

Mechanical properties and workability of self-hardening calcium phosphate cement as a function of the particle size distribution

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In this study, the mechanical properties of α -tricalcium phosphate (α -TCP)-tetracalcium phosphate (TTCP)-dicalcium phosphate dehydrate (DCPD) system bone cement, was studied. This research examined the effect of changes in the particle size distribution change of the starting materials. The composition of the α -TCP/TTCP/DCPD system bone cement was fixed at Ca/P=1.50. 20 groups of this cement were prepared with a main particle size distributions. The highest compressive strength of a specimen (P/L ratio=2.5) after curing for 7days in simulated body fluid (SBF) was 60 ± 2 MPa. Also, we intended to improve the workability maintaining the compressive strength through the addition of TCP granules. 5 groups of cement were prepared with respect to the blending ratio between granular and powdery TCP. Even if the best compressive strength of specimen was observed in the cement without granules at a powder to liquid (P/L) ratio of 2.5, a comparable compressive strength (58.36 MPa) could also be obtained in the cement by replacing half of powdery TCP with granules by weight. However, the granular cement exhibited proper workability unlike the powder one.

Key words: calcium phosphate, TCP granule, bone cement.

Introduction

Self-setting calcium phosphate cements are useful for various applications such as orthopaedic surgery and dentistry. Calcium phosphate cements have excellent biocompatibility and less heat evolution compared with conventional PMMA bone cement. However, the mechanical properties need to be improved. It is well known that the particle size and the activity of the starting materials are critical parameters influencing the mechanical properties (setting time and compressive strength) of hydraulic cements [1]. Calcium phosphate cement is typically composed of α -tricalcium phosphate (α -TCP), TTCP (tetracalcium phosphate) and DCPD (dicalcium phosphate dehydrate). Among these, α -TCP is the least soluble and thus controls the overall hardening reaction. Therefore in this work, an investigation was much to increase the compressive strength while maintaining a proper setting time by changing the α -TCP particle size distribution.

Materials and Methods

α -TCP and TTCP were prepared by calcination of a mixture of calcium hydrogen-phosphate (DCPA) and

calcium carbonate at 1500 °C for 6 h in a furnace, followed by quenching to room temperature. Subsequently the powders obtained were blended with DCPD. 0.5 mole of $\text{NH}_4\text{H}_2\text{PO}_4$ and 0.3 mole of citric acid were dissolved in a litre of deionized water to prepare a setting agent. The TCP granules were synthesized through sintering of green bodies at 1350 °C and subsequent grinding and sieving. Fig. 1 shows the synthesis of TCP, TTCP powders and the preparation and the analysis of Bone Cement

The composition of the TCP/TTCP/DCPD system bone cement was fixed at Ca/P=1.50 according to results in a previous study [1]. Table 1 shows the median particle size of the various raw materials. 20 groups of cement were prepared with the particle size distributions. Also, 5 groups of cement were prepared

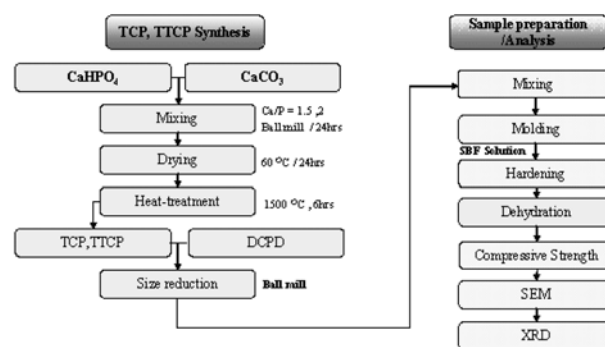


Fig. 1. Synthesis of TCP, TTCP and Sample preparation & Analysis of Bone Cement.

