J Mater Sci: Mater Med (2008) 19:737–744
DOI 10.1007/s10856-007-3198-z

Study of a hydraulic DCPA/CaO-based cement for dental applications

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Received: 16 April 2007 / Accepted: 29 May 2007 / Published online: 10 July 2007

Abstract A CPC was obtained by mixing calcium hydrogenphosphate (DCPA: $CaHPO_4$) and calcium oxide with either water or sodium phosphate (NaP) buffers. Physical and mechanical properties such as compressive strength (CS), initial (I) and final (F) setting times, cohesion time (T_C), dough time (T_D), swelling time (T_S), dimensional and thermal behavior, injectability ($t_{100\%}$), antimicrobial properties, setting reaction kinetics, and powder stability over time were investigated by varying different parameters such as liquid-to-powder (L/P) ratio (0.35 to 0.7 mL g^{-1}), molar calcium-to-phosphate (Ca/P) ratio (1.67 to 3), the pH (4, 7 or 9) and the concentration (0 to 1 M) of the NaP buffer. The best results were obtained with the pH 7 NaP buffer at a concentration of 0.75 M. With this liquid phase, physical and mechanical properties depended on the Ca/P and L/P ratios, varying from 3 to 11 MPa (CS), 6 to 10 min (I), 11 to 15 min (F), 15 to 45 min (T_S), 3 to 12 min ($t_{100\%}$), 16 min (T_D). This cement expanded during its setting (2.5–7%), and is thus appropriate for tight filling. Finally the cement has antimicrobial activity from Ca/P = 2 and the whole properties were conserved after 8 months storage. Given the mechanical, rheological and antimicrobial properties of this new DCPA/CaO-based cement, its use as root canal sealing or pulp capping material may be considered as similar to calcium hydroxide or ZnO/eugenol-based pastes, without or with a gutta-percha point.

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Introduction

Calcium hydroxide-based cements or pastes are currently used in dentistry for direct or indirect pulp capping, apexification, apexogenesis and root canal filling [1–4]. Calcium hydroxide presents certain advantages such as its antimicrobial and anti-inflammatory activities, but also some drawbacks as described in the introduction to a previous paper [5]. Ever since the studies of Brown and Chow [6] were published, calcium phosphate-based cements (CPCs) have attracted much interest in dental, maxillofacial and orthopedic surgery because of their good osteoconductivity for bone reconstruction. CPCs are able to harden in situ and present appropriate mechanical properties. Our intention is to prepare CPCs that conserve the advantages of calcium hydroxide-based pastes while avoiding or minimizing their drawbacks, particularly the lack of hardening, retraction on drying and their non negligible solubility. Two cements have already been developed in this goal. The first was from bis-dihydrogen phosphate monohydrate (or monocalcium phosphate monohydrate MCPM) and calcium oxide and is suitable for pulp capping [7–9]. The second, derived from calcium hydrogen phosphate dihydrate (or dicalcium phosphate dihydrate DCPD) and calcium oxide [5, 10], is suitable as a root canal filler and for endodontic treatments. These two cements exert antimicrobial activity, determined by the agar diffusion method [9, 10], when containing molar calcium-to-phosphate ratios of Ca/P ≥ 2 and Ca/P ≥ 1.67 respectively.

Generally, hydrated and anhydrous salts show differences in solubility and dissolution rates. The difference in

solubility can affect setting reaction kinetics and consequently the rheological and mechanical properties of the resulting cements. We therefore investigated the properties of a new cement prepared from calcium oxide and dicalcium phosphate anhydrous (DCPA, $CaHPO_4$) instead of DCPD.

Materials and methods

Chemicals

All chemicals were analytical reagent grade purchased from Aldrich (CaO) and Fluka (DCPA, NaH_2PO_4, $Na_2HPO_4{\cdot}12H_2O$). Commercial CaO was heated at 900 °C for 2 h to remove H_2O and CO_2 and was then stored in a vacuum desiccators. The median particle size d_{50} of the CaO was around 7 μm (d_{10}–d_{90} = 2–40 μm; specific surface area = 1.3 $m^2\ g^{-1}$, Mastersizer, Malvern Instruments). The commercial DCPA was used as received, its median particle size was around 5 μm but agglomerates of up to 60 μm were noted (estimation from SEM pictures).

