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Synthesis and Properties of Self-hardening Calcium Phosphate Cements for Biological Application

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Fine powders of α-tricalcium phosphate, tetracalcium phosphate and dicalcium phosphate were mixed together to prepare self-setting cements which form hydroxyapatite, one of the well-known biocompatible materials, as the end of products of hydration. Hardening behaviour of the cements was examined at the temperature range of 37~70°C and 150~250°C under the normal and hydrothermal condition respectively. The conversion of cements into hydroxyapatite was significantly improved at elevated temperature and the paste was strengthened by interlocking of hydroxyapatite crystals, indicating that the strength is determined by microtexture rather than the amount of conversion of cements into hydroxyapatite.

Key words : Calcium phosphate cement, Bioceramics, Hydroxyapatite, Phosphate chemically bonded ceramics

I. Introduction

Recently, calcium phosphate cements have been a subject of considerable interest in the field of biomaterials. Calcium phosphate cement[1-9] can be prepared from a mixture of calcium phosphate compounds such as tricalcium phosphate (TCP), dicalcium phosphate dihydrate (DCPD), dicalcium phosphate anhydrate (DCPA) and tetracalcium phosphate (TTCP). When the cement is mixed with water, it hardens with the formation of hydroxyapatite (HAp), which is biocompatable.

Many studies concerned with calcium phosphate cements are carried out under physiological conditions, for example at a temperature of 37°C at physiological pH, for an active application of self-setting property to fill the space created by the absence of bone as an artificial hard tissue. In such a case of in-vivo hydration, an attempt to increase mechanical strength of hardened HAp body would be restricted seriously by the fixed physiological conditions. A mechanical strength can be increased by the hydration under various ex-vivo conditions such as elevated temperature, hydrothermal condition, lowered pH of liquid component and soaking a hardened body in a calcium phosphate solution for microstructural improvement. And there may be many other attempts such as control of powder composition and liquid/powder ratio (L/P ratio), addition of previously prepared HAp powders as a seeding materials and/or fibrous calcium phosphates for cement-fiber composites.

In this study, calcium phosphate cements of different combination were prepared from DCPA, DCPD, α-TCP and TTCP, and mixed with water at various temperature of 37~250°C under normal or hydrothermal condition with or without addition of HAp seeds and/or phosphoric acid solution. Hardening properties of the cements were studied by means of X-ray diffractometry (XRD), scanning election microscopy (SEM) and mechanical strength test of hardened paste.

II. Experimental Procedure

TTCP[$Ca_4(PO_4)_2O$] was prepared by heating an equimolar mixture of calcium carbonate and DCPD($CaHPO_4 \cdot 2H_2O$) to 1350°C for 6 hours. α-TCP[$Ca_3(PO_4)_2$] was prepared from a mixture containing 1 mole of calcium carbonate and 2 moles of DCPA($CaHPO_4$) by same method. The synthesized TTCP and α-TCP were ground to the size under 15 μm by a ball milling. Commercial reagent grade DCPA and DCPD used for preparation of TTCP and α-TCP and for cement component were used as received. HAp powders for seed were prepared from a mixture (Ca/P molar ratio=1.67) of calcium hydroxide and diammonium hydrogenphosphate by mixing with water and curing for 48 hours at 25°C.

Three different calcium phosphate cements having the Ca/P molar ratio of 1.5~1.7 were prepared by mixing TTCP with DCPA, DCPD and α-TCP seperately. An additional calcium phosphate cement was prepared by using the α-TCP powder. HAp powders of 10% by weight were added to these 4 types of simple cements as a seed. To lower an initial pH of cement paste, phosphoric acid solution of concentration of 1.7 M was used instead of pure water as a liquid component of cement paste.

The cement pastes were prepared by mixing the powder component and liquid component with the liquid/powder ratio of 0.3, and packing into a stainless steel mold (13 mmD×11 mmH) without pressure. After forming, cement paste was wrapped by air-tight PE film and stored

in a 37°C, 50°C and 70°C humidity chamber for 1~24 hours. Some of samples were not wrapped and stored under hydrothermal conditions of 150~250°C for 9 hours by means of an autoclave.

