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Preparation and compressive strength of α-tricalcium phosphate based cement dispersed with ceramic particles

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Abstract

The preparation and strength of an α-tricalcium phosphate (α-$Ca_3(PO_4)_2$) cement with and without dispersed particles of polycrystalline 3 mol% Y_2O_3 doped tetragonal zirconia (3Y–TZP), polycrystalline alumina (Al_2O_3), and amorphous silica (SiO_2) were investigated. α-Tricalcium phosphate transformed completely to calcium deficient hydroxyapatite ($Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$) after curing in simulated body fluid at 37 °C for 120 h. The compressive strength of a cement without dispersed particles cured at 37 °C for 168 h was 42 MPa but increased to 48, 64, and 67 MPa by dispersing 7.5 wt.% of Al_2O_3, 3Y–TZP, and SiO_2 particles, respectively. The improvement of compressive strength seemed to depend on the affinity of the cement matrix and dispersed particles.

Keywords: B. Composites; C. Mechanical properties; D. Apatite; E. Biomedical applications; E. Structural

1. Introduction

A significant number of biomedical materials for the repair or augmenting of bone and teeth, have been developed [1–3]. Calcium phosphate cement is a self-setting material which can be prepared at body temperature and can be moulded during surgery. It reacts with water to transform mainly into hydroxyapatite, which is easily accepted by living tissue on implantation [4,5–15]. It can be used both as an injectable material in complicated bone defects and as a fixation between ceramics and natural bone tissue for surgical implantation. The first calcium phosphate dental cement was prepared with calcium oxide powder and orthophosphoric acid solution by Ostermann in 1832 [5]. Brown and Chow developed a calcium phosphate cement that consists of a mixture of dicalcium phosphate dihydrate and tetracalcium phosphate with water or a diluted orthophosphate solution [4,6]. Since that time various types of such cements which consist of α-tricalcium phosphate [7], α-tricalcium phosphate/dicalcium phosphate dihydrate [8], and monocalcium phosphate/tetracalcium phosphate[9], have been developed. The mechanical properties of cement are important in healing, however, the fracture strength of self-setting calcium phosphate cement is generally modest. Therefore, research has focused on improving its mechanical properties [14,15].

It is well known that microstructural modification by introducing the use of fibers and/or particles with high fracture strength results in improved mechanical properties [16]. Zirconia, alumina and silica particles are candidate materials to improve the mechanical properties of calcium phosphate cement since they possess excellent mechanical properties and are harmless to a living body [17,18]. In a previous paper [19] it was reported that compressive strength of calcium phosphate based cement could be improved by dispersing polycrystalline ceria doped tetragonal zirconia. On continuation of our studies on improving mechanical properties of biocompatible cement, a series of tests was performed to evaluate the mechanical properties of α-tricalcium phosphate cement containing dispersed particles of polycrystalline 3Y–TZP, polycrystalline Al_2O_3, and amorphous SiO_2.

2. Experimental procedure

α-Tricalcium phosphate powders (α-$Ca_3(PO_4)_2$, Taihei Chemical Industrial Co.) were used after ball-milling for 30 min using a planetary ball mill (P-7, Fritze Co.) to attain the specific surface area and average particle

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size of 3.8 $m^2 g^{-1}$ and 7 μm, respectively. Polycrystalline 3 mol% yttria-doped zirconia was prepared by sieving TOSOH Zirconia B53 to 45–63 μm using stainless steel meshes. Polycrystalline alumina was prepared by calcining Sumitomo Chemical Alumina, AKP-15 at 1600 °C for 1 h followed by ball-milling and sieving to 45–63 μm. Amorphous silica particles were prepared by ball-milling of Wako Amorphous Silica using a planetary ball mill followed by sieving to −26, 26–45 45–63, and 75–150 μm. These powders were designated as 3Y–TZP, Al_2O_3, and SiO_2, respectively. The scanning electron micrographs of 3Y–TZP and SiO_2 particles sieved to 45–63 μm are shown in Fig. 1. The polycrystalline 3Y–TZP consisted of dense, spherical, agglomerated particles with an average diameter of 50 μm, whereas SiO_2 particles consisted of random form particles.