Preparation of calcium phosphate cements

The liquid phase used was either pure water or 0.25, 0.45, 0.6, 0.75 or 1 M sodium phosphate (NaP) buffers, pH 4, 7 or 9 prepared from NaH_2PO_4 and $Na_2HPO_4{\cdot}12\ H_2O$. The powder, containing DCPA and CaO in various weight ratios, was incorporated into the liquid phase on a glass plate at 20 ± 1 °C as successive fractions, in the same manner as for dental zinc phosphate cements (one-sixth of the powder was added every 15 s) and kneaded with a spatula between each addition to produce a paste of workable consistency. After a total mixing time of 2 min, the paste was loaded into molds to measure compressive strength or setting times. The different molar calcium-to-phosphate (Ca/P) ratios tested ranged from 1.67 to 3 and the liquid-to-powder (L/P) ratios from 0.3 to 0.5 mL g^{-1}.

Measurements of mechanical strength and the different times

Compressive strength (CS) was measured at a loading rate of 1 mm min^{-1} with an Instron 4444 testing machine on samples (4 mm diameter × 6 mm height) stored for 24 h at 37 °C and 100% relative humidity (RH), as already described [7]. Initial (I) and final (F) setting times [11] were measured at 37 °C using Vicat needles 2 mm in diameter, 100-g loaded and 1 mm in diameter, 400-g loaded. The dough or working time (T_D) corresponds to the time during which the paste can be worked without losing the mechanical properties of the resulting cement [12]. T_D was determined as follows: after the 2 min of preparation, the paste was left on a glass plate at 20 °C for 1, 3, 5... or 13 min then worked again with the spatula for 1 min and loaded either into the molds to determine the CS or into the apparatus used to measure the final setting time and thus evaluate any changes in mechanical properties.

The cohesion time (T_C) was estimated by visual observation of the sample surface [13]. After preparation, the cement paste was loaded in a stainless steel cup (8.5 mm in diameter × 5 mm in depth) that was, after 1, 3, 5... min of waiting, immersed in Ringer's solution at 37 °C. The cohesion time corresponds to the time of immersion at which there is no departure of particles from the cement surface.

Swelling time [13] (T_S) was measured by first placing the cement paste in the stainless steel cup and storing the cup at 37 °C, 100% RH for different time periods, then immersing the cup in Ringer's solution at 37 °C for 10 min. The sample was then removed from the solution and tested in the same manner as for the final setting time. Swelling time corresponds to the storage time for which no deformation of its surface was observed after 10 min of immersion. Deformation was characterized by the depth to which the Vicat needle penetrated.

Effect of the kneading temperature

The effect of kneading temperature of on the mechanical properties of cements was evaluated by preparing cements with Ca/P = 1.67 and 3 and kneading the paste on the glass plate at 15, 20, 25 and 37 °C. The CS and the initial and final setting times were then measured.

Dimensional and thermal changes during setting

Cement expansion and the heat dissipated during setting were measured using a lab-made apparatus. A hole, 8.2 mm in diameter, was drilled through a Plexiglas cylinder (4 cm diameter × 4 cm height) thermostated at 37 °C. The cement paste was injected into the hole to cover a thermocouple that had previously been inserted. A Plexiglas plug (8.0 mm in diameter) was then inserted, packing down the cement, and an extensometer was placed at the top of the plug. The inner temperature of the cement and its expansion were recorded over time until they stabilized.

Injectability

The injectability [14] of the cement was estimated by the weight percentage of the cement paste that could be injected using a 2.5 mL syringe (Plastipak®) with an inner diameter of 8.5 mm, an opening 2 mm in diameter and 1 cm in length. Two grams of cement were prepared, loaded into the syringe, and mechanically injected at a constant pressure of

6.8 bar (lab-made apparatus) at different points after the start of mixing until the paste was no longer completely injectable. The mass of cement injected and the mass remaining in the syringe were accurately weighed and the percentage calculated.

Setting reaction kinetics and powder stability over time

X-ray diffraction (XRD) was used to monitor the setting reaction and verify the stability of the cement powder over time. At different intervals post-preparation, cement samples were crushed, washed with acetone to remove residual water, dried and analyzed by XRD. Cement powders with different Ca/P ratios (1.67, 2 and 2.5) were analyzed by XRD right after DCPA and CaO mixing, after four months and after one year storage in a closed jar. XRD patterns were recorded on an Automatic diffractometer composed of a Philips PW3830 HT generator, a horizontal goniometer (CGR) and X-ray tube Philips 2273/20 using a Cu anticathode ($K_{\alpha 1}$ 1,5405 Å) with a nickel filter followed by a quartz monochromator.

