h using zirconia media. The slurries were vacuum filtered. The precursor cakes were then fired on platinum foils in an open atmosphere furnace. Each mixture was sintered at 1100°C, 1200° or 1300°C for 1 h, followed by air quenching. The fired pieces were hand ground using an alumina mortar and pestle and further by vibratory milling.

2.2. Hydrolysis reactivity of α-TCP

The hydrolysis reactivity of α-TCP produced by different synthesis routes or with additives was examined by determination of solution pH and/or isothermal calorimetric analyses at 37 ± 0.2°C. Hydrolysis in water occurs according to:

$$3Ca_3(PO_4)_2 + H_2O = Ca_9(HPO_4)(PO_4)_5(OH) \quad (4)$$

For pH measurements 1 gram samples of α-TCP (or a α-TCP containing mixture) were suspended in distilled water to attain a liquid-to-solid mass ratio of 100 and stirred with a magnetic bar. The pH variation was monitored with a glass combination electrode every 30 seconds for 24 h. N_2 was bubbled for 1 h prior to the addition of solids and throughout the experiments.

The isothermal calorimetric system (Thermometric Corp., San Diego, CA) used consists of a closed reaction chamber and a thermostated water bath. A detailed description of the system can be found elsewhere [18]. The samples were placed in a reaction cell surrounded by thermopiles. After reaching thermal equilibrium, reaction was initiated by injecting distilled water into the reaction cell. Either two or three ml of D.I. water reacted with an equivalent mass of solid α-TCP or α-TCP-additive blends. The heat flow (dQ/dt) was recorded as a function of time for 24 h. By integrating the heat flow data over the reaction time, the total heat (Q) evolved was obtained.

2.3. Tensile strength

α-TCP-additive (90 : 10 wt%) mixtures were milled in anhydrous ethanol with zirconia media for 5 h, vacuum filtered and dried in an vacuum oven at 80°C for 12 h. Dry powder mixtures were compacted in a cylindrical die at a pressure of 4.25 MPa (500 psi) to obtain a green body with a suitable geometry for mechanical testing. The same amount of powder (0.6 ± 0.02 g) was pressed for every formulation. Coin shaped pellets were placed into plastic vials containing an equivalent amount of deionized water and immersed in a constant temperature water bath at 37°C. The samples were removed after 24 h or 48 h of reaction. Five samples were produced for each formulation at each reaction time, together with the phase-pure α-TCP control samples. After hydration, the samples were immersed in acetone for 30 min and vacuum dried. The fracture strengths of dried samples were then determined by the Brazilian test, in which circular discs are compressed diametrically in a physical testing machine. The tensile strengths

(σ_T) were determined according to $\sigma_T = 2P/\pi Dt$ where P is the maximum load, D sample diameter and t its thickness. Testing was performed on an Instron machine at constant cross head speed of 0.05 cm/minute.

2.4. X-Ray diffraction analyses

Powder X-ray diffraction (XRD) analyses were performed using a Scintag automated diffractometer, with Cu K_α radiation. The samples were scanned over a 2θ range of 20°–40° at a step size of 0.02° two-theta and a scan rate of 4° 2θ/min.

2.5. Powder characterization

The particle size was measured by using a laser diffraction particle size analyzer (Horiba Capa-700). The specific surface area measurements were performed with BET method employing a Quantachrome (Monosorb) surface area analyzer which uses 20 : 80 gas mixture of N_2 : He.

3. Results and discussion

3.1. Effect of synthesis route on hydrolysis reactivity

Fig. 1 shows the pH change in water at 37°C for α-TCP prepared according to Equations 1–3. Regardless of synthesis route, the sintering temperature was 1300°C and XRD analyses showed the fired products were phase pure α-TCP. The pH values of the slurries were approximately 9.35 immediately after addition of the α-TCP particulates. The changes in pH were remarkable for TCP2 and TCP3, only. The pH of the TCP1 slurry remained almost constant, reaching 9.27 after 24 h. The pH values of the TCP2 and TCP3 slurries after 24 h were 8.12 and 7.2, respectively. XRD analyses showed that only TCP3 was reactive and had partially converted to HAp.