The requisite amounts of 3Y–TZP, Al_2O_3, and SiO_2 were mixed with α-tricalcium phosphate powder in an alumina mortar. Cement paste was prepared by mixing with deionized water at a liquid/powder (L/P) ratio of 0.28 ml g^{-1}. The cement pastes were poured into stainless steel moulds 6 mm in diameter and 12 mm in height and held in saturated water vapor atmosphere at 37 °C for 12 h. After that the samples were stored in simulated body fluid (SBF) with ion concentrations [20] (Na^+ 142.0, K^+ 5.0, Mg^{2+} 1.5, Ca^{2+} 2.5, Cl^- 147.8, HCO_3^- 4.2, HPO_4^{2-} 1.0 and SO_4^{2-} 0.5 mM) and pH 7.4 nearly equal to those of human blood plasma at 37 °C. The compressive strength was determined using a universal testing machine (AG-2000G, Shimadzu Autograph, Shimadzu Co. Ltd.) at a cross-head speed of 0.5 mm min^{-1}. The average of six determinations was taken and the scatter indicated by error bar. The crystalline phase constitution of the reaction products was identified by X-ray diffraction analysis using graphite monochromatised CuK_α radiation. The microstructure was observed with a scanning electron microscope (S-430, Hitachi Co.). The concentrations of calcium and phosphate ions in the product and curing solution were determined by inductively coupled plasma-atomic emission spectroscopy (Optima3300, Perkin Elmer Co.).

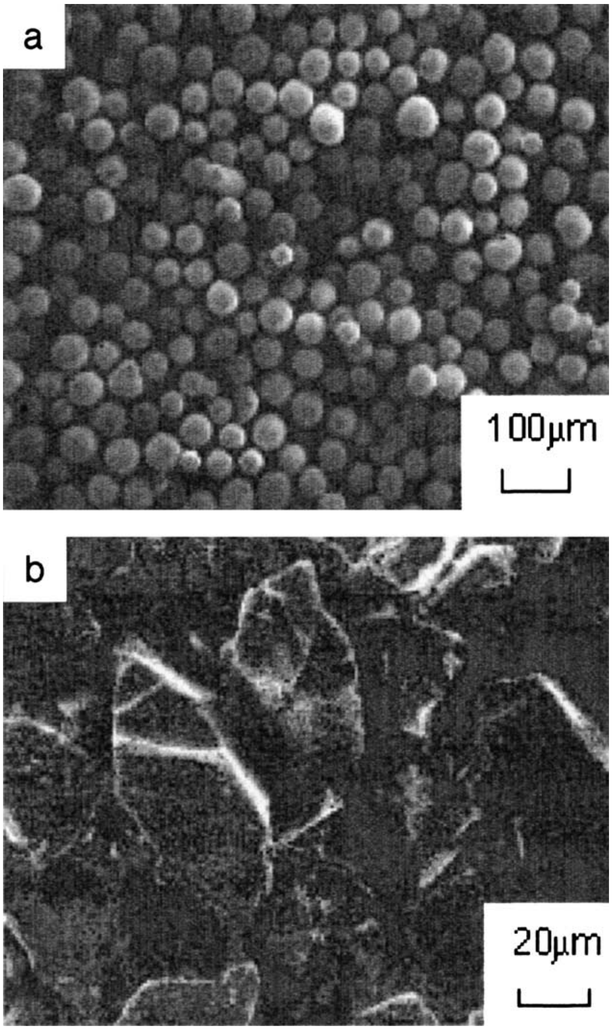

Fig. 1. Scanning electron micrgraphs of (a) polycrystalline 3Y–TZP and (b) amorphous SiO_2 particles sieved to 45–63 μm.

