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Development of calcium phosphate cement

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Abstract

Calcium phosphate cements were prepared by mixing α-type calcium phosphate, aqueous solutions of polyvinyl alcohol and citric acid, and silicate sand. Higher concentration of polyvinyl alcohol and citric acid gave a cured body having higher mechanical strength and 50% aqueous solutions of polyvinyl alcohol and citric acid were the highest concentration to be available in this hardening process. Polyvinyl alcohol gave better mechanical strength to a hard body than citric acid. Smaller particle size of silicate sand gave stronger mechanical strength to a cured body. The highest mechanical strength of a cured body was obtained when the mixing weight ratio of α-type calcium phosphate to silicate sand was1–0.5. The calcium phosphate cement showed very good adhesion strength for cement plates with an analogous component.

Keywords: Preparation; Composites; Mechanical properties

1. Introduction

In our working group, development of calcium phosphate cements were progressed.[1] α-Type tricalcium phosphate (α-TCP), tetracalcium phosphate (TeCP) and amorphous calcium phosphate were used as source materials of calcium phosphates. Citric acid, polyacrylic acid (PAA), polyvinyl alcohol (PVA) and some organic acids were used as stimulators of calcium phosphate cements. Hard bodies of calcium phosphate cements were prepared under many experimental conditions and mechanical strength of them was examined. The highest compressive strength of 120 MPa was obtained for a cured body made from α-TCP–PAA system and the highest compressive strength of 60 MPa was obtained for a hard body prepared from TeCP–PVA system. These values are very good mechanical strength in comparison with that of cements which are using now in orthopedic and dental fields. The calcium phosphate cements are a kind of polymer cement which is made by mixing inorganic cements and organic polymers. Organic polymers are added to compensate weak points of inorganic cements. It is generally accepted that the appearance of mechanical strength concerned with cured bodies of polymer cements is associated with the following three terms[2–4]:

(1) Formation of a cement hydrate.
(2) Formation of a matrix phase between cement hydrates and organic polymers.
(3) Chemical bond between cement hydrates and organic polymers.

In the case of calcium phosphate cement, the hydrate is hydroxyapatite (HAP). Calcium phosphate cement which is cured by only water does not have enough mechanical strength because unreacted water releases from the cement and this produces holes inside the cement.[1,5] It is useful to improve mechanical strength of the calcium phosphate cements by mixing organic polymers into the cements and forming a matrix phase between cement hydrates and organic polymer films.

By the way, calcium phosphate materials are expensive source materials and it is not beneficial in cost performance to use in fields other than biomaterials. Accordingly, to expand the application of calcium phosphate cements, it is necessary to make composite cement with a low cost resource-material. In this experiment, silicate sand was used for making a calcium-phosphate-composite cement with a low cost, and the effect of silicate sand on mechanical strength of the composite cement is discussed in this paper.

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2. Experimental procedure

α-TCP was made by heating an equimolar mixture of γ-type calcium diphosphate and calcium carbonate at 1250 °C for 2 h.[6] Silicate sand having average particle size of 3–140 μm was used as composite material. Polyvinyl alcohol and citric acid solutions were adopted as a hardening stimulator. Hard bodies were prepared by mixing α-TCP and silicate sand with various weight ratios and then adding a stimulator into the mixture. The effects of particle size of silicate sand, concentration of a stimulator and mixing weight ratio (*P*/*L*) of a powder sample to a stimulator on mechanical strength of a hard body were examined. Hydrogen ion exponent (pH) of a stimulator was adjusted by adding 1N sodium hydroxide to PVA solutions and sodium hydroxide powder to citric acid solutions. When a PVA solution was used as a stimulator, the cement paste was heated at 80 °C in an air bath for 24 h. While a citric acid solution was used as a stimulator, curing was done at room temperature (15–25 °C) for several minutes to 1 h. The X-ray diffractometric (XRD) technique was used for identification of chemicals contained in a prepared hard body. The SEM observation was adopted to analyze surface of a cured body. To test mechanical strength of a hard body, compressive strength and adhesion test of the calcium phosphate cement were examined. Adhesion force of the calcium phosphate cements to cement plates having the same component was measured according to the Japanese Industrial Standard (JIS) method.

3. Results and discussion

3.1. Hardening with PVA

According to preparatory experiment, pH 10 of polyvinyl alcohol solutions, hardening temperature of 80 °C, hardening time of 24 h and *P*/*L* ratio of 2.0 were adopted to cure calcium-phosphate-cement pastes, because the experimental condition was appropriate for hardening of the cement pastes of this system.

Dependence of compressive strength on the concentration of a PVA solution is shown in Table 1. Mixing ratio of silicate sand to α-TCP was 10% in this treatment. According to the result, regardless of the particle size of silicate sand, compressive strength of the hard body increased with increasing concentration of the PVA solution and bulk density of the cured body also increases with increasing PVA concentration. Fluidity of the PVA solution decreased with increasing concentration and workability of the cement paste decreased with increasing concentration of the PVA solution. It was difficult to prepare cement pastes with a PVA solution having a higher concentration than 50%.