Mineral phases of the pastes and percent of conversion of cement minerals[5] into HAp were confirmed and measured by XRD, with passage of time after mixing. Microstructure of the hardened paste were observed by SEM and mechanical strengths were assessed by diametral tensile strength (DTS, kg/cm^2) of hardened paste.[6]

III. Result and Discussion

1. Properties of synthesized powders

Synthesized TTCP, α-TCP and HAp seeds were confirmed by XRD to be nearly pure in mineral phase except for negligible amount of β-TCP formed in α-TCP. Microstructure of the TTCP showed very porous solid agglomerate with high surface area by virtue of using hydrates as a starting materials of synthesis and heating to relatively lower temperature for a long time instead of higher temperature for a short time. The microstructure would be favorable to dissolution during hydration of the cements by dissolution-precipitation mechanism. HAp powders were shaped like a chestnut bur slightly cohered each other.

2. Mineralogical changes occurring during 24 hours hydration

The extent of conversion (%) of the cement materials into HAp, measured by XRD with passage of time is shown in Fig. 1. The mode of increasing percent of conversion and total amount converted after 24 hours hydration varied with the type of plain cement, reaction temperature and addition of seed HAp or phosphoric acid.

In two plain cements composed of TTCP/DCPD and α-TCP, conversion took place easily than in the other cements. At 37°C, conversion did not take place in all pastes prepared from plain cement within 10 hours after mixing with water. But the effect of temperature on conversion of three cements except for one cement prepared from TTCP/α-TCP was enough to raise the curves of conversion considerably at 50°C, showing an advantage of ex-vivo hydration. The effect of more elevated temperature up to 70°C on the conversion was shown in the paste prepared from α-TCP only. Addition of seed HAp also raised the curves of conversion of the pastes except for the paste prepared from α-TCP. So, even in the cement prepared from TTCP/α-TCP, which did not show conversion at all temperatures by 24 hours hydration, the effect of seeding was shown. Relatively lower percent of conversion of two cements prepared from TTCP/DCPA and TTCP/α-TCP could be raised up to 85% using phosphoric acid solution of concentration of 1.7 M as a liquid component instead of pure water. The addition of phosphoric acid was most effective to increase the extent of conversion of these cements into HAp within several hours.

XRD patterns of various pastes are shown in Fig. 2.

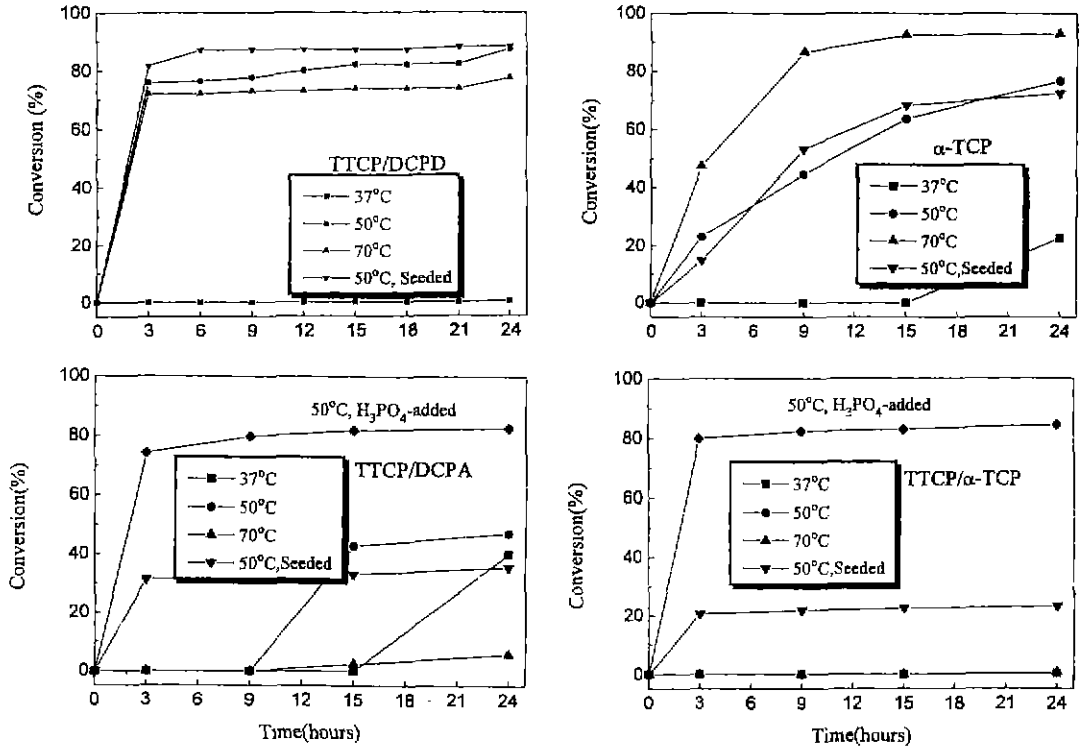
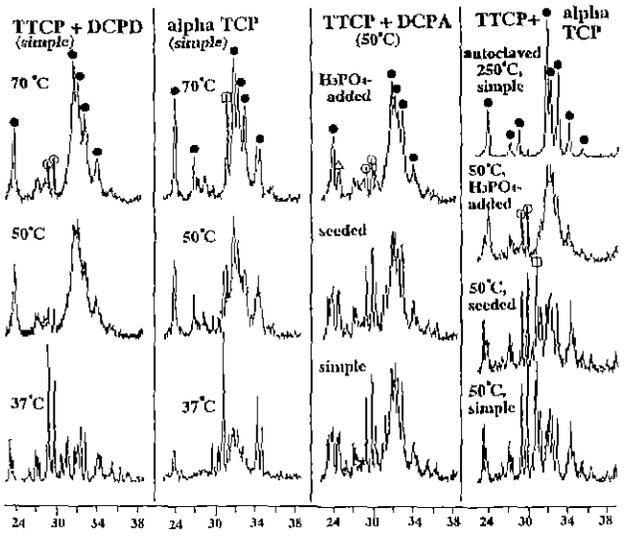