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Table 1. Median particle size of raw materials

	Ca/P=1.5		
	TCP	TTCP	DCPD
Particle Size	21.97		
Distribution (μm)	11.56	20.35	16.02
	9.7		
	7.44	6.73	7.82
	6.21		

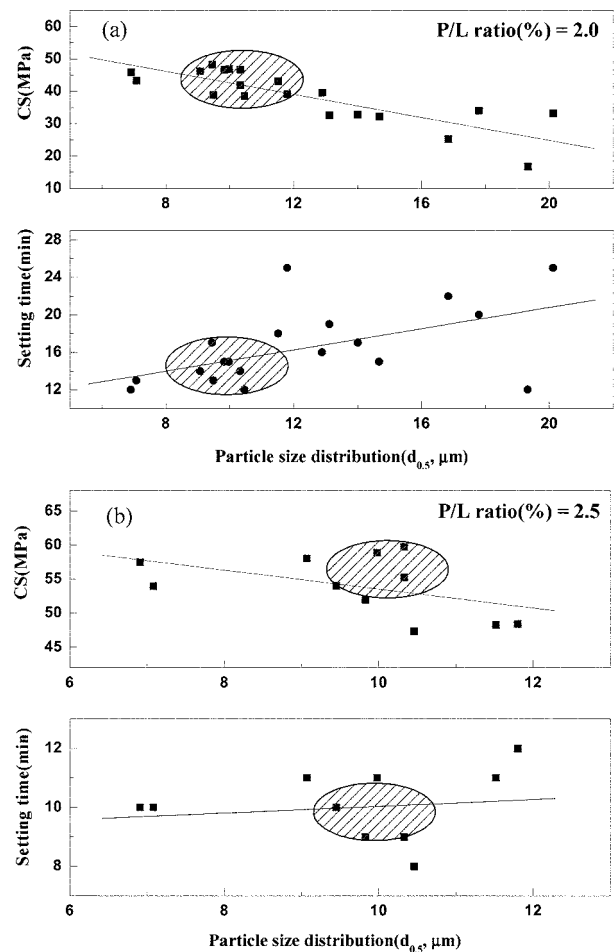
Table 2. Designation of sample with a mixing ratio (wt %) between granular and powdery TCP

	TCP type and size range	
	granule 45~90 μm	Powder 9~11 μm
G100	100	0
G80	80	20
G50	50	50
G20	20	80
R	0	100

with respect to the blending ratio between granular and powdery TCP. The weight percent of granules were 0, 20, 50, 80 or 100 and designated as R, G20, G50, G80 and G100, respectively, as summarized in Table 2. The average particle size of TTCP and DCPD was 7 μm and 16 μm , respectively. The hydration reaction was performed for 7days in simulated body fluid at 37 °C and RH 100. The powder to liquid (P/L) ratio was changed from 2.0 to 5.0 depending on the state of mixture. The compressive strength of hardened cement was measured for cube specimens with an edge length of 1 cm using an universal testing machine (INSTRON 4204, maruto) at a compression speed of 0.5 mm/minute. The setting time was also determined using a Vicat needle. The samples were characterized with X-ray diffractometry and scanning electron microscopy.

Results

Figure 2(a) shows the compressive strength with a change of particle size after curing for 7days in SBF at a P/L ratio=2.0. The compressive strength of the specimen with a particle size distribution from 9-11 μm was 49 ± 2 MPa, which was the best result at a P/L ratio=2.0. The setting time of this specimen with this particle size distribution was about 14 minute. To reduce the setting time and improve the compressive strength, we retried 11 groups of cement with a particle size distributions of 9-11 μm at a P/L ratio=2.5. Fig. 2(b) shows the compressive strength at a P/L ratio=2.5. The compressive strength of a specimen with a particle size distribution centered at 10 μm was about 60 ± 2 MPa, which was the best in this study. The setting time of the specimen with that particle size was about 11 minute. The particle size distribution of the highest