3. Results and discussion

The XRD patterns of the α-tricalcium phosphate (α-TCP) cement soaked in SBF solution at 37 °C for (a) 0, (b) 10, (c) 24, (d) 96, and (e) 120 h are shown in Fig. 2. Although a great portion of the powder before curing was made of α-tricalcium phosphate (α-TCP), a small amount of β-tricalcium phosphate (β-TCP) was contained. The XRD peaks corresponding to α-tricalcium phosphate decreased with time and hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$ appeared after 10 h. After 120 h curing XRD peaks of α-tricalcium phosphate completely disappeared, while the peak strength of β-tricalcium phosphate did not change. Fernandez et al. [12] reported that the calcium deficient hydroxyapatite, $Ca_9(HPO_4)(PO_4)_5OH$ was formed by curing α-tricalcium phosphate cement in water as shown by Eq. (1).

$$3Ca_3(PO_4)_2 + H_2O \rightarrow Ca_9(HPO_4)(PO_4)_5OH \qquad (1)$$

The lattice constants of hydroxyapatite formed after 168 h curing are shown in Table 1 together with those of stoichiometric hydroxyapatite. The product showed longer lattice constant *a* and shorter lattice constant *c* than those of stoichiometric hydroxyapatite, indicating the formation of calcium deficient hydroxyapatite.

The Ca/P atomic ratio of cement product and the concentrations of calcium ion and phosphate ion in the curing SBF solution are shown in Fig. 3 as a function of time. The Ca/P atomic ratio increased from 1.50 to 1.54 after 167 h curing, while both calcium ion and phosphate ion concentrations decreased with time. These results suggested that both calcium ion and phosphate ion in SBF solution were absorbed

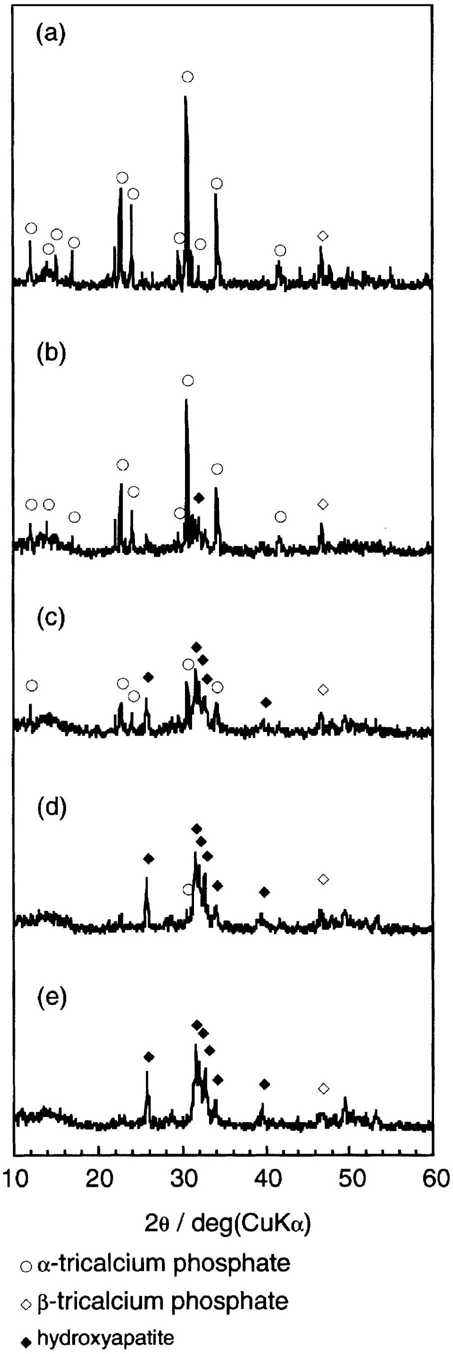

Fig. 2. X-ray diffraction patterns of α-tricalcium phosphate cements soaked in SBF solutions for (a) 0, (b), 10, (c) 24, (d) 96, and (e) 120 h at 37 °C.

with cement during curing. It is seen that the absorbed amount of calcium ion was ca. twice as larger as that of phosphate ion. Therefore, the curing product may contain higher amount of calcium ion than $Ca_9(HPO_4)(PO_4)_5OH$ and therefore, can be described as $Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$ $(0<x<1)$.

