Compressive strength and diametral tensile strength of some calcium-orthophosphate cements: a pilot study

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More than 100 different formulations of calcium-orthophosphate cements were subjected to determinations of the compressive strength and the diametral tensile strength after storage at room temperature for 24 h under 100% relative humidity (RH). It was found that setting occurred on more than 15 combinations of reactants. Further, it was shown that the mechanical properties of the cements which were obtained were also dependent on the water/powder ratio, the content of seed material and the storage conditions. Other factors which are thought to be of importance are the particle form and the particle size of the powder constituents as well as the addition of modifiers.

1. Introduction

In the literature [1–7], the compressive strengths or the diametral tensile strengths of several calcium-orthophosphate cements have been mentioned after storage under different conditions for different times. In the formulations, compounds like dicalcium phosphate (DCP), dicalcium-phosphate dihydrate (DCPD), tetracalcium phosphate (TTCP), alpha-tertiary calcium phosphate (α-TCP), beta-tertiary calcium phosphate (β-TCP), monocalcium-phosphate monohydrate (MCPM), and hydroxyapatite (HA) have been used. A summary is given in Table I.

In a previous study [8] a more systematic approach was designed to formulate calcium-orthophosphate cements. Essential points in this approach are: (a) that the cement powder contains one or two more-acidic components and one or two more-basic components which start to react to give calcium orthophosphates of intermediate acidity upon mixing with water. (b) that the mixture of reactants is composed in such a way that a calcium orthophosphate may be formed which is known to precipitate directly from aqueous solutions, and (c) that sometimes a seed material is added to avoid the necessity of nucleation of the precipitating calcium orthophosphate.

The first purpose of the present study was a quick screening of such formulations with respect to the compressive strength and the diametral tensile strength after storage for 24 h under 100% relative humidity (RH) at room temperature. In some cases the reproducibility of the effect of varying the water/powder ratio, the content of seed material or the storage conditions was investigated in order to have a first impression about the importance of such factors.

2. Methods and materials

The basic materials which were available as commercial products are mentioned in Table II. DCP, DCPD and precipitated hydroxyapatite (PHA) could be used as-received; other materials, like MCPM, CaO and $CaMgO_2$, had to be crushed and milled before use. Other basic products had to be synthesized. To that purpose, appropriate mixtures of $CaHPO_4$, $CaCO_3$, Na_2CO_3, K_2CO_3 and/or $CaCl_2$ were used. The synthesized products and the conditions of preparation are mentioned in Table III. The purity of the basic products was checked by X-rav diffraction.

Over 100 formulations were designed [8]. Pastes were made of these reactant mixtures by addition of water and intimate mixing at a glass slab. The pastes were used to fill cylindrical moulds 12 mm high having a diameter of 6 mm. The samples were stored in a desiccator above water at room temperature for 24 h. After storage, the samples were removed from the moulds. Half of them ($n = 6$–8) were used for determination of the compressive strength with an Instron Universal Testing Machine 4507 at a compression rate of 1 mm min^{-1}. The other half were used to determine the diametral tensile strength. Average values and standard deviations were calculated. In some cases the reproducibility or the effect of varying water/powder ratios, the content of seed materials or the storage conditions were studied. The compressive strength, C, was calculated by dividing the crushing force by the cross-section of the samples, whereas the diametral tensile strength, T, was calculated from the formula $T = 2F/\pi LD$ in which F is the crushing force, L is length and D is the diameter. Values for both T and F were expressed in MPa.

3. Results

The compressive strength, C, and the diametral tensile

TABLE I Literature data for the compressive strength, C (MPa), and the diametral tensile strength, T (MPa), reported for some calcium-orthophosphate cements

Ref.	Mixture of reactants	Modifier added	Water/powder ratio	C	T	Storage conditions
1	DCP + TTCP	–	0.5	34 ± 4	–	Immersion in water at 37 °C for 24 h
1	DCP + TTCP	HA	0.5	31 ± 7	–	Immersion in water at 37 °C for 24 h
2	DCP + TTCP	–	0.25	36 ± 1	–	100% relative humidity at 37 °C for 24 h
3	DCP + TTCP	–	?	21	–	?
1	DCPD + TTCP	–	0.5	31 ± 5	–	Immersion in water at 37 °C for 24 h
4	DCPD + TTCP	–	?	9 ± 3	–	Soaking for 24 h at 37 °C in 0.9% NaCl solution
4	DCPD + α-TCP	–	0.63	17 ± 3	–	Soaking for 24 h at 37 °C in 0.9% NaCl solution
5	MCPM + β-TCP	–	0.6–1.2	–	0.1–1.1	Immersion for several days at 37 °C in 0.9% NaCl solution
6	MCPM + β-TCP	Plaster	0.24–0.33	–	0.9–3.2	Immersion for several days at 37 °C in 0.9% NaCl solution
7	$CaO–SiO_2–P_2O_5–CaF_2$ glass	$(NH_4)_2HPO_4$	0.5	68	–	Implantation for 7 days in the muscles of a rat