Among the reasons for such diferences in reactivity are impurities in the precursors. It is known that cationic and anionic species such as sodium, potassium, magnesium and chloride alter the hydrolysis behavior of α-TCP [5]. However, the same $CaCO_3$ had been used in preparations of the all TCP powders. The phosphate sources in TCP2 and TCP3, ($CaHPO_4$ and $Ca_2P_2O_7$, respectively) were also synthesized from this $CaCO_3$. In fact $Ca_2P_2O_7$ is an anhydrate of $CaHPO_4$. The other phosphate source $NH_4H_2PO_4$ used in Equation 1 was free of impurities at concentrations higher than 0.005 wt% as determined by atomic emission spectroscopy. The variation in reactivity appears to be related to the physical properties of the α-TCP particles. As shown in Table I, the TCP3 has a greater specific surface area. Table I also shows that, although the average particle size does not differ greatly, the surface area of TCP3 was three times greater than TCP1-which was found least reactive by pH measurements. Thus the reactivity difference can be related to the surface area of the α-TCP precursor. It has been previously established that the low temperature aqueous formation of HAp progreses through a dissolution and precipitation mechanism [3, 19–23]. During HAp formation this way the solution becomes supersaturated with respect to HAp as a result of continuing dissolution of anhydrous calcium phosphate reactant(s); this is followed by precipitation of HAp. Under this circumstance the surface area of the solid reactant(s) becomes the rate-determining factor governing the reaction kinetics.

TABLE I The particle size and specific surface area of α-TCP synthesized at 1300°C from various reactants

α-TCP	Precursors	Median average particle size, (μm)	BET specific surface area, (m^2/g)
TCP1	$NH_4H_2PO_4 + CaCO_3$	5.5	0.22
TCP2	$CaHPO_4 + CaCO_3$	3.6	0.36
TCP3	$Ca_2P_2O_7 + CaCO_3$	3.1	0.65

Fig. 2 shows the effect of the sintering temperature on the reactivity of TCP3. This figure shows the pH variation during hydrolysis of particulate α-TCP synthesized from $Ca_2P_2O_7$ and $CaCO_3$ at 1100, 1200 and 1300°C. XRD analyses of the sintered powders prior to hydrolysis indicated presence of β-TCP for the powder synthesized at 1100°C. The products fired at 1200 and 1300°C were phase pure α-TCP. As shown in Fig. 2, for the all powders synthesized from $Ca_2P_2O_7$ and $CaCO_3$,

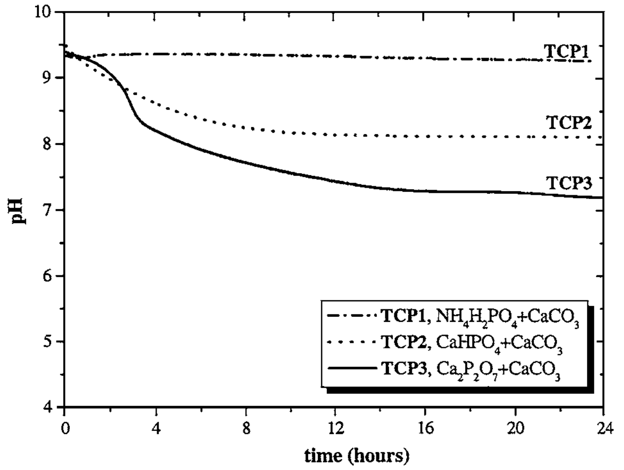

Figure 1 pH variations during hydrolysis of α-TCP synthesized at 1300°C from various precursors.