Time dependence of compressive strength and density of α-tricalcium phosphate cements with and without dispersed 7.5 wt.% 3Y–TZP particles is shown in Fig. 4. The compressive strength of the cement without additive increased up to 50 MPa after 50 h curing and then decreased to 42 MPa after 168 h curing. The density of the cement without additive also showed similar profile. The decrease in the density may be due to the dissolution-reprecipitation mechanism of the cement setting, i.e., α-tricalcium phosphate remained inside of the cement matrix dissolved into the curing solution and precipitated as calcium deficient hydroxyapatite on the surface of the cement. On the other hand, the compressive strength of the cement dispersed with 3Y–TZP particles increased up to 68 MPa after 50 h curing and then was almost constant although the density decreased as a similar manner of the cement without additive. It is clear that dispersion of 3Y–TZP particles is effective to improve the compressive strength of α-tricalcium phosphate cement.

Compressive strengths of α-tricalcium phosphate cements dispersed with various amounts of 3Y–TZP after 168 h curing are shown in Fig. 5. The compressive

Table 1
Lattice constants of cured product after 168 h at 37 °C

Sample	*a* (nm)	*c* (nm)
Product	0.9449	0.6804
$Ca_{10}(PO_4)_6(OH)_2$[a]	0.9418	0.6884

[a] JCPDS N. 9-432.

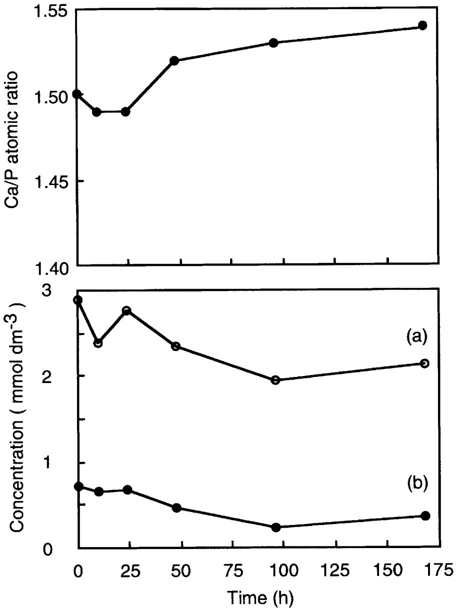

Fig. 3. Time dependence of Ca/P atomic ratio of cement product soaked in SBF solution at 37 °C, and the concentrations of (a) calcium ion and (b) phosphate ion in SBF solution.