Antimicrobial activity

The antimicrobial activity of the different cement formulations (Ca/P = 1.67, 2 and 2.5) was investigated using the agar diffusion method [14, 15]. Plates (90 mm in diameter) were filled with 25 mL casein soybean digest agar supplemented with 1% w/w sucrose and buffered at pH 7.4. 100-µL aliquot of the bacterial suspension was inoculated onto the surface of each agar plate (approximately 10^6 cells per plate, estimated using the Mac Farlan scale and checked by CFU counting after successive dilution). Two cement samples and one $Ca(OH)_2$ reference, surrounded by the plastic ring (8.5 mm in diameter × 5 mm in height), were placed symmetrically onto the plates. The plates were cultured aerobically in a closed jar (Baltimore Biological Laboratory) at 37 °C. The susceptibility of *Streptococcus mutans* (Sm), (clinical isolates controlled by API gallery bioMérieux® and gram reaction) to CPCs and $Ca(OH)_2$ was tested. The diameter of inhibition zones was measured periodically up to 12 days to detect any variations in inhibition over time. A minimum of four experiments was performed for each cement formulation as well as for calcium hydroxide.

Results

Compressive strength

The compressive strength of the cement was first determined for Ca/P = 1.67 (Fig. 1) using different concentrations of pH 7 sodium phosphate buffer (0 to 1 M) and L/P ratios (0.35 to 0.5 mL g^{-1}). The best CS values were obtained with the 0.75 M pH 7 NaP buffer irrespective of the L/P ratio. Sodium phosphate buffers with pH values of 4 and 9 were also tested as the liquid phase, but the results were not better than those obtained with the pH 7 buffer. Consequently, pH 7 NaP buffer at a concentration of 0.75 M was used as the liquid phase for subsequent experiments.

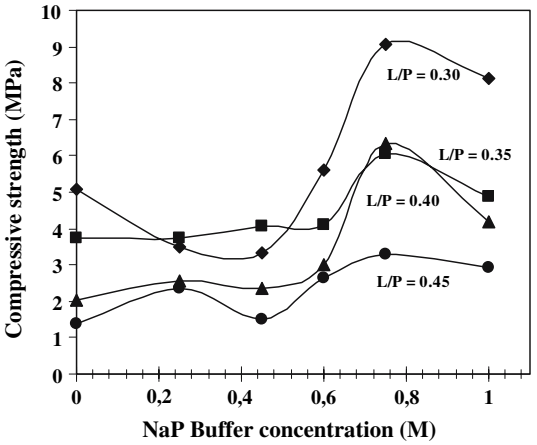

Fig. 1 Relation between compressive strength and pH 7 sodium phosphate buffer concentration; Ca/P = 1.67 and different L/P ratios in mL g^{-1} (indicated on each plot)

The CS was also measured for Ca/P ratios of 1.67–3 (Fig. 2). Globally, the CS value increased slightly with the Ca/P ratio. As observed for other types of cement [7, 15, 16], CS was reduced by increasing the L/P ratio (Figs. 1 and 2). For the sake of clarity, the standard deviations for each point (mean value of at least 10 samples) are not shown in the figures; but these were generally 10% or less of the mean value.

The CS of cements with L/P = 0.4 mL g^{-1}, 0.75 M pH 7 NaP buffer and Ca/P = 1.67 and 3 was also measured after different storage times at 37 °C and 100% RH. For

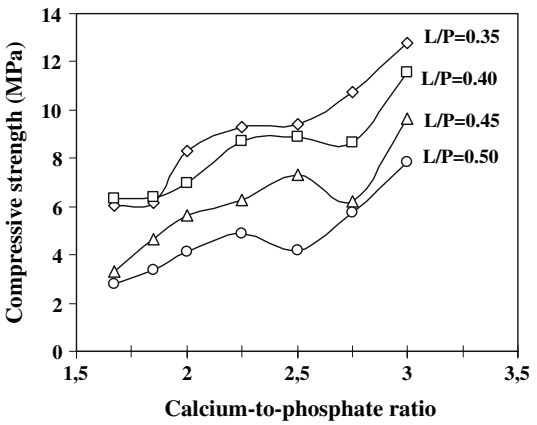

Fig. 2 Relation between compressive strength and calcium-to-phosphate ratio for different L/P ratios in mL g^{-1} (indicated on each plot); 0.75 M pH 7 NaP buffer

Ca/P = 1.67, the CS value was around 2 MPa after 30 min, 6.4 MPa after one day and stable at about 10.5 MPa after storage for three months. For Ca/P = 3, the CS values were 6.4, 11.5 and 24.2 MPa after 30 min, one day and three months respectively.