XRD diagrams of the cured bodies made with the 50% PVA solution are shown in Fig. 1. The diagrams show that HAP is formed in the cured bodies and the formation of HAP causes mechanical strength of the hard bodies. The formation of HAP can be progressed by hydration reaction of α-TCP.

Table 1
Dependence of compressive strength on concentration of PVA solution[a]

Concentration (%)	Sand (μm)	Bulk density (g/cm3)	Compressive strength (MPa)
5	140	1.20	0.4
	27	1.22	0.9
	3	1.23	1.7
10	140	1.25	2.3
	27	1.28	2.5
	3	1.29	2.7
20	140	1.28	6.1
	27	1.28	4.8
	3	1.30	7.6
30	140	1.30	7.8
	27	1.34	11.4
	3	1.39	12.6
40	140	1.33	7.9
	27	1.36	17.4
	3	1.40	22.0
50	140	1.40	9.6
	27	1.41	25.3
	3	1.45	31.1

[a] Addition ratio of silicate sand to α-TCP = 10%.

The effect of particle size of silicate sand on mechanical strength is also shown in Table 1. Compressive strength of the cured bodies increased with decreasing particle size of silicate sand and the highest mechanical strength of the cured bodies was obtained when silicate sand with the smallest particle size was used in every PVA concentration. The highest compressive strength of the cured bodies was 31.1 MPa when an addition amount of silicate sand to α-TCP was 10% and

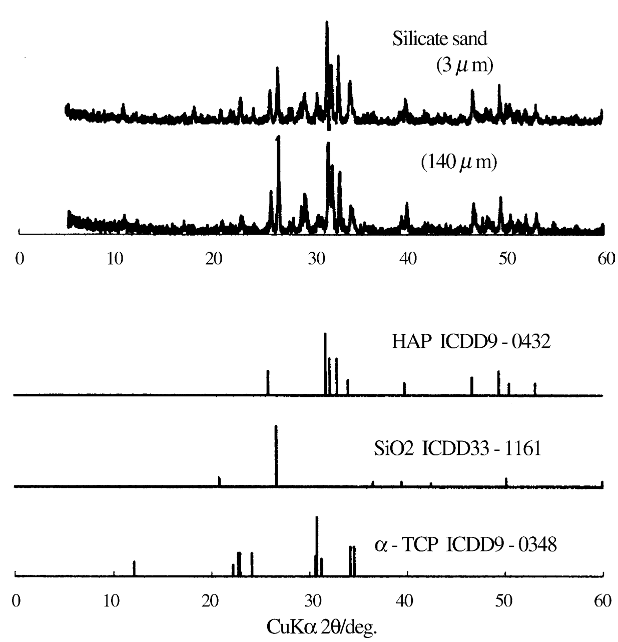

Fig. 1. XRD diagrams of hard bodies made with PVA solution.

Table 2
Dependence of compressive strength on addition amount of silicate sand

Sand (%)[a]	Concentration of PVA (%)	Bulk density (g/cm^3)	Compressive strength (MPa)
10	5	1.23	1.7
	10	1.28	2.7
	30	1.39	12.6
	50	1.45	31.1
20	5	1.25	4.2
	10	1.26	7.2
	30	1.30	17.4
	50	1.29	35.5
30	5	1.26	8.6
	10	1.28	14.6
	30	1.35	19.7
	50	1.36	38.1
40	5	1.27	10.6
	10	1.27	18.3
	30	1.39	23.3
	50	1.46	47.9
50	5	1.30	15.2
	10	1.31	25.5
	30	1.44	26.3
	50	1.50	49.4

[a] Average particle size of silicate sand was 3 μm.

Table 3
Dependence of compressive strength on concentration and pH of citric acid solution[a]

Concentration of citric acid (%)	pH of citric acid solution	Bulk density (g/cm^3)	Compressive strength (MPa)
10	2	1.21	5.7
	3	1.23	8.1
	4	1.26	13.3
20	2	1.23	10.1
	3	1.28	12.1
	4	1.36	18.5
30	2	1.25	13.1
	3	1.29	15.8
	4	1.38	16.2
40	2	1.26	14.6
	3	1.29	15.8
	4	1.38	17.4
50	2	1.30	14.5
	3	1.38	16.0
	4	1.43	17.8

[a] Average particle size of silicate sand = 3 μm.

this is fairly good strength in comparison with the strength of hard bodies made from usual cements.

The effect of addition amount of silicate sand on mechanical strength of the hard bodies was tested and the result is listed in Table 2. In this experiment, silicate sand with an average particle size of 3 μm was used because the silicate sand gave the best mechanical strength in above work. Compressive strength and bulk density of the cured bodies increased with increasing addition amount of silicate sand. According to XRD analysis, it was found that HAP was formed in every cured body and this can be attributed to appearance of mechanical strength of the cured bodies. The highest compressive strength of 49.4 MPa was obtained when hardening under the silicate-sand addition ratio of 50% and the PVA concentration of 50% was employed.