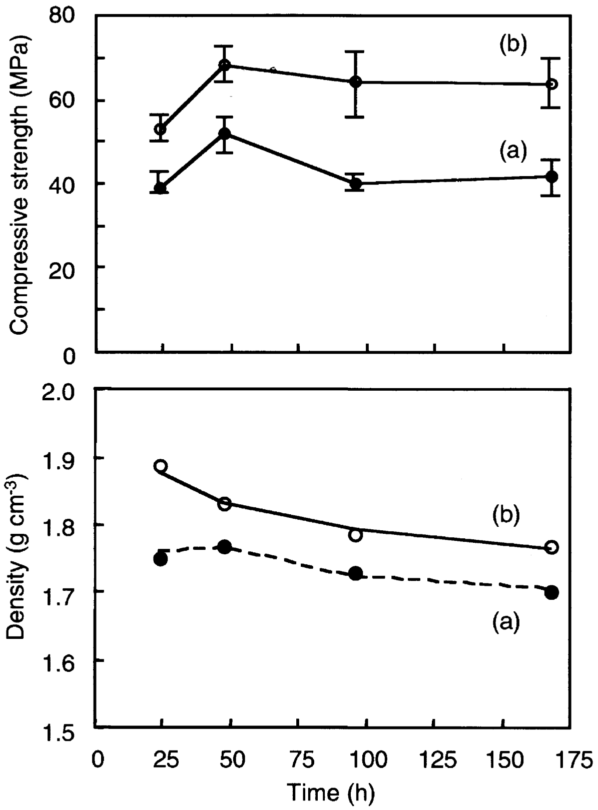

Fig. 4. Time dependence of compressive strength and density of α-tricalcium phosphate cement (a) without additive and (b) dispersed with 7.5 wt.% 3Y–TZP particles.

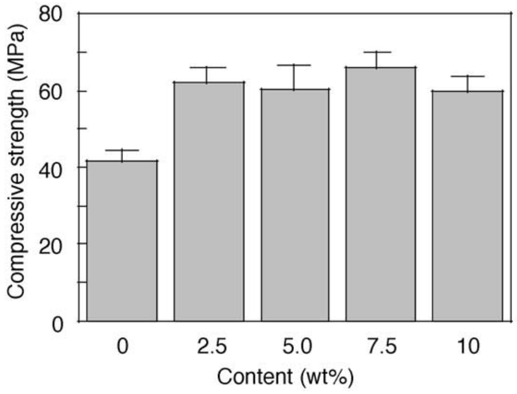

Fig. 5. Compressive strengths of α-tricalcium phosphate cements dispersed with various amounts of 3Y–TZP particles after 168 h curing.

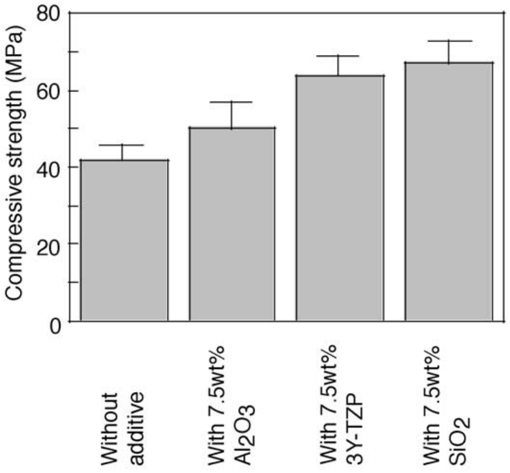

Fig. 6. Compressive strengths of α-tricalcium phosphate cements dispersed with 7.5 wt.% of 3Y–TZP, Al_2O_3, and SiO_2 particles after 168 h curing.

strength increased from 42 to 62 MPa by dispersing with 2.5 wt.% 3Y–TZP particles and then was almost constant up to 10 wt.% 3Y–TZP particles.

Compressive strengths of α-tricalcium cements dispersed with 7.5 wt.% of 3Y–TZP, Al_2O_3, and SiO_2 particles after 168 h curing are shown in Fig. 6. It is seen that dispersion of 3Y–TZP, Al_2O_3, and SiO_2 particles all were effective to improve the compressive strength and the improving effect was in the order $SiO_2 > 3Y$–$TZP > Al_2O_3$. These results suggested that the improvement of the compressive strength was not caused by the transformation toughening of TZP, but the affinity between the hydroxyapatite and dispersed particles probably played an important role in improving the compressive strength.

Scanning electron micrographs of the fracture surfaces of α-tricalcium phosphate cement dispersed with 7.5 wt.% of 3Y–TZP, Al_2O_3, and SiO_2 particles after 168 h curing are shown in Fig. 7. It is seen that the cement matrix clearly separated from Al_2O_3 particle, but partly remained on the surface of 3Y–TZP and SiO_2, indicating the affinity of cement matrix and 3Y–TZP and SiO_2 particles was higher than that of cement matrix and Al_2O_3 particles. It was reported that Zr–OH and Si–OH formed by the reaction of zirconia and silica with water promptly combined with Ca^{2+} and promoted the formation of hydroxyapatite [21]. Such characterisitics of zirconia and silica may play important role to construct strong binding of cement matrix and dispersed 3Y–TZP and SiO_2 particles, and consequently to improve the compressive strength of the cement.