The different times

The different times, such as initial and final setting times, dough time, cohesion time and swelling time that describe cement behavior during its setting, were measured for the cements with the different Ca/P and L/P ratios presented in Table 1.

The initial I and final F setting times were virtually independent of the Ca/P ratio (1.67–3 range) and L/P ratio (0.35–0.45 mL g^{-1}): I = 8 ± 1 min and F = 11.0 ± 1.5 min The difference between I and F was also constant (around 3–4 min for the three L/P ratios tested). The dough or working time exceeded 16 min for all the different Ca/P ratios tested. Indeed, even kneading the paste 16 min after its preparation, the CS after one day remained constant for the different Ca/P ratios (Fig. 3).

The same stability was observed for the final setting time F (around 11–13 min). The cohesion time was very short ($T_C \approx 3$ min) for all Ca/P and L/P ratios. The

Table 1 The different times measured and experimental conditions tested

Times	L/P (mL g^{-1})	Ca/P
Initial setting time	0.35–0.4–0.45	1.67–1.85–2–2.25–2.5–2.75–3
Final setting time	0.35–0.4–0.45	1.67–1.85–2–2.25–2.5–2.75–3
Dough time	0.4–0.45	1.67–1.85–2–2.25–2.5–2.75–3
Cohesion time	0.4–0.45	1.67–1.85–2–2.25–2.5–2.75–3
Swelling time	0.4–0.45	1.67–1.85–2–2.25–2.5–2.75–3

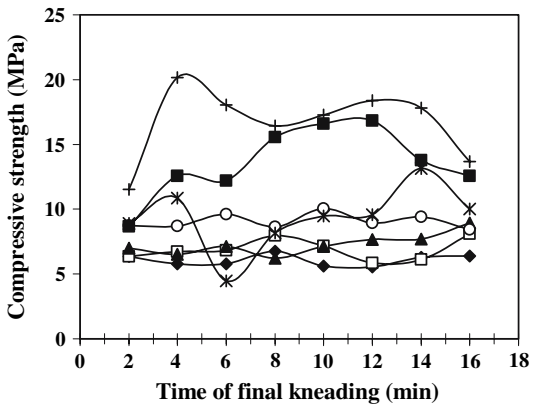

Fig. 3 Determination of the working time: relation between compressive strength and the time at which the last kneading was stopped (measured from the beginning of starting material mixing) for cements with Ca/P ratios of (◆) 1.67, (□) 1.85, (▲) 2, (○) 2.25, (★) 2.5, (■) 2.75 and (+) 3; L/P = 0.4 mL g^{-1}, 0.75 M pH 7 NaP buffer

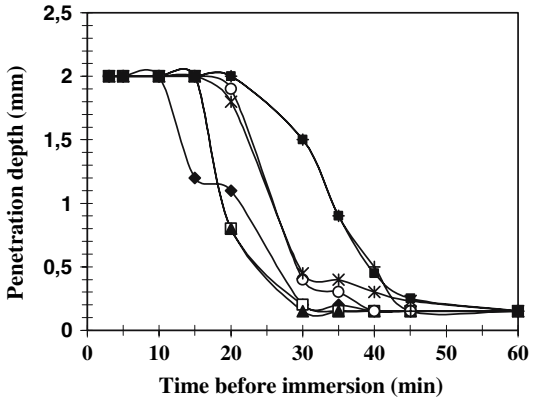

Fig. 4 Determination of the swelling time: relation between the penetration depth of the Vicat needle and the time at which the cement sample was immersed in Ringer's solution (measured from the beginning of starting material mixing) for cements with Ca/P ratios of (♦) 1.67, (□) 1.85, (▲) 2, (○) 2.25, (★) 2.5, (■) 2.75 and (+) 3; L/P = 0.4 mL g^{-1}, 0.75 M pH 7 NaP buffer

swelling time (Fig. 4) was around 30 min for cements with a Ca/P ratio of 1.67, 1.85 or 2, but when the Ca/P ratio increased, this increased substantially: T_S = 40 min for Ca/P = 2.25 and 45 min for Ca/P = 2.5–3.

Effect of kneading temperature

Changes in the initial and final setting times with the temperature at which the cements were prepared on the glass plate are represented in Fig. 5. The I and F decreased with the temperature of kneading. The compressive strength at one day remained constant for cement with Ca/P = 1.67 and increased slightly for higher Ca/P ratios.