**Fig. 2.** Change of initial setting time and compressive strength with particle size distribution in each composition. (a) P/L=2.0 (b) P/L=2.5.**Table 3.** Compressive strength and Setting time of granular bone cement

	Compressive strength (MPa)						
	2.0	2.5	3.0	3.5	4.0	4.5	5.0
G100	—	—	—	—	27.2	30.28	28.91
G80	—	—	—	39.20	47.53	34.25	—
G50	—	34.40	41.31	58.36	39.41	—	—
G20	—	39.79	51.89	×	—	—	—
R	49.00	60.00	×	—	—	—	—

compressive strength sample was 10.20 μm (α -TCP =9.7 μm , TTCP=6.73 μm and DCPD=16.02 μm).

Table 3 shows the compressive strength as a function of the percentage of granules. The compressive strength of specimen R (P/L ratio=2.5) after curing for 7days in SBF solution was 60.0 ± 2 MPa, which was the best in this work. But the workability of specimen R (P/L ratio=2.5) was not suitable for handling and a further increase of P/L ratio was impossible. A similar value of the compressive strength (58.36 MPa) was also observed in sample G50 with a P/L ratio of 3.5. However the workability of specimen G50 (P/L ratio

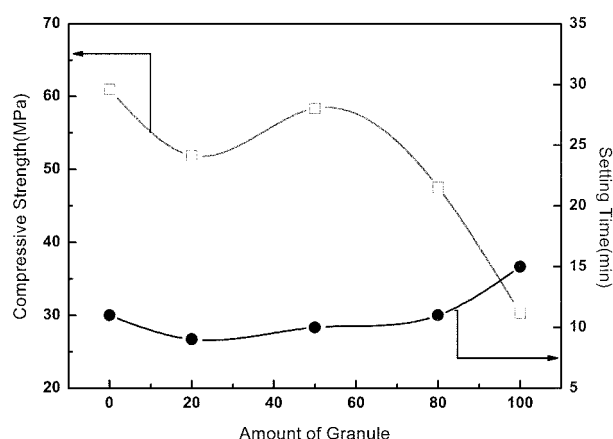


Fig. 3. Compressive strength and Setting time of granular bone cement.

=3.5) was much improved as can be seen from the fact that the P/L ratio in G50 could be further increased to 4.0. The setting time was tested for the specimen with the best compressive strength at each composition. It is well known that a suitable setting time is about 8-12 minute including mixing time. As shown in Fig. 3, the initial setting time of all compositions was about 10 minute, except for G100.

Figure 4(a) shows the X-ray diffraction patterns of a specimen with about a 10 μm particle size distribution after curing for 7days in SBF. The formation of the HAp phase after curing for 1day was observed. As time lapsed, the TCP peak decreased and the HAp peak increased. Fig. 4(b) shows the X-ray diffraction patterns of a specimen with about a 20 μm particle size

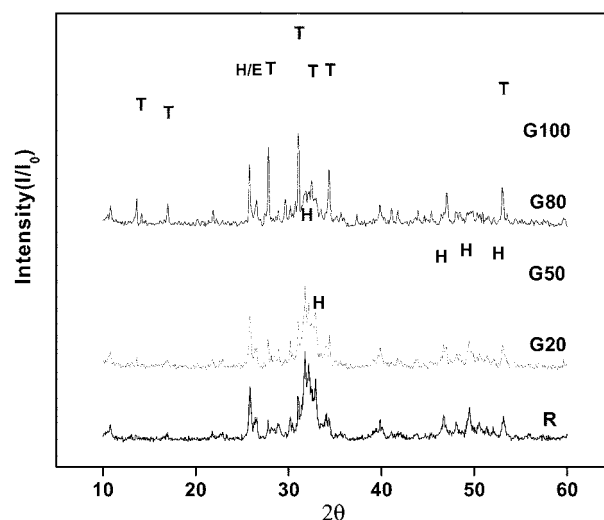


Fig. 5. XRD patterns of Bone Cement (7days). (T: α -Tricalcium phosphate, H: Hydroxyapatite)

distribution after curing for 7days in SBF. The specimen was composed of only the TCP phase until 3days and the formation of the HAp phase after curing for 7days was observed. However, some TCP phase still remained after 7days. The result in Fig. 4 suggests a change of HAp conversion with the particle size distribution. It also suggests that the transformation during the setting reaction is not sufficient when the particle size of the starting materials was around 20 μm .

