Effect of heat treatment on setting behavior and compressive strength of tetracalcium phosphate cement

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Due to its superior biocompatibility and osteoconductivity, calcium phosphate cement (CPC) has been suggested for use as a filling material for dental and orthopedic applications [1–4]. The primary reaction product of most CPCs, after being implanted for a while, is various kinds of apatite [5], which is the main inorganic component of human bones and teeth [6, 7].

Tetracalcium phosphate (TTCP), a member of the calcium phosphate family, is known to have a high chemical activity and reacts with aqueous solution at room temperature [8]. The obtained hardened material has a high affinity for the living body and is therefore frequently used as a constituent in CPC powder [9–11].

Despite many advantages, there are problems for CPC during practical application, including working/setting time being too short or too long and dispersion upon early contact with blood or aqueous media. Appropriate working/setting times are critical for surgical applications. In the laboratory, a monolithic TTCP powder with nano-sized whiskers grown on surface was recently developed [12], which demonstrated excellent mechanical properties and biological responses with a relatively short working/setting time. The present work provides a simple heat treatment method for prolonging the working/setting time, while maintaining the strength, of the TTCP cement.

The TTCP powder used for the study was fabricated in-house from the reaction of dicalcium pyrophosphate ($Ca_2P_2O_7$) (Sigma Chem. Co., St. Louis, MO, USA) and calcium carbonate ($CaCO_3$) (Katayama Chem. Co., Tokyo, Japan) by a weight ratio of 1:1.27. The powders were mixed uniformly in ethanol for 12 hr, followed by heating in an oven to let the powders dry. The dried powder mixture was then heated to 1400 °C and allowed to react and form TTCP [13]. Since a "whisker treatment" [12] has been very effective in enhancing the properties of TTCP cement, the same treatment was used to treat the TTCP powder for the present study.

The whisker-treated TTCP powder was heat-treated in an air furnace (N 7/H, Nabertherm®, Germany). Different heat-treatment temperatures (140–400 °C) and times (30 and 120 min) were used for the study. To form a CPC paste, the TTCP powder was mixed with a diammonium hydrogenphosphate ($(NH_4)_2HPO_4$) hardening solution with a pH value of 8.6 and liquid/powder ratio of 0.3 ml/g. After mixing for 1 min, the cement paste was uniformly packed in a stainless steel mold which has an opening of 6 mm diameter and 12 mm depth (ASTM F 451-99a) for the preparation of samples for compressive strength testing. After mixing for 15 min, the CPC samples were removed from the mode and immersed in 20 ml Hanks' physiological solution [14] at 37 °C. Since short-term (typically within 20–30 min after implantation) and long-term strengths are both important for CPC, the compressive strengths of CPC immersed for 20 min, 1 day and 7 days were measured.

The working time of the CPC was determined as the duration for which the paste was no longer moldable, while setting time was measured according to ISO 1566 standard method. The compressive strength was measured using a desktop mechanical tester (Shimadzu AGS-500D, Tokyo, Japan) at a crosshead speed of 1.0 mm/min.

X-ray diffraction (XRD) was carried out to identify the phase changes of CPC during immersion using a Rigaku D-MAX B X-ray diffractometer (Tokyo, Japan) with Ni-filtered CuKα radiation operated at 30 kV and 20 mA at a scanning speed of 0.25°/min. A Fourier transform infrared spectroscopy (FTIR) system (Jasco, FT/IR-460 Plus, USA) in transmission absorption mode with a spectral resolution of 2 cm^{-1} was used to characterize the various functional groups of the TTCP powder under various heat-treatment conditions.

One major result of this study was that the working/setting time of the present monolithic TTCP-derived CPC could be significantly changed by applying a simple heat treatment to TTCP powder. As can be seen from Table I, all the investigated heat treatment conditions caused the working/setting time to become longer than those without the heat treatment. For example, when the TTCP powder was heat-treated at 300 °C or lower, the working and setting times of the CPC increased by 50–75% and 60–80%, respectively. When the TTCP powder was heat-treated to 400 °C for 30 min, the working/setting time largely increased to a surgically inconvenient level. When the TTCP powder was heat-treated to 400 °C for 120 min, the cement paste was hardly set.