Dimensional and thermal changes during setting

The cement expanded continually during its setting for all the Ca/P ratios tested (Fig. 6). This expansion reached a

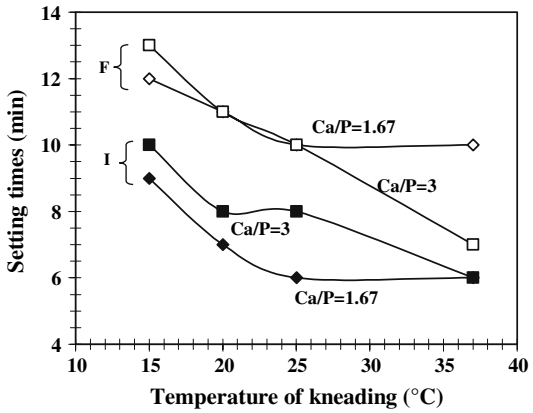

Fig. 5 Relation between initial (I) and final (F) setting times and kneading temperature; CaP = 1.67 and 3, L/P = 0.4 mL g^{-1}, 0.75 M pH 7 NaP buffer

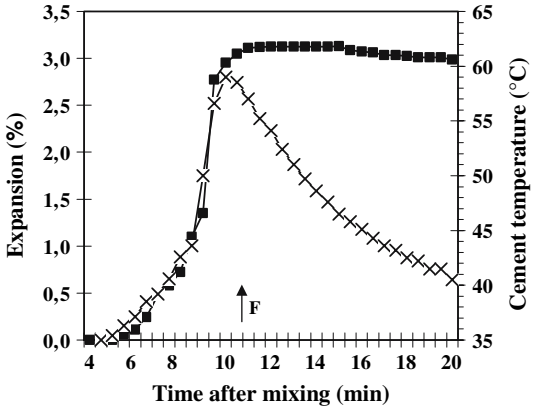

Fig. 6 Relation between expansion volume (■) or inner temperature (×) and time after mixing for a cement with CaP = 1.67 and L/P = 0.4 mL g^{-1}, 0.75 M pH 7 NaP buffer

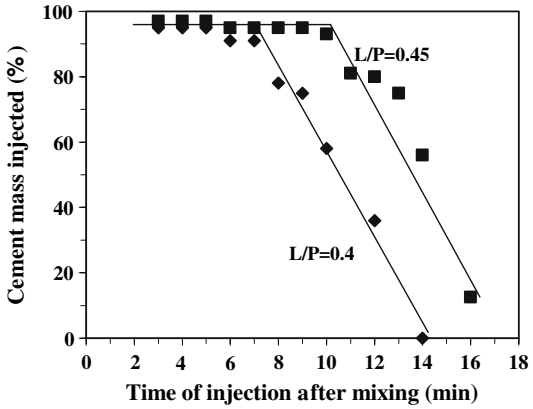

Fig. 8 Determination of the time required for 100% injectability: relation between the mass of cement paste injected and the time of injection measured from the beginning of starting material mixing; Ca/P = 1.67, L/P = 0.4 and 0.45 mL g^{-1}, 0.75 M pH 7 NaP buffer

maximum at a time point corresponding approximately to the final setting time. Maximum expansion increased with the Ca/P ratio from 3% (Ca/P = 1.67) to 7% (Ca/P = 2.5) but was virtually independent of the L/P ratio. The temperature of the cement rose during setting then decreased (Fig. 6). The temperature also reached a maximum (θ_{max}) at a time point corresponding to the final setting time. The difference between θ_{max} and 37 °C was recoded as $\Delta\theta$. The variations in $\Delta\theta$ with the Ca/P and L/P ratios are represented in Fig. 7. $\Delta\theta$ increased with the Ca/P ratio but decreased slightly as the L/P ratio increased.

Injectability

The time required for 100% injectability corresponds to the sharp break in the plot of the mass percentage injected versus the time at which the cement was injected measured from the beginning of starting material mixing (Fig. 8). The time required for 100% injectability decreased markedly for L/P ratio of 0.4 mL g^{-1} as the Ca/P ratio increased (from 8 min, Ca/P = 1.67 to 2 min, Ca/P = 3) but was longer (11 min) and independent of the Ca/P ratio when L/P was 0.45 mL g^{-1}.