Figure 5 shows the X-ray diffraction pattern of specimens with a change of TCP particle size after curing for

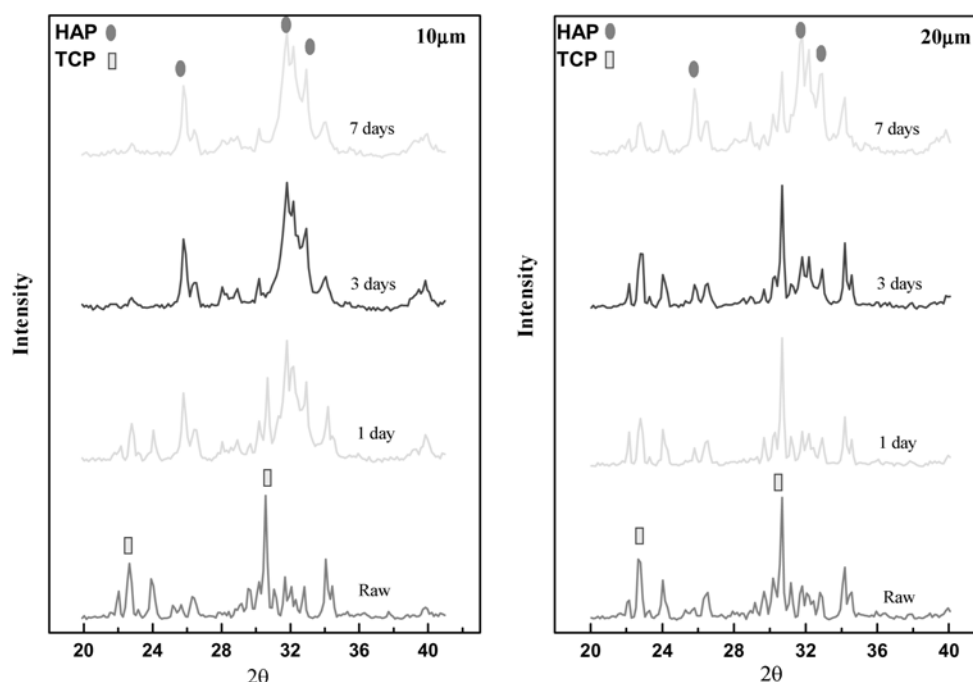


Fig. 4. XRD patterns with change of particle size distribution; (a) 10 μm (b) 20 μm

7days in SBF. The specimens R and G20 were composed of HAp phase after hardening. However, specimen G50 consisted of TCP and HAp, while G80 and G100 were composed of only TCP. The result in Fig. 5 suggests that the transformation to HAp during the setting reaction is not complete for the samples with the higher granule contents. To increase the strength of cements, two aspects need to be considered. First, the setting reaction should be carried out homogeneously in the overall specimen leaving the unreacted part as a minimum. Second, the specific strength of the final product needs to be as high as possible [2, 3].

Table 3 shows that the compressive strength requires an optimum condition in the P/L ratio except for the groups with smaller granular contents (R, G20). With an increase of P/L ratio, the initial increase of strength can be attributed to the decrease of porosity, while the final decrease of strength is ascribed to an insufficient homogeneity in the reaction throughout the specimen.