Fig. 1. Effect of temperature and addtives on the conversion ratio of cement component into Hydroxyapatite.



(●: HAp, ○: TTCP, △: DCPA, □: alpha TCP)

Fig. 2. XRD patterns of pastes prepared from various components under different conditions, for 24 hours except for one autoclaved sample (9 hours).

Small amounts of cement minerals remained with the HAp converted from them after 24 hours hydration except for DCPD. The effects of phosphoric acid were remarkable in pastes prepared from TTCP/DCPA and TTCP/α-TCP so that unreacted α-TCP existed at all temperatures could be eliminated by using phosphoric acid solution. As shown in Fig. 2, complete elimination of TTCP could be accomplished in the paste prepared from TTCP/α-TCP by hydration under hydrothermal condition of 250°C for 9 hours by means of autoclave.

3. Strength and microstructure of the pastes

Diametral tensile strengths of the various paste are shown in Fig. 3 and Fig. 4. Generally, the strength of hardened paste prepared from α-TCP showed relatively

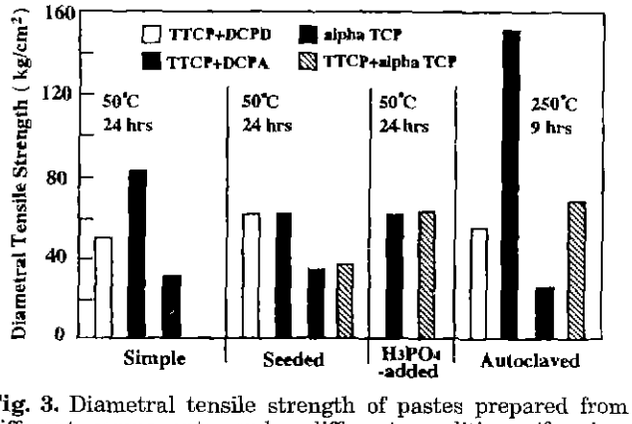


Fig. 3. Diametral tensile strength of pastes prepared from different components under different conditions (forming under pressure of 0.2 kg/cm²).

