

Effects of Particle Size Distribution of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ on Self-hardening Bone Cement

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ABSTRACT

This research examined the effect, which it follows in particle size distribution change of $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$ (DCPD). We used two kinds of compositions; tetracalcium phosphate (TTCP)/dicalcium phosphate dihydrate (DCPD) composition and α -tricalcium phosphate (α -TCP)/TTCP/DCPD composition. As the result, the mean particle size of the DCPD decreased, the setting time shortened at all compositions. The reference powder (DR), which did not milling, showed about 2 times strength value compared with other milling sample. Especially, the compressive strength of 60 : 20 : 20 sample ($\text{DR}(d_{0.5})=12.08 \mu\text{m}$) after curing 7 days in simulated body fluid solution was $40 \pm 0.5 \text{ MPa}$, which was the highest. This resulted from the packing density at α -TCP/TTCP/DCPD combination.

Key words : Self-hardening, TCP, DCPD, Particle size distribution, Setting time

1. Introduction

Self-hardening bone cements (SHBCs) have attracted much attention in biomaterials because of their excellent biocompatibility and bio-replacing behavior over long periods of time.¹⁻⁴⁾ Since the development in 1987⁵⁾ of the first self-setting calcium phosphate cement consisting of tetracalcium phosphate (TTCP) and dicalcium phosphate anhydrous (DCPA) or dicalcium phosphate dihydrate (DCPD), many different combinations of calcium and phosphate-containing compounds have been investigated as potential calcium phosphate cement materials and the properties of the various cements reported.⁶⁾ And in these materials, one or more ambient-temperature reactions involving phase transformation of calcium phosphate compounds cause the hardening of the cement.⁷⁾ It is well known that the particle size of the starting materials influences the mechanical properties (setting time, compressive strength and so on) of hydraulic cements and conversion rate to the final product via their dissolution rate which is faster with small particles.^{8,9)}

In this study, α -tricalcium phosphate (α -TCP), tetracalcium phosphate (TTCP) and the dicalcium phosphate dihydrate (DCPD) of three phases, it investigated the effect which it follows in particle size distribution (PSD) change of the DCPD and with the each composition ratio it regulates the ratio of powder to liquid ratio with the quality which it follows in physical properties change of the bone cement which appears namely, to investigate the initial setting

time, hydration, and the compressive strength, etc.

2. Experimental

α -TCP and TTCP were prepared by heating a mixture of DCPD and calcium carbonate at 1500°C for 6 h in furnace, followed by quenching at room temperature. In order to investigate the effect which it follows in particle size distribution each $12.08 \mu\text{m}$ (DR), $6.05 \mu\text{m}$ (DB), $3.45 \mu\text{m}$ (DP2), and $3.12 \mu\text{m}$ (DP4) with it pulverized the DCPD of reagent grade and it used. Compositions were reference specimens (TTCP:DCPD=50 : 50) and 3 phases (TCP:TTCP:DCPD=60 : 20 : 20 and 70 : 15 : 15). And the cement was prepared by mixing 2 and 3 compositions powder with an aqueous solution containing $0.5 \text{ M NH}_4\text{H}_2\text{PO}_4$ as accelerant. The hydration reaction was performed to 1, 3, and 7 days in simulated body fluid at 37°C . The powder to liquid (P/L) ratio was fixed by 2.0. After hardened samples of $\phi 6 \times 12 \text{ mm}$ were used for compressive strength test. Also it measured the setting time. The sample obtained from the crushed materials after hardened was tested by X-Ray Diffractometer (XRD), and the microstructure was observed by Scanning Electron Microscopy (SEM).

Table 1. Median Particle Size of Raw Materials

	Particle size distribution (μm)	Remark
TCP	5.79	Synthesized powder
TTCP	2.45	Synthesized powder
DCPD	DR	Raw(reagent grade)
	DB	
	DP2	$d_{0.5}$ after milling
	DP4	

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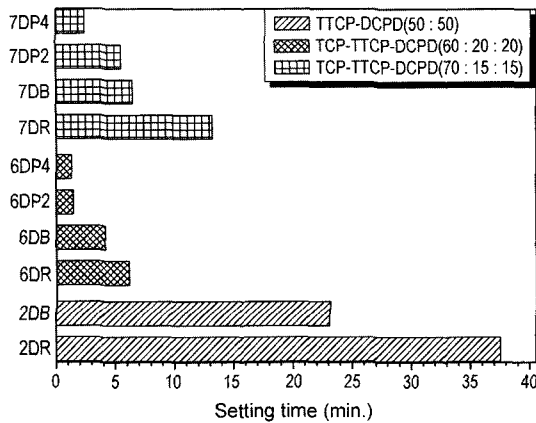


Fig. 1. Change of initial setting time with each composition.