Setting reaction kinetics

For the cement with Ca/P = 1.67, 1 h after solid phase and liquid phase mixing, hydroxyapatite (HA) appeared (diffraction peak at 15.9 °θ) and CaO (diffraction peak at 18.8 °θ) was totally hydrated as $Ca(OH)_2$ (diffraction peak at 9.08 °θ) (Fig. 9). The proportion of HA increased slowly

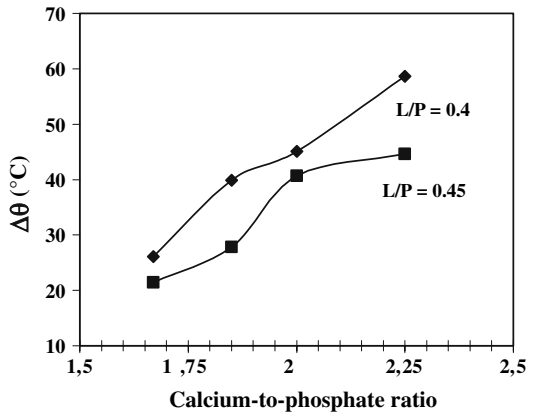

Fig. 7 Relation between $\Delta\theta = \theta_{max}$–37 °C and the Ca/P ratio for two L/P ratios, 0.4 and 0.45 mL g^{-1}, 0.75 M pH 7 NaP buffer

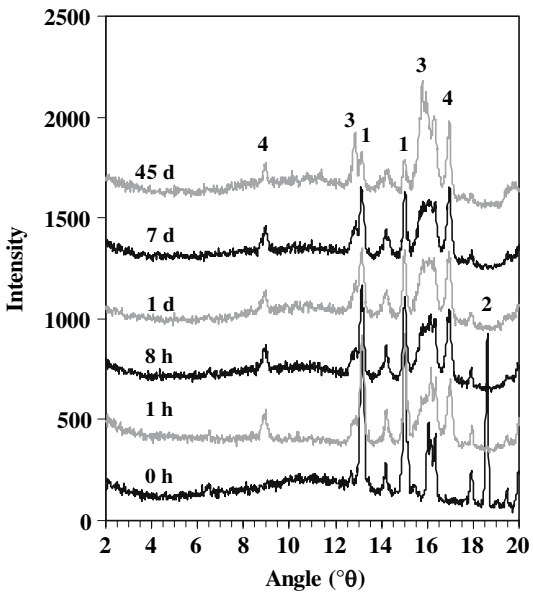

Fig. 9 XRD patterns of the cement (Ca/P = 1.67) at different intervals after solid and liquid phase mixing (indicated on each pattern). **1** = DCPA; **2** = CaO; **3** = HA and **4** = $Ca(OH)_2$

with time, but never reach completion. DCPA (13.3 °θ and 15.2 °θ peaks) and $Ca(OH)_2$ (9.08 °θ and 17.16 °θ peaks) remained after 45 days. The amount of remaining calcium hydroxide after 45 days increased according to the Ca/P ratio.

Powder stability and cement characteristics over time

The XRD patterns of cement powders recorded one day, four months and one year after preparation did not reveal any evolution regardless of Ca/P ratio. CS at one day, I, F, 100% injectability, expansion and heat variation during setting were tested after 1, 2, 3 and 12 months storage for the cements with Ca/P = 1.67 and 2. CS remained constant (7 ± 1 MPa for Ca/P = 1.67 and 9 ± 1 MPa for Ca/P = 2). Similarly the initial setting time was unchanged (I = 7–8 min) and the final setting time (F = 11 min) was slightly increased at 12 months (13.5 ± 0.5 min). Heat variation during setting and cement expansion were slightly decreased. However, after one year, the cement was longer easily injectable.

Antimicrobial activity

The antimicrobial property was tested with powders freshly prepared and after 8-month storage. It was compared to pure calcium hydroxide as reference [9, 10] (Fig. 10). Right after cement formulation, the antimicrobial activity of CPCs was 30 ± 5, 65 ± 3 and 85 ± 5% of the $Ca(OH)_2$ one for Ca/P = 1.67, 2 and 2.5 respectively. After storage for 8 months, it was 0, 60 ± 2% (Fig. 10) and 81 ± 3% of the $Ca(OH)_2$ one respectively. The storage for 8 months did not affect the bacterial growth inhibition for cements with Ca/P = 2 and 2.5 (P = 0.18 and 0.21 respectively, one-way ANOVA statistical test, significance level of 0.05).