Figure 6 shows SEM photographs of specimens with a change of particle size after curing for 7days in SBF solution. In the specimen with a 10 μm particle size distribution((a) and (b)), the structure with a HAp from 1day was developed on the surface of the hardened

body. In specimen with a 20 μm particle size distribution((c) and (d)), the structure of HAp hardly appeared and the TCP morphology is dominant at 1day. However, petal-like HAp started to appear around 7days. As time lapsed, petal-like HAp developed and the microstructure became more compacted.

Figure 7 shows the SEM photographs of specimens with a change of TCP particle size after curing for 7days in SBF solution. In specimens G20 and G50, petal-like HAp could be observed on the surface of the hardened body even though some TCP granules still remained. For specimens G80 and G100, the HAp was hardly visible and a granular morphology of TCP was dominant.

Figure 8 shows the FTIR spectra of the product formed by hydrolysis of bone cement after curing for 7days in SBF solution with a change of particle size. The bands at 550-600 and 1020-1120 cm^{-1} are assigned to PO_4^{3-} . The absorption bands at 630 and 3540 cm^{-1} suggest the presence of structural OH^- groups in the hydrated products. These bands are assigned to a OH^- librational mode and to the stretching mode respectively. The decrease in absorption intensity of the OH^- band suggests the formation of calcium-deficient hydroxyapatite (CDHA) [4]. The band at 1650 cm^{-1} can be

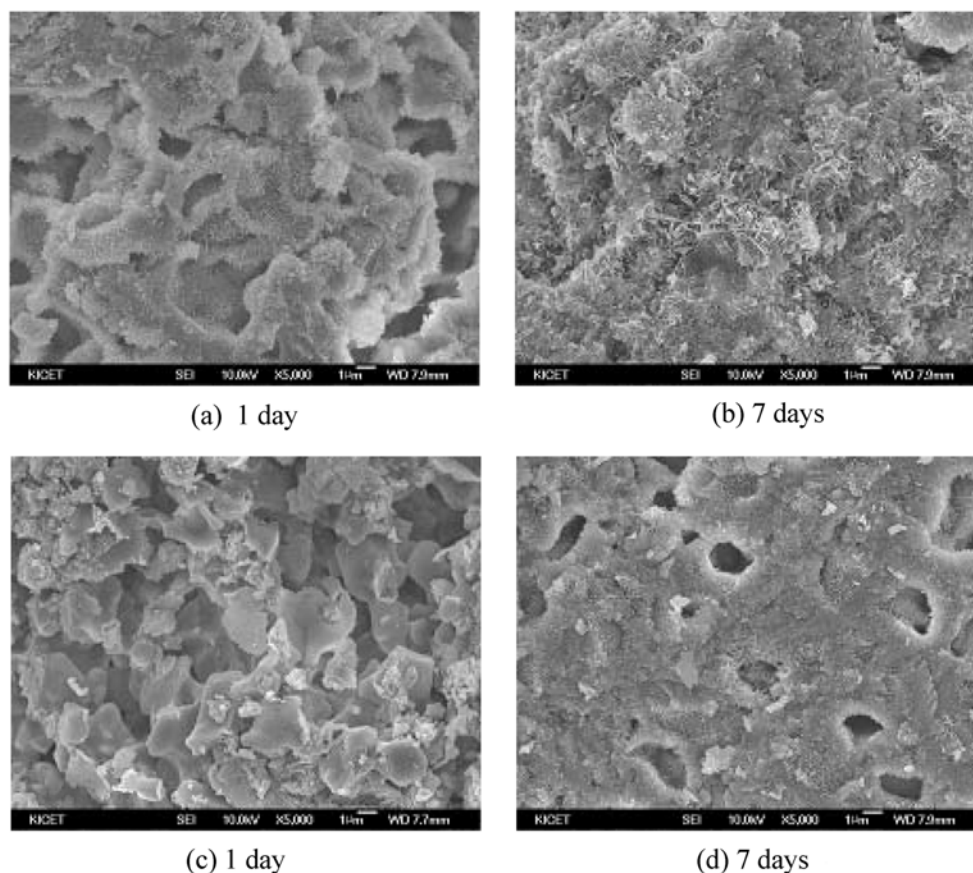


Fig. 6. SEM photographs with change of particle size distribution; 10 μm ((a) and (b)) and 20 μm ((c) and (d))