The compressive strength of the TTCP cement could also be modified by heat-treating the TTCP powder. As indicated in Table II, when the TTCP powder was heat-treated at 140 °C for 30 min, the compressive strengths

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0022–2461

TABLE I Working and setting times of non-heat-treated and heat-treated TTCP cement

	Working time (min)	Setting time (min)
Non-heat-treated	8.0 ± 1.2	9.5 ± 1.3
140°C, 30 min	12.0 ± 0.8	15.8 ± 0.8
120 min	12.3 ± 0.4	15.3 ± 0.5
200°C, 30 min	12.5 ± 0.4	15.8 ± 0.2
120 min	13.3 ± 0.1	16.0 ± 0.1
250°C, 30 min	12.0 ± 0.2	14.3 ± 0.2
120 min	12.0 ± 0.3	14.0 ± 0.5
300°C, 30 min	12.0 ± 0.5	15.0 ± 0.5
120 min	13.8 ± 0.4	17.3 ± 0.4
400°C, 30 min	16.5 ± 0.1	23.0 ± 0.2
120 min	45.0 ± 3.4	[a]

[a] cement is hardly set.

TABLE II Compressive strengths of non-heat-treated and heat-treated TTCP cement

	Compressive strength (MPa)		
	20 min	1 day	7 days
Non-heat-treated	49.2 ± 6.3	90.3 ± 8.1	70.5 ± 8.0
140°C, 30 min	17.5 ± 2.6	86.5 ± 8.3	38.8 ± 0.9
120 min	18.0 ± 3.0	72.6 ± 14.6	69.6 ± 9.9
200°C, 30 min	44.9 ± 5.4	85.2 ± 13.3	85.1 ± 12.3
120 min	65.9 ± 9.4	96.0 ± 7.2	80.1 ± 14.4
250°C, 30 min	41.7 ± 4.3	66.7 ± 6.2	86.5 ± 13.7
120 min	42.8 ± 5.0	88.6 ± 7.4	58.5 ± 9.1
300°C, 30 min	29.7 ± 3.9	91.1 ± 16.1	80.4 ± 10.6
120 min	25.6 ± 2.6	52.3 ± 10.7	54.3 ± 2.4
400°C, 30 min	16.1 ± 0.9	28.5 ± 1.7	36.2 ± 3.5

of CPC immersed in Hanks' solution for 20 min and 7 days both largely decreased, although its 1 day-strength did not change much. When TTCP powder was heat-treated at 200 °C for 30 min, both 20 min and 7 days-compressive strengths significantly increased.

When the powder was treated at 200 °C for 120 min, the 20 min and 1 day-compressive strengths further increased to 65.9 and 96.0 MPa (the highest 1 day-strength), respectively. Its 7 days-strength, however, declined to 80.1 MPa. When the powder was treated at 250 °C for 30 min the compressive strength of the CPC continued to increase even after immersion for 7 days. While the heat-treatment at 300 °C for 30 min still showed relatively high 1 day and 7 days-strengths, the heat treatment at 300 °C for 120 min or at 400 °C caused the compressive strength of the CPC to largely decline. From a practical point of view, among all heat treatment conditions investigated in this study, the heat treatment at about 200–300 °C for about 30–120 min appears to be a suitable range for prolonging the working/setting time, while maintaining (in some cases even increasing) the compressive strength of the TTCP cement.

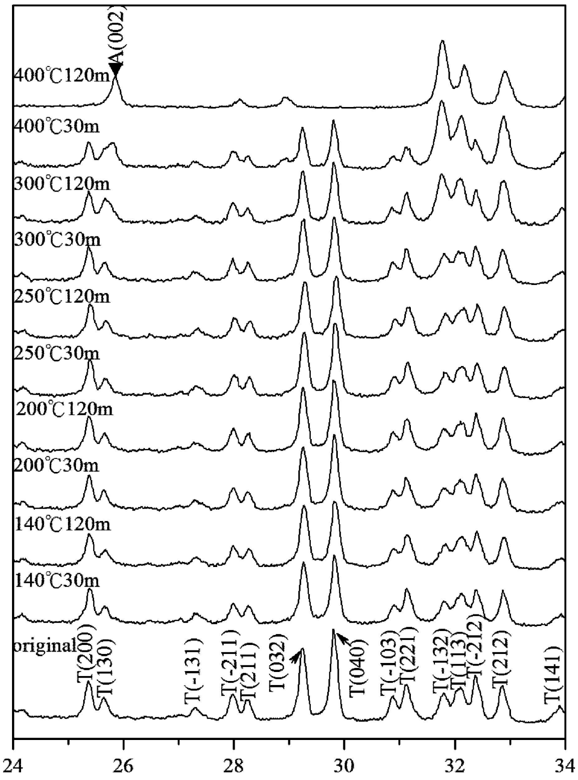

Figure 1 XRD patterns of non-heat-treated and heat-treated TTCP powder (A: apatite; T: TTCP).