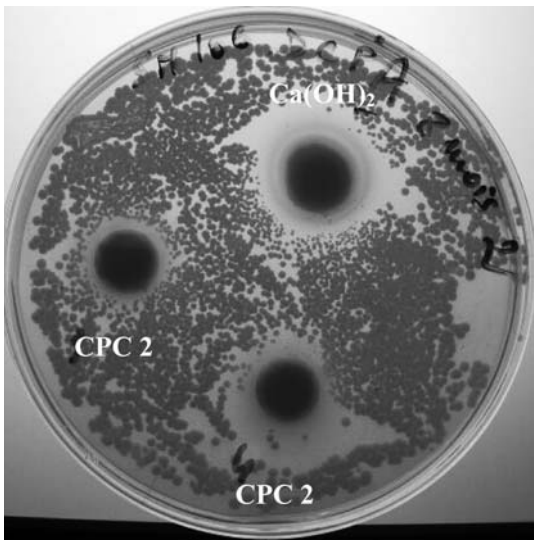

Fig. 10 Photography of a plate showing the disposition of samples and the *S. mutans* growth inhibition zone around samples: (up) pure $Ca(OH)_2$, and (down) CPCs with Ca/P = 2 after 8-month storage

Discussion

The root canal of a tooth has an inner diameter of about 0.2–0.3 mm and a length of 12–15 mm. Before filling, the root canal is generally enlarged by scraping with endodontic files to a diameter of 0.6–1 mm. This facilitates the penetration of the sealer and allows the smear layer removal. A root canal filler must have rheological properties that allow it to penetrate easily into the main canal to the apex, but also into the lateral canals and if possible into the dentinal tubules. In this operation, the paste is introduced into the root canal as several applications using either a Lentulo spiral, a syringe with a blunted needle or by turning a file counterclockwise. Finally, the paste can be laterally or vertically condensed with a gutta-percha point to improve its penetration into lateral canals and dentinal tubules. This requires a regular kneading of the cement paste, which must not be detrimental to its final properties. The total time to correctly fill a root canal is around 15 min.

Because osseous tissues do not tolerate basic pH, calcium phosphate cements developed for orthopedic purposes have Ca/P ratios of 1.67 or less, value corresponding to stoichiometric hydroxyapatite. For dental uses, and more especially for endodontic applications, the materials used can be alkaline to exert antimicrobial activity. This is why Ca/P ratios over 1.67 were tested in this work. During setting, the starting materials convert into a mixture of hydroxyapatite (or calcium deficient hydroxyapatite) and calcium hydroxide (Eq. 1).

$$6\ CaHPO_4 + (4 + x)\ CaO + (x - 2)\ H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + x\ Ca(OH)_2 \quad (1)$$

The precipitation of HA gives the cement its appropriate mechanical properties and the release of hydroxyl ions from calcium hydroxide ensures antimicrobial activity [3]. The increase in the Ca/P ratio raises the calcium oxide content in the starting powder, thus increasing the amount of calcium hydroxide after setting and the number of hydroxyl ions potentially releasable. The antimicrobial activity of the two cements previously developed was effectively dependent on the Ca/P ratio [9, 10].

The cements prepared from DCPA and CaO, and a 0.75 M pH 7 NaP buffer as liquid phase, generally showed a compressive strength after one day of 2.5–12 MPa and setting times at 37 °C of 7–13 min (Fig. 2) when the Ca/P

ratios were 1.67–3 and the L/P ratios were 0.35–0.5 mL g^{-1}. The increase in the Ca/P ratio had a variable effect on the different parameters describing cement behavior during and after setting. Compressive strength was improved (Fig. 2). The initial and final setting times and the dough time (Fig. 3) remained constant while the swelling time (Fig. 4), volume expansion and temperature rise during setting were increased (Fig. 7). With an L/P ratio of 0.4 mL g^{-1}, the time required for 100% injectability was acceptable for Ca/P = 1.67 but this decreased substantially as the Ca//P ratio increased. Increasing the L/P ratio improved the injectability (Fig. 8) and diminished the rise in temperature (Fig. 7) without any change in setting times and expansion, but to the detriment of the CS (Fig. 2).

The setting times, dough time and injectability of this cement comply with the characteristics required for root canal fillers. Its compressive strength is sufficient to ensure hard sealing but not too high to allow easy removal with an ultrasonic instrument. Its expansion characteristics are consistent with hermetic filling and the swelling of the cement, in contact with liquids remaining in lateral canals and tubules, could facilitate paste penetration into these and the diffusion of hydroxyl ions for antimicrobial activity.

The setting reaction results in a mixture of calcium deficient hydroxyapatite and calcium hydroxide. The hydroxyapatite network which gives the cement its hardness acts as a drug delivery system releasing hydroxyl ions. Because hydroxyapatite is less soluble than calcium hydroxide at physiological pH, and this cement is more resistant than calcium hydroxide pastes, it could be used as definitive sealing material with or without gutta-percha point. Since the post-setting components of the cement are bioresorbable and osteoconductive, any transfer of the paste through the apex would not be contra-indicated, unlike ZnO/eugenol-based cements. This could even be advantageous in cases of periapical inflammation.