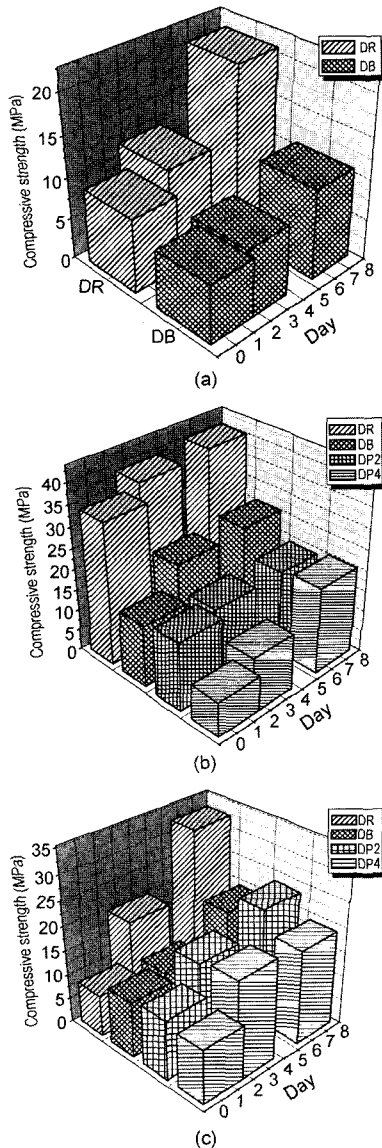


Fig. 2. Compare the compressive strength with DCPD particle size distribution in each composition. (a) TTCP: DCPD (DB & DR)=50:50 (b) TCP:TTCP:DCPD=60:20:20, and (c) TCP:TTCP:DCPD=70:15:15.

3. Results and Discussion

Fig. 1 shows the initial setting time of samples with particle size distribution of DCPD. The initial setting time of TCP-TTCP-DCPD combination was shorter than that of TTCP-DCPD combination. In case of the initial setting time of reference sample (DR), TTCP-DCPD combination was about 37 min, but the composition of 60:20:20 were about 6 min. Also, the initial setting time of 70:15:15 compositions were about 13 min longer than that of 60:20:20 compositions. With the mean diameter of DCPD increased, the setting time shortened.

The compressive strength of samples with various particle size of DCPD in TTCP-DCPD and TCP-TTCP-DCPD combination shows the Fig. 2. The compressive strength of sample DR was higher than that of other samples at each combination. Especially, the compressive strength of 60:20:20 sample (DR($d_{0.5}$)=12.08 μm) after curing 7 days in simulated body fluid solution was 40 ± 0.5 MPa, which was the highest. This resulted from the packing density at TCP-TTCP-DCPD combination.

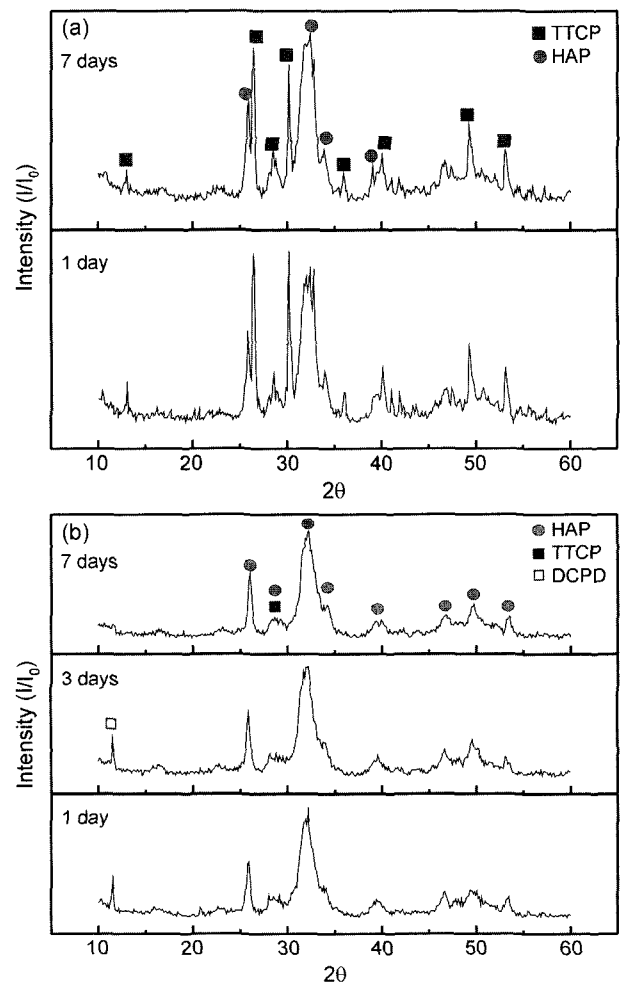


Fig. 3. XRD patterns of the reference sample in two compositions (TTCP-DCPD); (a) 50:50 (DR) and (b) 50:50 (DB).