TABLE II Raw chemicals used either directly or after milling as basic materials, or used as chemicals to prepare other basic materials

Name	Formula	Brand	Catalogue number
Calcium hydrogen phosphate	$CaHPO_4$	Merck[a]	2144
Calcium carbonate	$CaCO_3$	Merck	2076
Calcium chloride, anhydrous	$CaCl_2$	Merck	2388
Calcium hydrogen phosphate dihydrate	$CaHPO_4{\cdot}2H_2O$	Merck	2146
Tricalcium phosphate[b]	$Ca_3(PO_4)_2$	Merck	2143
Sodium carbonate, anhydrous	Na_2CO_3	Merck	6392
Calcium hydroxide	$Ca(OH)_2$	Merck	2047
Potassium carbonate	K_2CO_3	Merck	4924
Calcium oxide from marble	CaO	Merck	2109
Calcium phosphate monobasic-1-hydrate	$Ca(H_2PO_4){\cdot}H_2O$	Panreac[c]	141225
Calcium oxide, natural	$CaMgO_2$	Panreac	151234

[a] E. Merck, Darmstadt, Germany.
[b] This product appeared to be a precipitated hydroxyapatite, PHA.
[c] Montplet y Estéban S.A., Barcelona, Spain.

TABLE III Basic products prepared by heating appropriate mixtures of $CaHPO_4$, $CaCO_3$, Na_2CO_3, K_2CO_3 and/or $CaCl_2$ in a furnace at high temperatures

Abbreviation	Basic product	Formula	Conditions of preparation
α-TCP	α-tertiary calcium phosphate	$Ca_3(PO_4)_2$	Heating for 6 h at 1300 °C and quenching in air to room temperature
TTCP	Tetracalcium phosphate	$Ca_4(PO_4)_2O$	Heating for 12 h at 1500 °C and cooling in a furnace to room temperature
β-TCP	β-tertiary calcium phosphate	$Ca_3(PO_4)_2$	Heating for 4 h at 1100 °C and cooling in a furnace to room temperature
SHA	Sintered hydroxyapatite	$Ca_{10}(PO_4)_6OH_{2-2x}O_x$	Heating for 10 h at 1100 °C and cooling in a furnace to room temperature
SP	Spodiosite	$Ca_2(PO_4)Cl$	Heating for 6 h at 700 °C and cooling in a furnace to room temperature
–	Calcium potassium phosphate	$CaKPO_4$	Heating for 6 h at 900 °C and cooling in a furnace to room temperature
SWH	Sodium whitlockite	$Ca_{10}Na(PO_4)_7$	Heating for 6 h at 1000 °C and cooling in a furnace to room temperature
CA	Chloroapatite	$Ca_{10}(PO_4)_6Cl_2$	Heating for 6 h at 800 °C and cooling in a furnace to room temperature

strength, T, of some calcium-orthophosphate cements are shown in Table IV after storage at room temperature for 24 hours under 100% relative humidity. For comparison, mixtures which did not react but simply dried out after preparation had a compressive strength of about 0.2 MPa and a tensile strength of about 0.05 MPa. The values in Table IV show that there are many formulations in the system of calcium orthophosphates which might be of practical use in surgery or dentistry.

TABLE IV Calcium-orthophosphate cement formulations having a compressive strength larger than 1 MPa after storage for 24 h at room temperature under 100% relative humidity