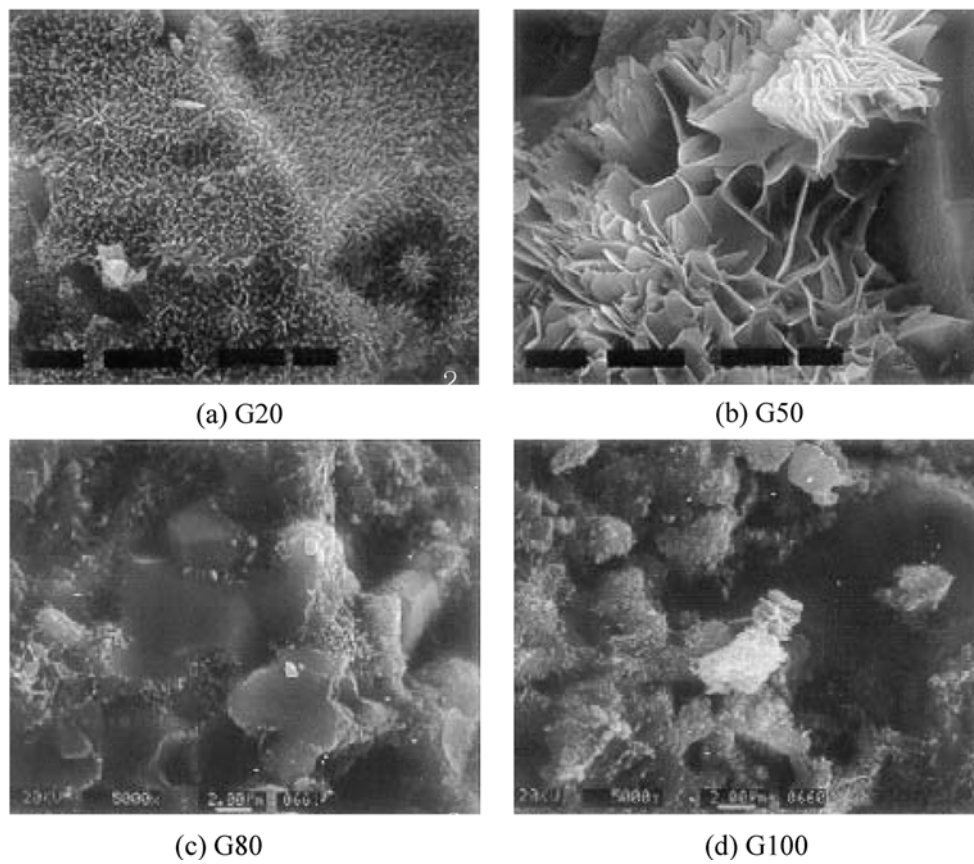


Fig. 7. SEM photographs ($\times 5,000$) of Bone Cement in SBF solution (7days).