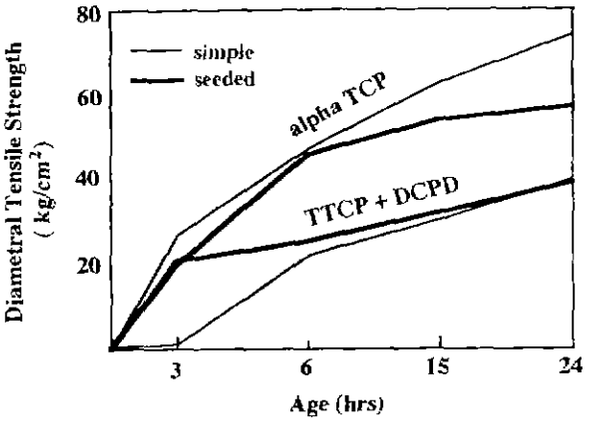


Fig. 4. Strength development of pastes prepared with and without seeds at 50°C (forming: pressureless).

higher value and the highest value (above 150 kg/cm²) could be obtained in this cement after hydration under hydrothermal condition. The strength of this cement increased with an increase in hydration temperature and percent of conversion apart from the addition of seeds or phosphoric acid. But some increases in strength caused by seeding were detectable in other samples and remarkable increases caused by addition of phosphoric acid were in cements prepared from TTCP/DCPA and TTCP/α-TCP.

The strength of pastes prepared from TTCP/DCPD and TTCP/DCPA could not be increased by autoclaving while percent of conversion could be increased extremely by autoclaving. Moreover, the paste prepared from TTCP/α-TCP which showed full conversion after autoclaving did not show expected strength. This means that the strength of a hardened paste is not proportional to percent of conversion always probably because of the factors concerned with the shape of produced HAp and microstructure of hardened paste.

SEM micrographs of fractured surface of hardened pastes were shown in Fig. 5 and Fig. 6. The shape of HAp crystals produced from different cements at 50°C were nearly same and petal-like except for the differences in size and homogeneity as a whole. Dense and homogeneous structure formed by interlocking of HAp crystals were observed easily in the paste prepared from H_3PO_4-added TTCP/DCPA in which addition of phosphoric acid caused in an increase in percent of conversion and diametral tensile strength. Rounded spheres formed with HAp cluster were observed in the paste prepared from seeded α-TCP in which unexpected decrease in strength was caused by seeding nevertheless the increase in percent of conversion. Thus, the strength of a paste is affected largely by the microstructure rather than degree of conversion into HAp.

Under the hydrothermal condition, the shapes of HAp crystals were completely different from those produced under the normal condition. Regardless of the complete

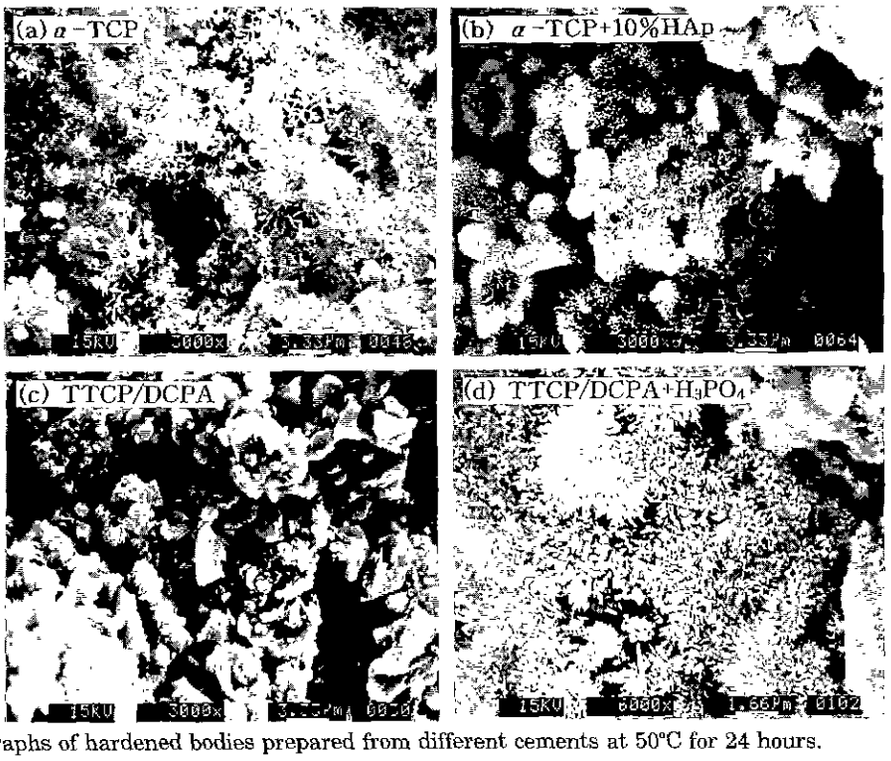


Fig. 5. SEM micrographs of hardened bodies prepared from different cements at 50°C for 24 hours.