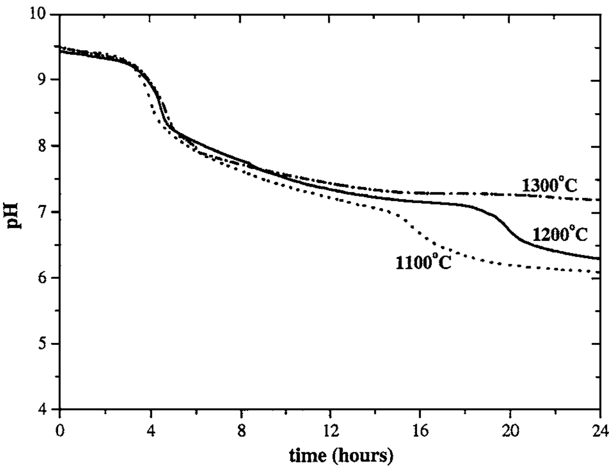

Figure 2 The variation in pH during hydrolysis of TCP3 sintered at various temperatures by reaction of $Ca_2P_2O_7$ and $CaCO_3$.

rapid increases in pH were observed immediately after the addition of α-TCP powder to the D.I. water (pH ~ 6). The pH reached a maximum of about 9.35 within $\sim$10 min. Subsequently, the pH values decreased first slowly followed by a relatively faster rate of decrease after 3 h of reaction. The powders synthesized at 1100 and 1200°C show a further reduction in pH to values near 6 after 15 h and 18 h, respectively.

XRD analyses of the solids present after 24 h of hydrolysis indicate that TCP produced at 1300°C contained the highest proportion of unreacted α-TCP. (see Fig. 3) TCP powders fired at lower temperatures showed virtually complete reaction; only a trace amount of α-TCP was found together with HAp. A final pH below 6 is characteristic of complete conversion to HAp. A prior study using isothermal calorimetry and XRD analyses showed the pH changes observed can be related with the events occurring during the hydrolysis reaction [15]. The pH decrease after 3 h is associated with the primary dissolution of TCP and the nucleation of HAp crystallites. The second decrease is related with the further transformation to HAp resulting in the uptake of OH^- from the solution. The pH does not change after a limiting value was reached (pH ~ 6), i.e. after the α-TCP had completely transformed to HAp. The absence of the final pH decrease for α-TCP synthesized at 1300°C indicates it to be less reactive than the other two. This was also confirmed by XRD as shown in Fig. 3.

Thus XRD analyses and pH variations illustrate the sintering temperature of 1200°C to be high enough to avoid the formation of β-TCP, while producing reactive α-TCP powder. Reaction at higher temperature leads to dead-burning associated with microstructural coarsening known to occur in high temperature solid-state reactions. [24] An increase in the firing temperature from 1150 to 1300°C for TCP3 leads to a reduction in the specific surface from 2.3 m^2/g to 0.65 m^2/g. When this occurs the dissolution is retarded commensurately. The typical pH variation during hydrolysis of reactive α-TCP precursor is represented by the pH variation (Fig. 2) for the powder synthesized at 1200°C. This powder was used in the remainder of the study.

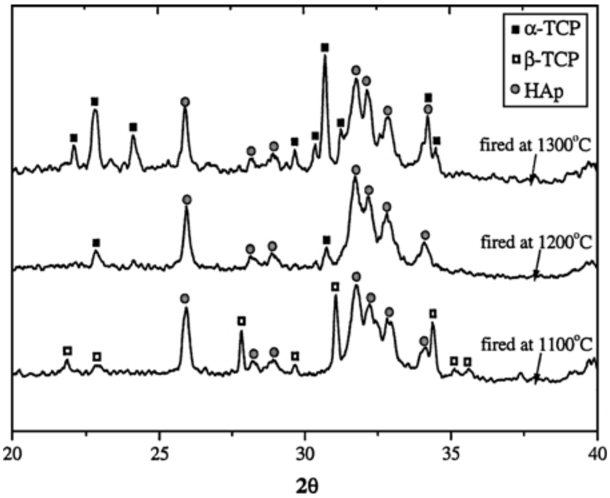

Figure 3 XRD patterns of the products formed after 24 h by hydrolysis of TCP synthesized at various temperatures by reaction of $CO_2P_2O_7$ and $CaCO_3$.