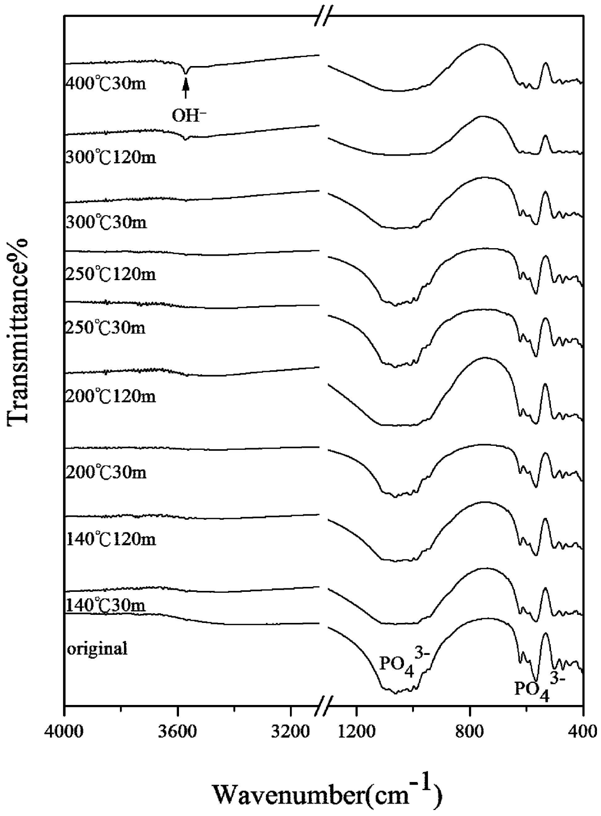

Figure 2 FTIR spectra of non-heat-treated and heat-treated TTCP powder.

To further understand the heat-treatment effect, XRD was performed on all heat-treated TTCP powders and their derived CPC immersed in 37 °C Hanks' solution for 20 min, 1 day and 7 days. The XRD pattern of non-heat-treated TTCP powder showed a typical TTCP crystal structure (Fig. 1). Except the conditions of 300 °C/120 min and 400 °C, the XRD patterns of all heat-treated TTCP powders remained essentially the same as that of non-heat-treated powder. When the TTCP powder was heated to 300 °C for 120 min or to 400 °C for 30 min, apatite peaks were observed, indicating that a phase transition from TTCP to apatite