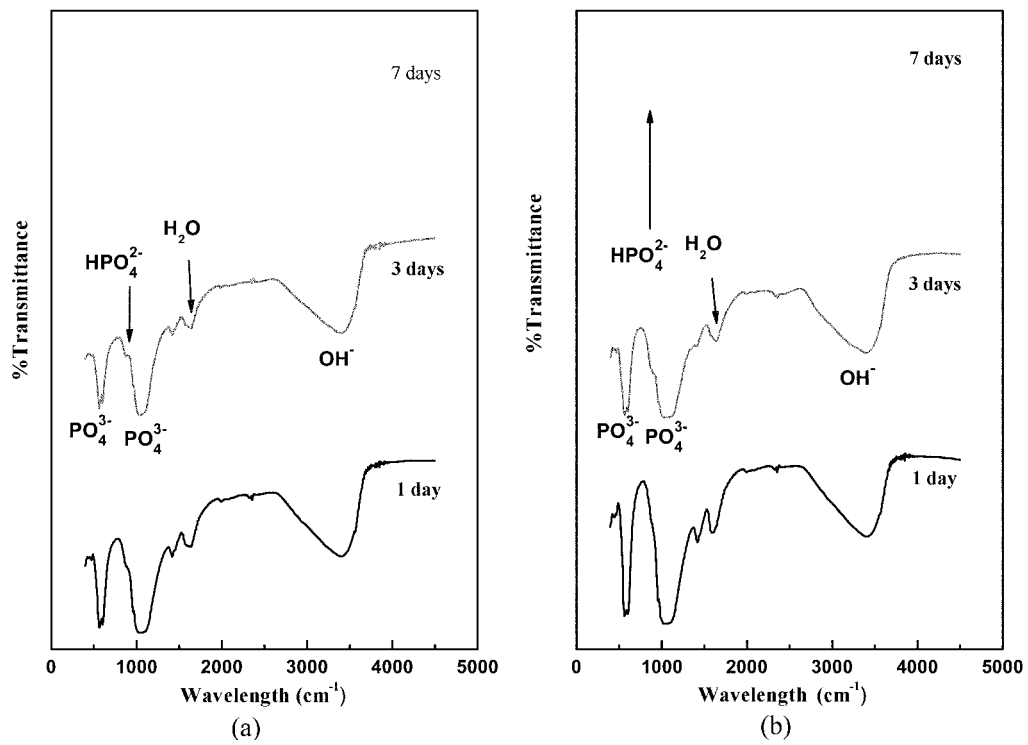


Fig. 8. IR spectra with change of particle size distribution; (a) 10 μm (b) 20 μm .

assigned to water.

The band at 875 cm^{-1} can be assigned as HPO_4^{2-} , which is unique to calcium-deficient minerals. As time lapsed, the band at 875 cm^{-1} was increased.

Discussion

To get high strength cements two aspects need to be considered. First, the setting reaction should be carried out homogeneously in the overall specimen leaving the unreacted part as a minimum. Second, the end product needs to be composed of the phase with a higher specific strength. The increase of strength with the P/L ratio is attributed to a decrease of porosity. The setting and hardening properties of calcium phosphate cements are due to the progressive dissolution of the TCP phase and the formation of an entangled network of calcium-deficient hydroxyapatite (CDHA) crystals.

Studies have shown the existence of two rate-controlling mechanisms during TCP hydration. Initially, the controlling mechanism is dissolution-precipitation and the surface area of the reactants plays a key-role during the process. After a certain time, a diffusion-controlled mechanism through a hydrated layer of crystals covering the TCP particles takes place [5, 6]. The hydration property of calcium phosphate cements may be a combination of physical and chemical processes. The physical factors include porosity, surface area and crystallinity. Factors tending to increase the rate or extent of hydration include increases in porosity, reductions in crystal size, an increase in number of crystal imperfections, and a decrease in grain size. The chemical factors depend on material composition.

With the introduction of granular TCP, the P/L ratio could be effectively increased and thus the advantage in workability could be realized while maintaining a similar level of compressive strength. However, a further increase of TCP granules rather decreased the compressive strength in spite of the decrease in porosity. This was attributed to an incomplete reaction in forming HAp that has the best specific strength in the system. The relative chemical inertness of granules might have prevented the reaction. This study has shown the two important factors in synthesizing self-setting cements with superior strength when introducing TCP granules. First, the P/L ratio should be determined in a consideration of not only of a minimization of porosity but also completeness of reaction. Second, even though the introduction of granules is positive in enhancing the workability, they need to be controlled so that sufficient conversion to HAp can be ensured.

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