Compressive strengths of α-tricalcium phosphate cement dispersed with 7.5 wt.% of SiO_2 particles of various particle sizes after 168 h curing are shown in Fig. 8. The compressive strength increased at first with increasing particle size up to 45–63 μm and then decreased. These results suggested that although the strengthening effect such as crack pinning, crack deflection, etc. increased with increasing dispersed particle size, the flaw size in the cement also increased with increasing dispersed particles size. Consequently, the particle size of 45–63 μm was optimum to improve the compressive strength of α-tricalcium phosphate cement.

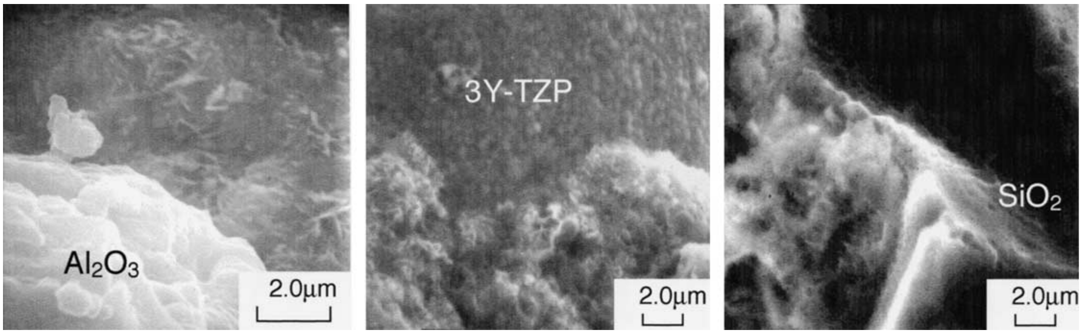

Fig. 7. Scanning electron micrographs of the fracture surfaces of α-tricalcium phosphate cement dispersed with 7.5 wt.% of 3Y–TZP, Al_2O_3, and SiO_2 particles soaked after 168 h curing.

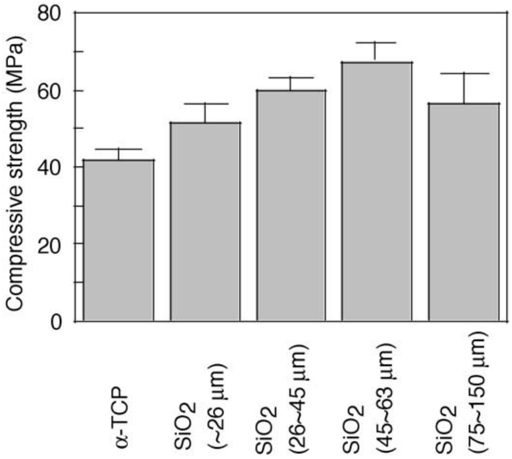

Fig. 8. Compressive strengths of α-tricalcium phosphate cement dispersed with 7.5 wt.% of SiO_2 particles of various particle sizes after 168 h curing.

4. Conclusions

α-Tricalcium phosphate (α-$Ca_3(PO_4)_2$) cement with a liquid/powder (L/P) ratio of 0.28 cm^3g^{-1} was completely transformed into hydroxyapatite in 120 h at 37 °C after mixing with water. Dispersion of 3Y–TZP, Al_2O_3, and SiO_2 particles were effective to improve the compressive strength and the improving effect was in the order $SiO_2 > 3Y\text{–}TZP > Al_2O_3$. The improvement of the compressive strength was not caused by the transformation toughening of TZP, but the affinity between the cement matrix and dispersed particles probably played an important role to improve the compressive strength.

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