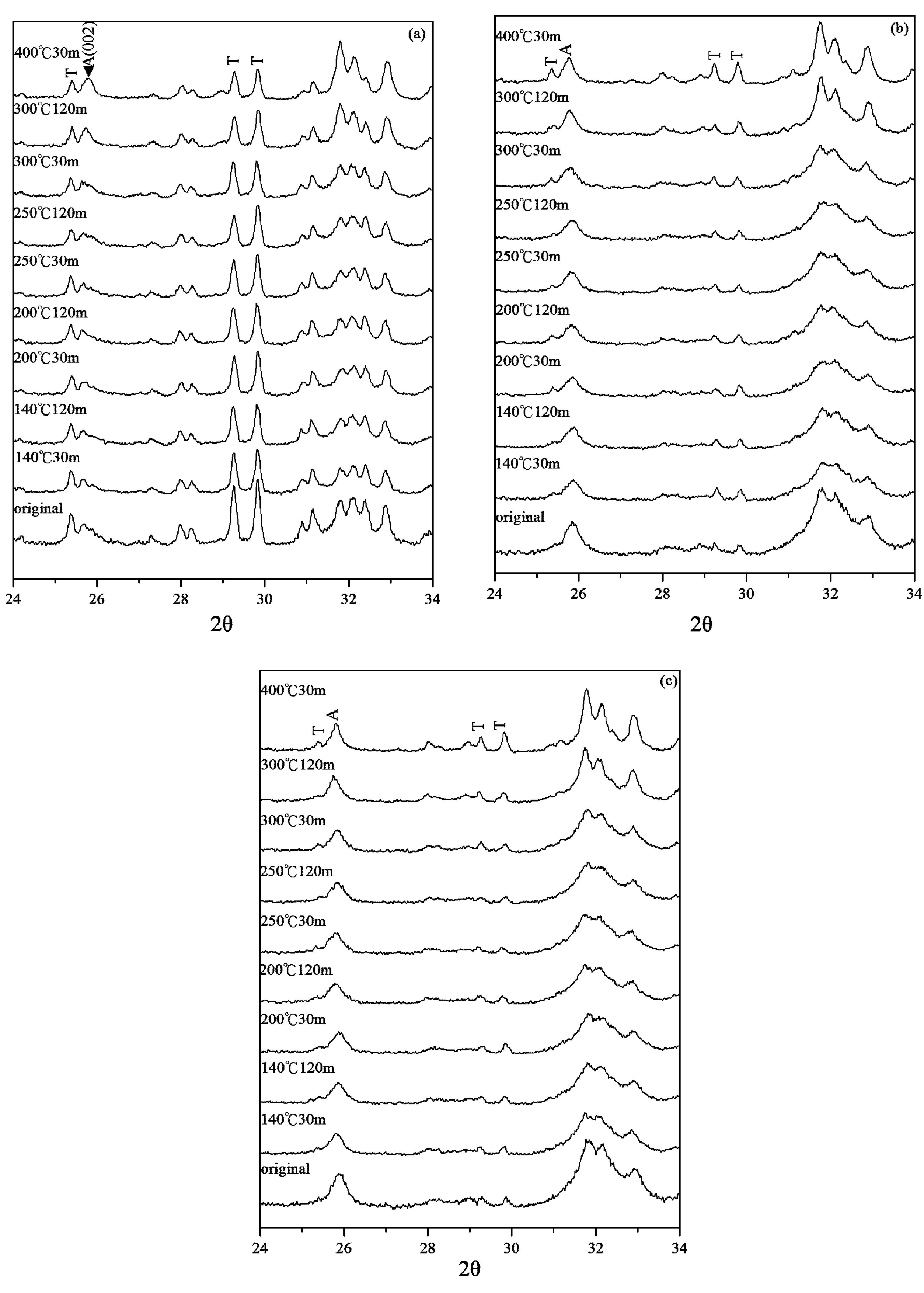

Figure 3 XRD patterns of non-heat-treated and heat-treated TTCP cement immersed in Hanks' solution for 20 min (a), 1 day (b) and 7 days (c).

had occurred. An example for the identification of the apatite phase can be seen from the apatite (002) peak sitting on the right "shoulder" of TTCP (130) peak [15]. The change in the preferred orientation between 31.5 and 32.6°C under such heat-treatment conditions is also believed to result from the formation of apatite, which usually displays a broad peak in this angular regime. When the powder was treated to 400 °C for 120 min, apatite emerged as the dominant phase. Since the primary focus of this study was on the properties of TTCP cement, any heat treatment condition beyond 400 °C/30 min was not pursued in this study.

The formation of apatite under these heat treatment conditions was reconfirmed by the presence of OH band at 3570 cm^{-1} in FTIR spectra (Fig. 2). This OH band has been identified by Doi *et al.* [16] and Fernández-Pardas *et al.* [17]. The fact that the large increases in working/setting time occurred under the same heat treatment conditions suggests that these increases in working/setting time are closely related to the TTCP-apatite phase transition.

The XRD patterns of CPC samples immersed in Hanks' solution for 20 min are similar to those of TTCP powders, except that apatite peaks can be seen from CPC samples under all heat treatment conditions (Fig. 3a). Again, the largest apatite peaks are observed in CPC samples being heat-treated at 400 °C. When immersed for 1 day, the apatite phase became dominant in the CPC samples derived from non-heat-treated or lower temperature-treated TTCP powders. In those higher temperature-treated CPC samples TTCP phase still dominated (Fig. 3b). The XRD patterns of 7-day-immersed samples show a similar trend (Fig. 3c). These XRD results indicate that heat treatment of the TTCP powder at higher temperatures enhanced the initial formation of apatite, but somehow slowed down the further formation of apatite during the immersion of CPC in Hanks' solution. It is speculated that the initial formation of apatite covering the surface of TTCP powder during heat treatment at higher temperatures caused the powder to become less reactive that, in turn, slowed down the further formation of apatite during immersion. Furthermore, the comparison between the XRD results and compressive strength data (Table II) indicates that the compressive strength of CPC is closely related to the relative amount of apatite formed in the CPC. The immersed CPC derived from the highest temperature (400 °C-treated powder had the smallest amount of apatite and the lowest compressive strength. On the other hand, those CPC samples having larger amounts of apatite also had higher compressive strengths.

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Received 4 August
and accepted 27 October 2004