Fig. 3 shows the X-ray diffraction pattern of TTCP-DCPD combination samples measured 1, 3, and 7 days after mix-

ing and storage in simulated body fluid solution. As shown in Fig. 3(a), formation of HAP from (no milling) sample DR

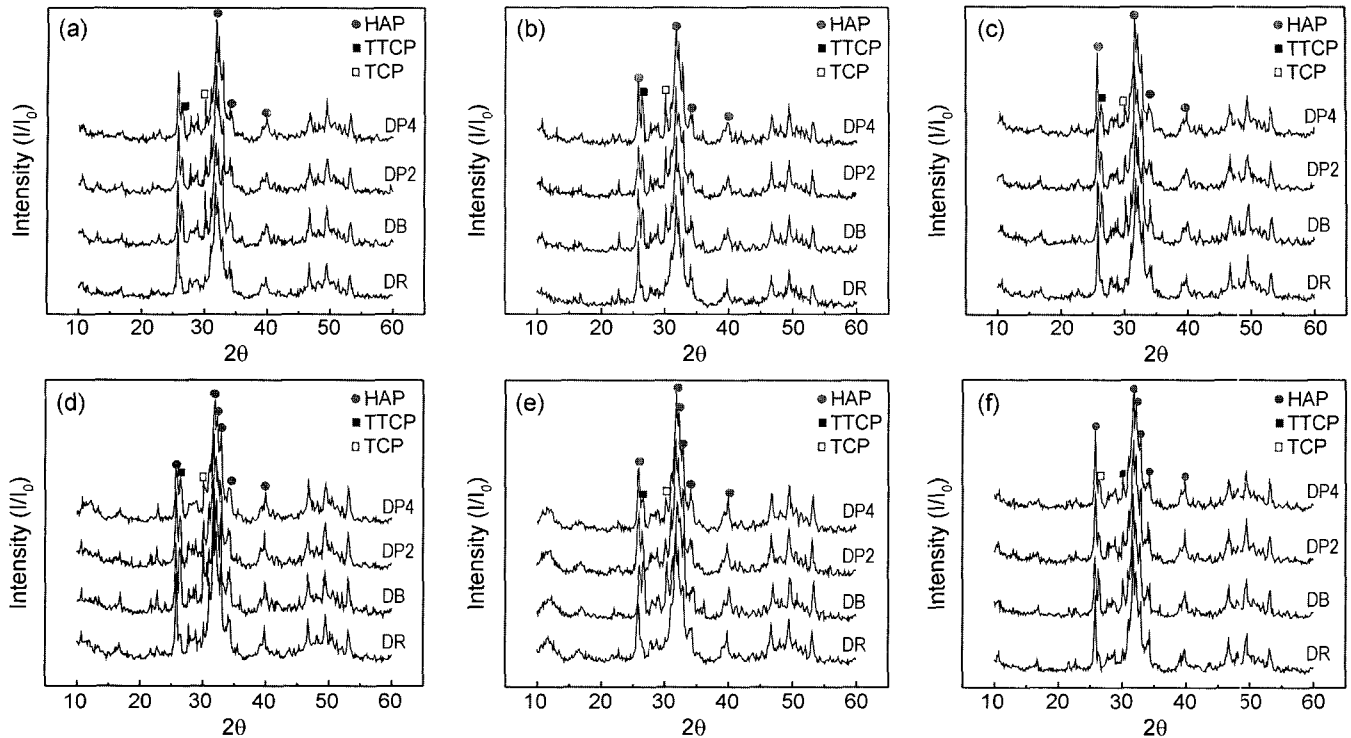


Fig. 4. XRD patterns of the TCP:TTCP:DCPD with change of DCPD particle size distribution in each composition; 60 : 20 : 20 ((a) 1 day (b) 3 days (c) 7 days) and 70 : 15 : 15 ((d) 1 day (e) 3 days (f) 7 days).