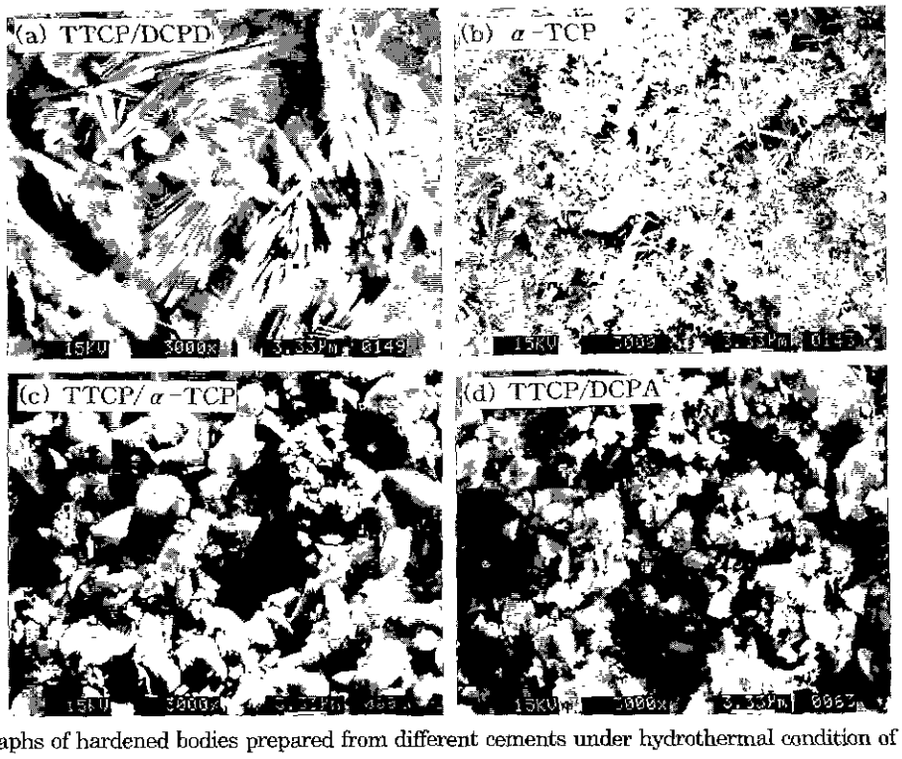


Fig. 6. SEM micrographs of hardened bodies prepared from different cements under hydrothermal condition of 200°C for 9 hours.

conversion into HAp, there was no tendency of appearance or interlocking of fiber-like or plate-like phase in the paste prepared from TTCP/DCPA and TTCP/α-TCP. Instead of that, new types of HAp were found in the pastes prepared from TTCP/DCPD and α-TCP. In later case, in which the maximum diametral tensile strength was obtained, especially, fibrous HAp formed a well-interlocked, dense and homogeneous microtexture.

IV. Conclusions

Hardening properties of pastes prepared from various

calcium phosphates under the normal and hydrothermal conditions were studied with the effects of addition of seed and phosphoric acid. Results obtained are as follows;

Hydration product of the cements was hydroxyapatite and degree of conversion of cement mineral into hydroxyapatite was largely affected by elevated temperature, hydrothermal treatment, seeding and addition of phosphoric acid. Mechanical strength of a hardened paste was developed by interlocking of microcrystals of hydroxyapatite formed during hydration and largely affected by the morphology of microstructure rather than degree of conversion. The highest diametral tensile strength of plain cement was obtained in the paste hardened under hydrothermal condition, in which long fiber-shaped hydroxyapate formed a well-interlocked, dense and homogeneous microtexture.

Acknowledgment

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