3.2. Hardening with citric acid

According to preliminary test, hardening of citric acid solutions gave a good result at P/L ratio of 2.0 and at room temperature. Therefore, the P/L ratio and the hardening temperature were adopted in this experiment.

The effect of pH value and the concentration of citric acid on mechanical strength of the hard bodies were studied and the result is listed in Table 3. From the result, compressive strength and bulk density of the hard bodies increased with increasing concentration and pH value of the citric acid solution. The result indicated that the hard body treated with higher concentration and pH of citric acid solution had a finer structure and larger compressive strength. While, referring to compressive strength of the hard bodies prepared with PVA solutions, that of the hard bodies made with citric acid solutions was low. The hard bodies which were prepared with citric acid solutions did not show an XRD diagram of HAP. This can reasonably be understood because hardening process was progressed in an acidic solution. The hard bodies showed XRD peaks due to only starting materials and did not show any other new XRD peaks. Accordingly, newly formed hydrate-cements would be amorphous and the mechanical strength of the hard bodies should come from the amorphous hydrate-cement. Mechanical strength of an amorphous hydrate-cement is usually weaker than that of crystalline one. It is generally concluded that calcium phosphate reacts with organic acid to produce a precursor of HAP and the precursor forms a matrix of chemical bonding between calcium cations and carboxyl groups of organic acid, and the matrix causes mechanical strength of the hard bodies. Citric acid solutions showed pH 2 and hardening time of the cement pastes with the stimulators was several minutes, and it was difficult to make a shape of the cement. Hardening time was prolonged by addition of sodium hydroxide into the citric acid solutions and shape-making of the cement pastes became easy.

The effect of addition of silicate sand into the cement was examined by using a citric acid solution of pH 3 and the result is indicated in Table 4. The result showed that compressive strength and bulk density of the hard bodies increased with increasing addition amount of silicate sand and concentration of citric acid. A cured body which was prepared with 50% citric acid solution of pH 3 and 50% of addition amount of silicate sand gave the highest compressive strength of 27.6 MPa and only the cured cement showed weak XRD peaks and a SEM photograph of needle crystal due to HAP inside the body.

Table 4
Dependence of addition amount of silicate sand and concentration of citric acid on compressive strength[a]

Sand (%)[a]	Concentration of citric acid (%)	Bulk density (g/cm^3)	Compressive strength (MPa)
10	10	1.24	5.2
	20	1.26	7.7
	30	1.25	9.7
	40	1.29	10.2
	50	1.30	12.1
20	10	1.25	7.1
	20	1.28	10.1
	30	1.30	9.9
	40	1.31	10.9
	50	1.33	12.9
30	10	1.33	9.3
	20	1.33	10.4
	30	1.34	11.3
	40	1.36	12.1
	50	1.37	13.4
40	10	1.35	10.7
	20	1.36	14.6
	30	1.38	16.6
	40	1.39	17.0
	50	1.40	18.5
50	10	1.36	16.4
	20	1.38	17.7
	30	1.41	19.8
	40	1.42	22.7
	50	1.44	27.6

[a] Average particle size of silicate sand = 3 μm.

In comparison with mechanical strength of the hard bodies prepared with PVA solutions, mechanical strength of the hard bodies cured with citric acid solutions showed a lower value. While, hardening time of the cement pastes with PVA solutions takes more than 1 day even at hardening temperature of 80 °C and that of the cement pastes with citric acid solutions takes only few minutes to 1 h even at room temperature. Further, curing time of the cements of citric acid solutions can be controlled by addition of sodium hydroxide into the solution.

3.3. Adhesion force of calcium phosphate cement

Adhesive strength of the calcium phosphate cements was measured at 20 and 80 °C by the method of JIS adhesion test. The result is listed in Table 5. According to the result, any calcium phosphate cement showed much higher adhesive strength than the required JIS adhesive strength of 0.6 MPa. Adhesive strength of the calcium phosphate cements increased with increasing addition amount of silicate sand.

Table 5
Adhesion strength of calcium phosphate cement under standard state[b]

Curing condition[a]	Sand (%)[b]	Adhesive strength (MPa)[c]
A	0	1.9–3.0
	10	2.5–3.7
	50	4.7–4.9
B	0	2.3–3.6
	10	2.6–3.8
	50	4.1–4.7

[a] A: curing at 20 °C for 1 week, B: curing at 80 °C for 1 day.
[b] 40% PVA solution and silicate sand with average particle size of 3 μm were used.
[c] The lowest and highest numbers are listed.

3.4. Application

According to the above result, the calcium phosphate cement containing silicate sand has enough mechanical strength for construction materials and building materials. Calcium phosphates are materials with a high cost. The cost of the calcium phosphate composite-cement can be reduced by adding silicate sand and mechanical strength of the composite cement also can be improved in comparison with usual calcium phosphate cements not containing silicate sand. The calcium phosphate composite-cement may be applicable to the field of biomaterials, because the composite cement has enough mechanical strength and is considered to have biocompatibility.

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