3.2. Hydrolysis with HAp seeding

Fig. 4 compares the rates of heat evolution during hydrolysis of α-TCP and the mechanical mixtures containing 1, 5 and 10 wt% HAp. XRD analyses indicated that all reactions reached completion by 24 h and only HAp was present. The rate curves show that pure α-TCP reacts completely by 18 h, after which no further heat was evolved. The heat evolution behavior is typical in that a heat peak occurs a very short time after mixing and is followed by heat peaks associated with the induction (HAp nucleation) and bulk transformation (growth) events. [23] After the mixing peak, the rate of heat evolution decreases to a minimum after approximately 3 h, after which a second maximum is observed. The third peak indicates major heat release and bulk transformation to HAp.

Heat evolution from the 1 wt% HAp-TCP mixture has the same features as phase pure α-TCP while showing a nucleation peak occurring 1 h earlier than that for pure α-TCP. Similarly, the growth peak shifts to shorter times. Complete transformation to HAp occurs at around 14 h, 4 hours shorter than in the absence of HAp seeds. At higher proportions of HAp addition, i.e. 5 and 10 wt%, hydrolysis occurs without a nucleation period. However, the effect of seeding on reaction time is the same for both 1 wt% and 10 wt% additions, approximately around 14 h. The inset in Fig. 4 shows that 5 wt% HAp is adequate to cause disappearance of nucleation period in α-TCP hydrolysis.

3.3. Hydrolysis of α-TCP-additive blends

The calorimetric rate curves for the hydrolysis of α-TCP-additive blends in water at 37°C are shown in Fig. 5. These curves were normalized to the weight proportion of the α-TCP present. The inset to Fig. 5 shows the corresponding total heats, evolved during 24 h of reaction. The total heat of reaction for the hydrolysis of phase-pure α-TCP is 133 kJ. The lower heat outputs for the α-TCP-additive formulations indicate all the additives used in this study inhibited hydrolysis of α-TCP to some extent. The presence of $CaCO_3$ strongly inhibited the hydrolysis reaction. The inhibitory effects of DCP and DCPD are relatively weak and occur the same degree, whereas $CaSO_4 \cdot 1/2H_2O$ exhibits a moderate effect. The retarding effect from strongest to weakest is $CaCO_3 > CaSO_4 \cdot 1/2H_2O >$ DCPD > DCP.

The rate curves in Fig. 5 show how a particular additive changes the HAp formation mechanism. In all cases there is a mixing peak of short duration at the onsets of the reactions; these almost overlap with the ordinate of Fig. 5. The α-TCP-$CaCO_3$ mixture did not produce significant heat suggesting minimal conversion. In the presence of $CaSO_4 \cdot 1/2H_2O$ the second calorimetric peak-representing the HAp growth-broadens and shifts to longer times. This heat curves resembles that for phase-pure TCP with slower reaction rate. The rate of heat evolution for α-TCP-DCP blend showed smaller calorimetric peaks than for pure α-TCP; the same distinct stages of hydrolysis are observable.

The α-TCP-DCPD mixture rate curve differs from the others. Heat evolution occurs more rapidly at short