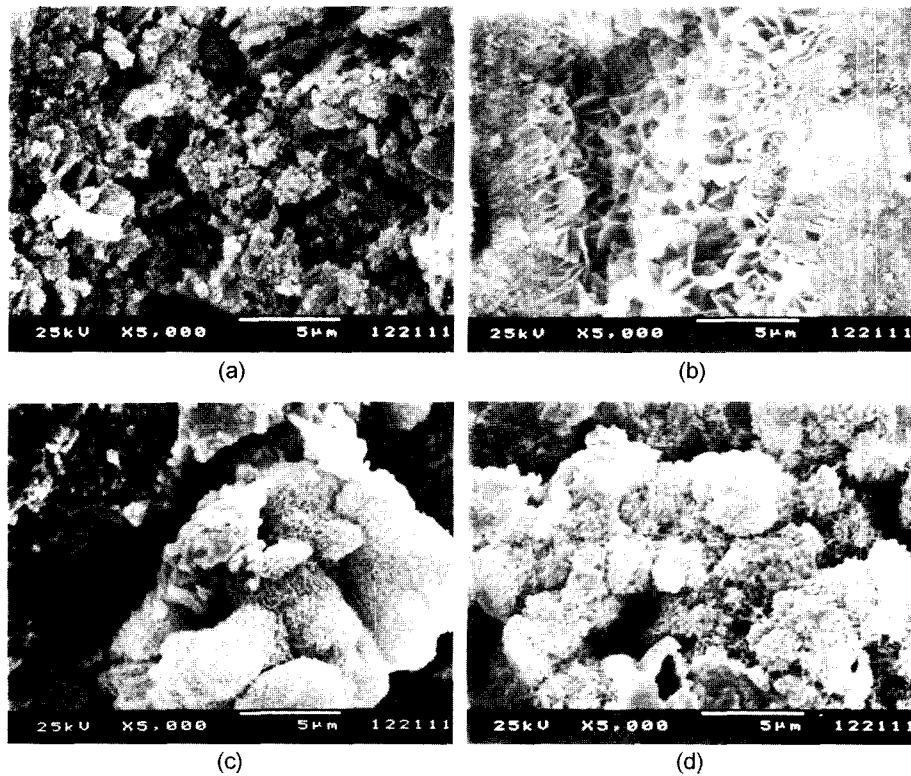


Fig. 5. SEM photographs with change of DCPD particle size distribution in composition of TTCP:DCPD (50 : 50); DR ((a) and (b)) and DB ((c) and (d)).

after curing 1 day was observed. Some TTCP still remained unreacted by 7 days. As shown in Fig. 3(b), also, formation of HAp from (ball milling) sample DB after curing 1 day was observed. Some DCPD still remained unreacted by 3 days. Finally, DCPD completely disappeared at 7 days. This finding may suggest HAp conversion.

In case of reference sample (DR), this shows the XRD peak of Fig. 4, a peak of TTCP near $ab. 30^\circ$ and $ab. 28^\circ$ (2 θ) neighboring TCP in 1 day was not almost existed. This verifies that a change happened with HAp of all amorphous form. As for this result, because it is matched with the compressive strength measurement result, it is for a change to have happened with HAp quickly by the ion elution of Ca^{2+} and PO_4^{2-} etc. Contrary to this, the specimen (DB, DP2, and DP4) decreases XRD peaks of TCP and TTCP according to the day passes being increased in all

compositions. Also, it is able to verify that it was getting up at a HAp peak of a crystalline. Figs. 5~6 shows SEM photographs of each composition of 1 day and 7 days with varied a DCPD particle size. Fig. 5 shows result of the microstructure of the specimen, which is crushed by raw materials (a, b) and ball mill (c, d) in a 2 compositions. As matching with the previous XRD result, in case of 1 day, the structure of HAp hardly appeared. However, HAp in the petal-like phase started to appear from the inside as the day progressed. The hardened body confirmed this. In case of the specimen (DB) by ball milling, the morphology of a circular particles of a chestnut bur type co-existing with needle-like crystalline were observed as time progressed. SEM photographs of the hardened body with DCPD particle size distribution as show in Fig. 6 in the composition of three phases. In 1 day, the hardend body