Formulation number	Reactants	Reactants Ca/P ratio	Intended seed material	Intended seed material in the cement powder (%)	Cement-Paste water/powder ratio (g/g)	C (n=6–8)	T (n=6–8)	C/T
1	α-TCP, MCPM, $CaMgO_2$	1.28	–	–	0.55	12.0	2.8	4.3
2	α-TCP, DCP	1.33		–	0.30	9.9	2.1	4.7
3	α-TCP, MCPM	1.33	SHA	40	0.45	6.3	1.5	4.2
4	α-TCP, MCPM, Ca MgO_2	1.28	β-TCP	40	0.55	5.9	1.8	3.3
5	α-TCP, DCPD	1.33	PHA	40	0.55	5.6	1.2	4.7
6	α-TCP, MCPM	1.33	PHA	40	0.65	5.2	1.0	5.2
7	TTCP, MCPM	1.50	–	–	0.50	4.9	1.4	3.5
8	TTCP, DCP	1.50	PHA	40	0.50	4.8	1.1	4.4
9	TTCP, MCPM	1.00	DCPD	10	0.40	3.6	–	–
10	β-TCP, MCPM	1.00	–	–	0.40	3.6	0.9	4.0
11	MCPM, CaO	1.33	SHA	40	0.50	3.2	0.7	4.6
12	TTCP, MCPM	1.33	–	–	0.50	2.8	0.8	3.5
13	α-TCP	1.50	PHA	40	0.50	2.7	0.5	5.4
14	TTCP, DCP	1.33	–	–	0.30	2.4	0.8	3.0
15	MCPM, CaO	1.50	PHA	40	0.60	2.3	0.4	5.8
16	α-TCP, DCP	1.33	PHA	40	0.50	2.3	0.5	4.6
17	MCPM, CaO, $CaMgO_2$	1.28	–	–	0.70	2.1	0.6	3.5
18	$CaKPO_4$, SP, DCPD	1.33	PHA	40	0.55	2.1	0.5	4.2
19	TTCP, MCPM, $CaMgO_2$	1.28	β-TCP	40	0.55	2.0	0.4	5.0
20	$CaKPO_4$, SP, DCP	1.33	PHA	40	0.55	1.7	0.3	5.7
21	TTCP, DCPD	1.33	PHA	40	0.55	1.6	0.4	4.0
22	MCPM, CaO	1.50	SHA	40	0.50	1.5	0.4	3.8
23	SWH, CA, DCPD	1.33	PHA	40	0.50	1.3	0.3	4.3
24	MCPM, CaO	1.33	–	–	0.60	1.3	0.25	5.0
25	TTCP, DCP	1.33	PHA	40	0.55	1.2	0.28	4.0
26	SWH, CA	1.50	PHA	40	0.35	1.2	0.27	4.0

TABLE V Effect of the water/powder ratio of some formulations on the compressive strength, C, and the diametral tensile strength, T, after storage under 100% relative humidity at room temperature for 24 h

No.	Reactants	Ca/P ratio	Seed	% seed	Water/powder ratio	C	T	C/T
3	α-TCP, MCPM	1.33	SHA	40	0.45	6.3 ± 0.8	1.50 ± 0.08	4.2 ± 0.7
27	α-TCP, MCPM	1.33	SHA	40	0.35	5.9 ± 0.3	1.38 ± 0.07	4.3 ± 0.4
2	α-TCP, DCP	1.33			0.30	9.9 ± 0.4	2.1 ± 0.1	4.7 ± 0.5
28	α-TCP, DCP	1.33			0.35	0.30 ± 0.05	0.04 ± 0.02	

According to Table V some systems are sensitive to variations in the water/powder ratios, others are hardly dependent over a certain range. Table VI shows that the reproducibility is not so good. In this respect it is suggested that milling of the constituents should be carried out under controlled and standardized conditions.

From Table VII it is observed that the addition of seeds of the calcium phosphate which is formed during the setting reactions does not necessarily lead to the reinforcement of the material. Table VIII shows that the properties of some calcium-orthophosphate cements are marginally improved by soaking in water during longer periods, whereas other formulations seem to need soaking in water in order to reach their bulk strength and maintain it over longer periods. From Table IX, it can be concluded that soaking in an aqueous solution instead of storage under 100% relative humidity may either increase or lower the strength, or hardly affect it.

4. Discussion

It is shown that at least 15 combinations of reactants among the calcium orthophosphates lead to setting after mixing with water at room temperature. Up to now the highest compressive strength reported for calcium-orthophosphate cements after storage *in vivo* is 36 MPa. This is too low a value to apply these cements under load-bearing conditions. However, one value obtained after storage *in vivo* was as high as 68 MPa. We estimate that values of more than 100 MPa for the compressive strength are necessary for applications under load-bearing conditions. However, these applications may not depend so much on the compressive strength but more on the fracture toughness.