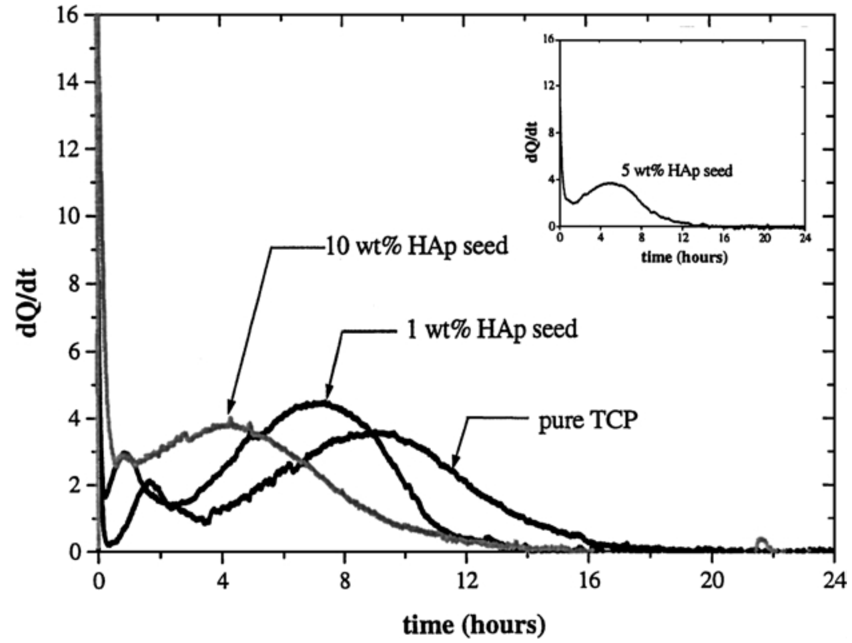

Figure 4 Rates of heat evolution for the hydrolysis of α-TCP in the presence of various proportions of HAp seeds.

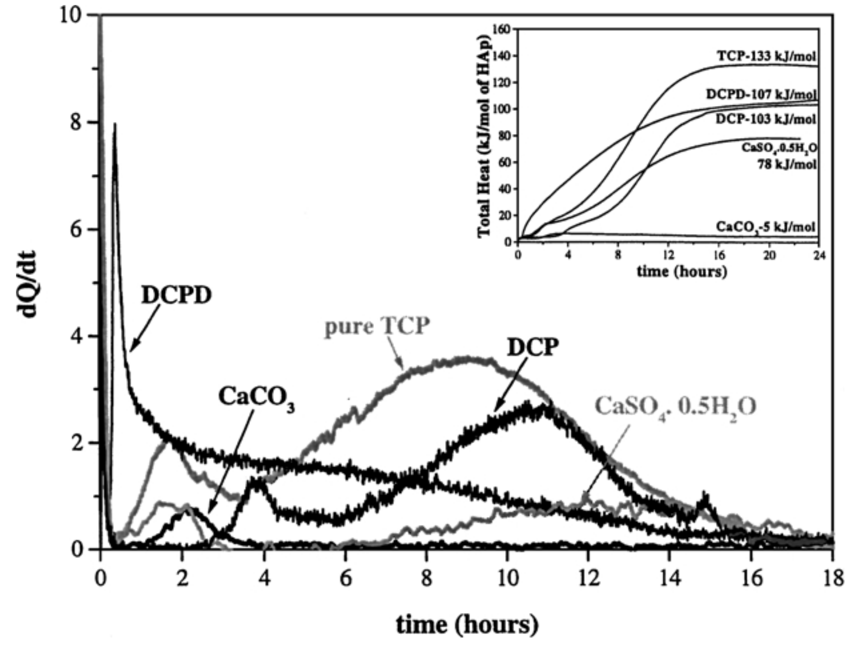

Figure 5 Calorimetric rate curves for the hydrolysis of α-TCP and various α-TCP-additive (90 : 10 wt%) formulations in water at 37°C. The inset figure is total heat evolution curves for each formulation. The curves are labeled with the abbreviations for the additives.

times but continually decreases at longer times. There are no distinct peaks following the initial mixing peak. In this regard heat evolution behavior similar to that observed when HAp seeds are present.

The XRD analyses (see Fig. 6) showed DCPD to be the only additive that completely disappeared by 24 h. Therefore the α-TCP-DCPD rate curve is cumulative of two processes occurring at the same time. The first is hydrolysis of α-TCP to HAp by dissolution and precipitation and the second one is the decomposition of DCPD. It has been shown that in the presence of water DCPD decomposes into anhydrous DCP at 36–45°C [25, 26]. Temperature, time and pH strongly effect the decomposition and the decomposition product. It has been reported by Fulmer and Brown that DCP formation may be accompanied with the formation of HAp [27]. They showed that although the hydrolysis of DCPD to HAp is incomplete in water at 38°C, complete conversion to HAp without DCP formation may occur under basic conditions depending on the buffering capacity of the surrounding solution [27]. The absence of DCPD or DCP according to XRD analyses suggests a similar effect in the presence of the basic α-TCP component, favoring the DCPD-to-HAp conversion.