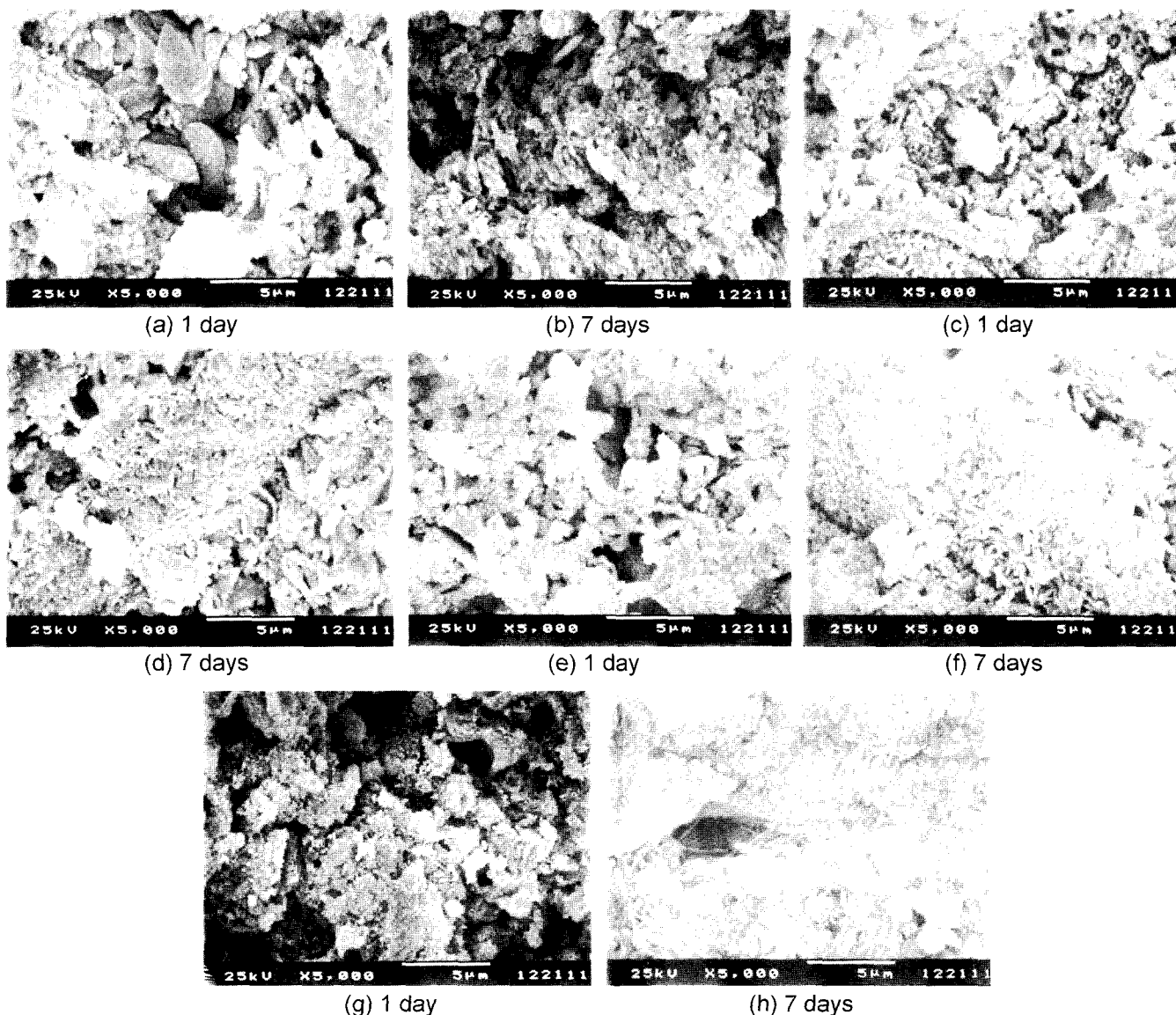


Fig. 6. SEM photographs with change of DCPD particle size distribution in the composition of 60 : 20 : 20; DR ((a) and (b)) DB ((c) and (d)) DP2 ((e) and (f)) DP4 ((g) and (h)).

can see the poor densified structure. As time lapsed, density confirmation is apparent due to the HAp product developing a hardened body.

4. Conclusions

As a result of the influence of the particle size distribution of DCPD in three compositions system, it was able to get the following conclusion. The result which measures an initial setting time, as the smaller the mean particle size of the DCPD and it is shortened it will be able to confirm setting time. And the result which measures compressive strength it follows in each composition, in cases of compared with compressive strength of 3 phases and reference raw specimen, raw specimen (DR) shows the strength value of about 2 times in different DCPD grain size. Specially, in case of 60 : 20 : 20 (DR) specimen, it showed 40 ± 0.5 MPa in 7-days. This is judged with the fact that due to the difference of packing ratio of the particle for it follows in grain size distribution of the DCPD. Also x-rays diffraction peak analysis result, the day passes to follow, it shows to occurring to transition with the hydroxyapatite (HAp). And in case of raw specimen (DR) of 3 phases, it will be able to confirm a change with peak pattern of the typical HAp of amorphous form in different DCPD particle size distribution.

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