TABLE VI Reproducibility of some formulations

No.	Reactants	Ca/P ratio	Seed	% seed	Water/powder ratio	C	T	C/T
4	α-TCP, MCPM, $CaMgO_2$	1.28	β-TCP	40	0.55	5.9 ± 0.6	1.8 ± 0.2	3.3 ± 0.6
29	α-TCP, MCPM, $CaMgO_2$	1.28	β-TCP	40	0.55	2.4 ± 0.5	1.0 ± 0.2	2.4 ± 1.0
1	α-TCP, MCPM, $CaMgO_2$	1.28			0.55	12.0 ± 0.4	2.8 ± 0.2	4.3 ± 0.4
30	α-TCP, MCPM, $CaMgO_2$	1.28			0.55	8.0 ± 0.8	1.9 ± 0.3	4.2 ± 1.1

TABLE VII Effect of the seed content on the properties of some cements

No.	Reactants	Ca/P ratio	Seed	% seed	Water/powder ratio	C	T	C/T
10	β-TCP, MCPM	1.00	DCPD	0	0.55	3.6 ± 0.2	0.90 ± 0.05	4.0 ± 0.4
31	β-TCP, MCPM	1.00	DCPD	20	0.55	2.9 ± 0.3	0.68 ± 0.07	4.3 ± 0.8
32	β-TCP, MCPM	1.00	DCPD	30	0.55	2.7 ± 0.3	0.60 ± 0.10	4.5 ± 1.1
33	β-TCP, MCPM	1.00	DCPD	40	0.55	2.3 ± 0.3	0.40 ± 0.02	5.8 ± 0.9

TABLE VIII Effect of the conditions of storage on the properties of some cements

No.	Storage conditions	C	T	C/T
29	24 h, room temperature, 100% RH	2.4 ± 0.5	1.0 ± 0.2	2.4 ± 1.0
29	85 days, 37 °C, soaking in water	4.8 ± 0.6	1.4 ± 0.3	3.4 ± 1.1
30	24 h, room temperature, 100% RH	8.0 ± 0.8	1.9 ± 0.3	4.2 ± 1.1
30	85 days, 37 °C, soaking in water	9.8 ± 1.2	3.2 ± 0.2	3.1 ± 0.6
28	24 h, room temperature, 100% RH	0.30 ± 0.05	0.04 ± 0.02	
28	85 days, 37 °C, soaking in water	24.5 ± 3.0	4.5 ± 0.3	5.4 ± 1.1

TABLE IX Effect of soaking in Ringer solution at 37 °C for one day, compared to storage under 100% relative humidity at room temperature, on the strength C or T of some cement formulations

Formulation number	Reactants	Reactant Ca/P ratio	Intended seed material	Intended seed material in the cement powder (%)	Cement paste water/powder ratio (g/g)	R
5	α-TCP, DCPD	1.33	PHA	40	0.55	0.06
6	α-TCP, MCPM	1.33	PHA	40	0.55	0.35
8	TTCP, DCP	1.50	PHA	40	0.65	0.06
16	α-TCP, DCP	1.33	PHA	40	0.50	0.8
18	$CaKPO_4$, SP, DCPD	1.33	PHA	40	0.55	0.8
19	TTCP, MCPM, $CaMgO_2$	1.28	β-TCP	40	0.55	0.33
21	TTCP, DCPD	1.33	PHA	40	0.55	1.3
26	SWH, CA	1.50	PHA	40	0.35	0.3
34	TTCP, DCPD	1.33	–		0.40	17
35	TTCP, DCPD	1.67	PHA	7	0.25	7
36	TTCP, DCPD	1.50	PHA	40	0.50	13
37	TTCP, DCPD	1.67	PHA	7	0.25	21

R = Compressive strength after soaking for 1 day at 37 °C in Ringer solution divided by the compressive strength after storage for 1 day under 100% relative humidity at room temperature

In this study it was established that factors which influence the mechanical properties of calcium orthophosphate cements are the formulation, the water/powder ratio, the seed content and the storage conditions. Further, we suggest that the content of any modifier [6] and the milling conditions (particle form, particle size) of the constituents are also important factors.

It is unknown yet what levels of strength, hardness and fracture toughness will be reached, once these calcium-phosphate cements have been developed to their full capacity. For comparison, compressive strengths of the established dental cements are mostly in the range 50–150 MPa. On the other hand, it is uncertain whether the mechanical strength will be the most pronounced criterion for selecting calcium-phosphate cements for application in surgery and dentistry; for example, the excellent biocompatibility and osteoconductivity of calcium phosphates like HA and β-TCP gives reason to think that calcium-phosphate cements may be applied, in the future, primarily for replacement and augmentation of bone tissue, thus the question remains unanswered as to whether these materials are suitable to function under load-bearing conditions.

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