The variations in pH during hydrolysis of blends (see Fig. 7) are consistent with the results obtained by calorimetry analyses. $CaSO_4 \cdot 1/2H_2O$ and DCP do not change the occurrence of three pH regimes during the hydrolysis of α-TCP. The pH decrease in the early stages of reaction of the α-TCP-DCPD blend is due

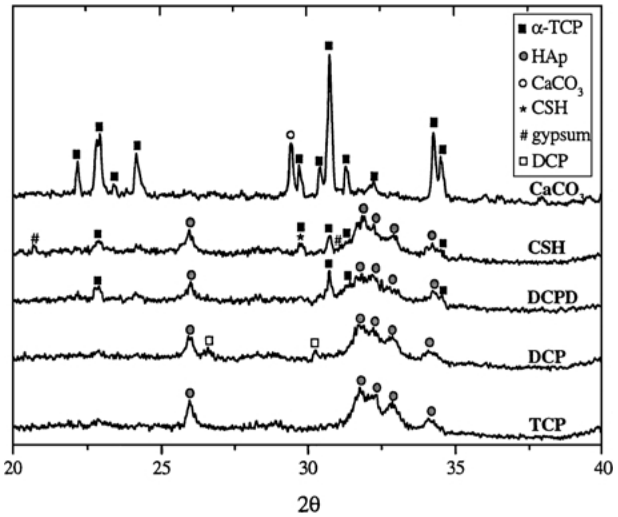

Figure 6 XRD patterns of the products of α-TCP-additive formulations after 24 h of reaction. The patterns are labeled with the abbreviations for the additives (CSH = $CaSO_4 \cdot 1/2H_2O$).

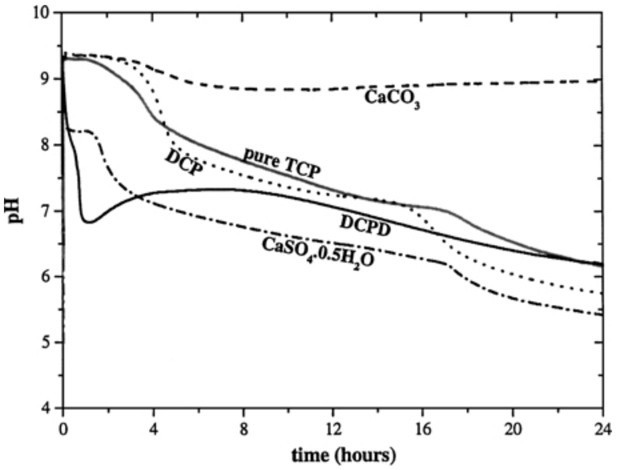

Figure 7 pH variations during hydrolysis of α-TCP-additive formulations. The curves are labeled with the abbreviations for the additives.

to the simultaneous dissolution of α-TCP and DCPD. These three mixtures approached a pH value near 6 indicating HAp formation. In the mixtures containing $CaCO_3$ HAp formation did not occur.

3.4. Mechanical properties

The effects of the additives on the diametrical strength as a function of hydrolysis time are shown in Table II. The changes in strength with time followed a similar trend for all formulations. The average strength of α-TCP compacts prior to hydrolysis were 0.36 ± 0.03 MPa. This initial strength value is representative for the other sets containing the additives. The strengths increased significantly during the first 24 h of reaction and leveled off or changed very slightly afterwards. The average diametral strength of the α-TCP samples was 7.26 ± 0.6 MPa after 24 h. The mixture containing DCP showed similar strength gain as the control α-TCP samples and attained reaching almost the same strengths at 24 h it was 7.1 ± 1.2 MPa for TCP-DCP blend. Their strengths did not increase between 24 h and 48 h of hydrolysis. The XRD analyses shown in Fig. 6, indicated the absence of unreacted α-TCP after 24 h. The DCPD-containing samples had a lower 24 h strength (5.51 ± 0.5 MPa) than phase-pure α-TCP, due to the unreacted α-TCP. However, this mixture reached almost the same value (6.74 ± 1.1 MPa) as that of phase-pure α-TCP after 48 h, once all the α-TCP was hydrated to HAp.