Finally, the mechanical properties of this cement are not overly affected by slight variations in the L/P ratio (Figs. 1, 2) or the temperature at which the cement paste is prepared (Fig. 5). This is important from a practical standpoint because the conditions of cement preparation in a dentist's surgery can be less reproducible than in a research laboratory where preparation conditions are standardized to ensure the repeatability of the results and to investigate the effect of different parameters on cement properties.

The replacement of DCPD by DCPA in preparation of calcium phosphate cements results in some minor differences in the mechanical and rheological properties of the cements produced. The liquid-to-powder ratio that gives the best paste workability characteristics before setting was 0.6 mL g^{-1} for DCPD/CaO as starting materials [5] and 0.4 mL g^{-1} for DCPA/CaO. At these L/P ratios, an increase in the Ca/P ratio (i) decreased compressive strength after one day for DCPD but increased it for DCPA; (ii) did not change the initial setting time, final setting time or working time for either of the two cements; (iii) resulted in a longer swelling time for DCPA than for DCPD; (iv) resulted in greater ultimate expansion for DCPA than for DCPD; (v) decreased injectability for DCPA more markedly than for DCPD. The main difference observed between these two cements concerned their inner temperature variations during setting since the maximum temperature θ_{max} reached during the setting of DCPD/CaO cements did not exceed 57 °C while for DCPA/CaO cements, it was already of 60 °C for Ca/P = 1.67 and rose to 95 °C for Ca/P = 2.25 (Fig. 7), and this for all the Ca/P and L/P ratios.

These differences in behavior can be partly explained as follows. The theoretical crystal density [17] corresponds to 2.32 g cm^{-3} for DCPD and 2.89 cm^{-3} for DCPA. This difference was also found in the relative density of the powder measured by weighting the same volume of commercial DCPD and DCPA powders packed down in the same way. The DCPA powder was 1.68 times denser than the DCPD powder despite a smaller mean particle size (DCPA 5 μm and DCPD 8 μm). Therefore, to obtain the same Ca/P ratio in the mixture with CaO, the volume of DCPA powder used was lower than the volume of DCPD powder, and the amount of liquid phase used to obtain a paste of workable consistency was smaller. Normally, a decrease in the L/P ratio diminishes setting times and increases compressive strength, which was not because with a Ca/P ratio of 1.67, I, F and CS were identical. This is probably due to the difference between DCPA and DCPD solubility's. Although anhydrous salts are generally more soluble than the corresponding hydrated salts, DCPA is less soluble than DCPD [17]. Consequently, oversaturation is reached more slowly and the setting is delayed. The thermal changes and expansion that occur during setting are due to the presence of calcium oxide (ocalexic-like behavior [18]) which is converted to calcium hydroxide (thermal effect) and then precipitates (expansion effect). Because, the dissolution of DCPA is slow and poor in comparison with DCPD, the concomitant dissolution and hydration of CaO was relatively more marked and the associated effects (thermal changes and expansion) were more marked in DCPA/CaO cement than in DCPD/CaO cement. The amount of CaO in the starting mixture increased with the Ca/P ratio and consequently the θ_{max} was higher (Fig. 7). This substantial increase in the inner temperature of the cement during setting may explain why compressive strength increased with the Ca/P ratio (Fig. 2) without any affect on the different times because of the retrograde solubility of DCPA and $Ca(OH)_2$ which slow down their dissolution. Studies of the mechanisms involved in the setting reaction and of its kinetics for the DCPD/CaO

and DCPA/CaO-based cements, including calorimetric measurements, will be required to confirm these hypotheses.

Finally, for similar values of the Ca/P ratio, DCPA/CaO-based cements exert a slightly better growth inhibition against *Streptococcus mutans* than DCPD/CaO-based cement [10] (×1.2 times), owing to a greater amount of available $Ca(OH)_2$ resulting from the slow and incomplete transformation of starting materials to HA (Fig. 9) in contrast with the DCPD/CaO setting reaction for which transformation was complete after 2 h [5].

Conclusion

The mechanical, rheological and antimicrobial properties of this new DCPA/CaO-based cement render it as appropriate as DCPD/CaO-based cement for use as a root canal sealing material or for pulp capping. Moreover, these properties are conserved after powder storage; lapsing time over 8 months. In comparison with DCPD/CaO-based cement, its main drawback is the temperature it reaches transiently during setting. Considering this last point, a Ca/P ratio of 2 in the powder seems a best compromise between compressive strength, expansion, heat evolution and antimicrobial potency.

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