TABLE II Diametrical strengths of α-TCP-additive formulations after 24 h and 48 h of hydrolysis

α-TCP-additive (90 : 10 wt%)	24 h	48 h
α-TCP	7.3 ± 0.6	7.0 ± 0.4
α-TCP-DCP	7.1 ± 1.2	7.1 ± 0.3
α-TCP-DCPD	5.5 ± 0.5	6.7 ± 1.1
α-TCP-$CaSO_4 \cdot 1/2H_2O$	8.4 ± 0.9	7.8 ± 0.9
α-TCP-$CaCO_3$	3.8 ± 0.3	3.5 ± 0.4

The blends containing $CaSO_4 \cdot 1/2H_2O$ and $CaCO_3$ determined the upper and lower bounds for the strength values of the mixtures examined. The $CaSO_4 \cdot 1/2H_2O$-containing mixture showed the highest strength at any hydrolysis time, although the reactivity, i.e. conversion of α-TCP to HAp was limited as determined by low calorimetric heat values. Its average diametral strength after 24 h was 8.36 ± 0.9 MPa. This additional strengthening is due to hydration of $CaSO_4 \cdot 1/2H_2O$ to gypsum. The extra XRD peaks corresponding to gypsum are indicated in Fig. 6. Lemaitre *et al.* reported extended setting times for a α-TCP-MCPM cement accompanied with additional strengthening in the presence of $CaSO_4 \cdot 1/2H_2O$ [28].

The $CaCO_3$-containing α-TCP blends reached an average strength of 3.49 ± 0.4 MPa after 48 h; approximately 50% lower than carbonate free α-TCP. XRD analysis showed only very limited HAp formation even after 48 h. The pH measurements and calorimetry analyses indicate carbonate ion not only retards the early dissolution of α-TCP but also inhibits the precipitation of HAp. Carbonates either in as solids or in the reactant liquid were previously found to decrease the reactivity and retard HAp formation for similar calcium phosphate systems. [29, 30]. The retarding effect of $CaCO_3$ is related to its pH buffer ability. As shown in Fig. 7 the presence of the $CaCO_3$ additive drives the solution pH towards basic conditions. This leads to a decrease in the apparent solubility of α-TCP as expected for all calcium phosphates exhibiting increasing solubility with decreasing pH [7]. As discussed earlier, due to the suppression of the dissolution step, precipitation of HAp does not occur. This is also in accord with the findings showing formation of carbonate-substituted apatite in the presence of a third component, such as MCPM [2] or DCPA [31], in the cement formulation. These acidic compounds decrease the solution pH suppressing the pH buffering effect of $CaCO_3$ and favoring the conditions for dissolution.

4. Summary

The ability of α-TCP to form HAp is greatly influenced by its synthesis temperature and by the α-TCP particle characteristics. pH measurements showed that reactivity of α-TCP is reduced by a low specific surface area and by overfiring. The rate of hydrolysis can be increased by HAp seeding at a weight proportion greater than 1%. A low proportion of HAp seeds resulted in shortened times for both the nucleation and the growth events. At higher additions (>5 wt%) hydrolysis occurs by growth of HAp without any intrinsic nucleation stage.

The additives investigated did not improve the hydrolysis rate but did change the HAp formation mechanism. All the α-TCP-additives mixtures, excluding α-TCP-$CaCO_3$, reached nominally the same strength values as governed by the transformation of α-TCP to HAp. The only improvement in strength was observed in the presence of $CaSO_4 \cdot 1/2H_2O$. Although α-TCP hydrolysis was limited, hydration of $CaSO_4 \cdot 1/2H_2O$ to gypsum resulted in slightly higher diametral strengths. At the other extreme $CaCO_3$ was detrimental to hardening. The presence of inert DCP and the decomposition of DCPD did not have any meaningful effect on the strength of final HAp.

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