Materials Science and Engineering C 33 (2013) 527–531

Contents lists available at SciVerse ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Influence of water content on hardening and handling of a premixed calcium phosphate cement

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ARTICLE INFO

Article history:
Received 24 January 2012
Received in revised form 12 September 2012
Accepted 28 September 2012
Available online 6 October 2012

Keywords:
Premixed
Calcium phosphate cements
Injectability
Strength
Setting time
Water content

ABSTRACT

Handling of calcium phosphate cements is difficult, where problems often arise during mixing, transferring to syringes, and subsequent injection. Via the use of premixed cements the risk of handling complications is reduced. However, for premixed cements to work in a clinical situation the setting time needs to be improved. The objective of this study is to investigate the influence of the addition of water on the properties of premixed cement. Monetite-forming premixed cements with small amounts of added water (less than 6.8 wt.%) were prepared and the influence on injectability, working time, setting time and mechanical strength was evaluated. The results showed that the addition of small amounts of water had significant influence on the properties of the premixed cement. With the addition of just 1.7 wt.% water, the force needed to extrude the cement from a syringe was reduced from 107 (±15) N to 39 (±9) N, the compression strength was almost doubled, and the setting time decreased from 29 (±4) min to 19 (±2) min, while the working time remained 5 to 6 h. This study demonstrates the importance of controlling the water content in premixed cement pastes and how water can be used to improve the properties of premixed cements.

1. Introduction

Calcium phosphate based materials are considered ideal for bone replacement, since they resemble the mineral phase of bone; calcium deficient hydroxyapatite. The first calcium phosphate paste was patented in 1975 by Driskell et al. [1], and the first calcium phosphate cements (CPC) were reported in the early 1980's [2,3]. Brushite and apatite are the two main types of CPC found, differing mainly in pH. In an acidic environment (pH<~4.2) the cement precipitates to brushite [4,5]; although monetite has also been reported [6]. At a higher pH however, apatite precipitation occurs [7]. Both types of CPC have good biocompatibility and are used clinically [8–11]. Furthermore, promising in vivo results have been shown for monetite based materials [12]. When the cements are compared in vivo, the acidic cements have been shown to resorb faster than apatite cements due to their increased solubility in physiological pH [13]. This allows for faster bone in-growth to occur into the cement-filled defect [12]. The mixing of commercially available water-based CPCs at present has to be done in the operating room, since hardening starts immediately after mixing. Each product has specific mixing equipment and instructions that can be quite tedious, making them difficult to work with. All stages of mixing, transfer, and injection are time sensitive, and must be performed within approximately 10 min. If the preparation of the cement goes over the allotted time, the cement hardens and injection of the cement is no longer possible. To overcome the mentioned problems, premixed calcium phosphate cements (pCPC) have been developed over the last few years. A pCPC is based on calcium phosphate powders mixed with a non-aqueous water-soluble liquid; e.g. glycerol or poly(ethylene glycol) [14–16]. Since the setting of these cements commences when the liquid phase is exchanged with water or body fluid, these cements could be stored and delivered in a syringe. This eliminates the stress related to the preparation of conventional water-mixed CPC's in the operating room. Both apatite [17,18] and acidic [15,16] pCPCs have been reported. In vivo evaluation of pCPCs has demonstrated similar behavior as conventionally water-mixed cements [19,20], making them a viable alternative. Although the water-mixed acidic cements set within a few minutes [15], due to the slow water–glycerol exchange the setting of the acidic pCPC is more time consuming [15,16]. To make the pCPC interesting commercially, the setting time needs to be reduced. It is probable that addition of small amounts of water to the cement mixture could reduce the setting time but it is not known how much is needed in order to achieve clinically relevant times. The objective of this study was to investigate the influence of small amounts of water on injectability, setting time, working time and mechanical properties of an acidic premixed cement mixture.

2. Method

2.1. Cement preparation

The powders used in the study were β-tricalcium phosphate (β-TCP, Fluka) and monocalcium phosphate hydrate (MCPH, Alfa

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http://dx.doi.org/10.1016/j.msec.2012.09.026

Aesar). The MCPH was dried in 110 °C for 3 days in order to remove all water, resulting in monocalcium phosphate anhydrous (MCPA) [21]. MCPA was used to facilitate the control of water content in the cement mixture. β-TCP and MCPA were stored in a desiccator over silica gel. For all cements the molar ratio used for MCPA and β-TCP was 1:1. Glycerol (anhydrous, Sigma) was used as a mixing liquid. Water was deliberately added to the mixture in percent of the total weight; 0, 1.7, 3.4, 5.1, and 6.8 wt.%, and four batches were made per group. The powder to glycerol (P/G) ratio was kept at 4.0 g/ml for all cements. Therefore, the total powder to liquid ratio (P/L) was lower for cements containing more water. A vacuum mixer (Twister, Renfert) was used for all mixing. First water was added to glycerol and hand mixed for some seconds before MCPA was added and all components were mixed for 50 s using the vacuum mixer. β-TCP powder was added and everything was mixed twice for 50 s. Between each mixing the cement attached to the wall and paddle was loosened in order to obtain homogenous cement pastes.

2.2. Working time

Working time of the cements was evaluated by preparing two batches with 0, 1.7 and 3.4 wt.% water each. Cements with higher than 3.4 wt.% water content could not be injected after 15 min and were, therefore, not evaluated further. The P/G for 1.7 and 3.4 wt.% was 4.0, while the P/G for 0 wt.% was slightly lower at 3.75, in order to start with comparable extrusion forces at $t=0$. Syringes with a barrel diameter of 8.55 mm and an outlet diameter of 1.90 mm were filled with approximately 1 ml of paste at $t=0$ and the syringes were stored in a dry environment at room temperature until they were tested. The force needed to extrude the paste from the syringe at a cross-head speed of 60 mm/min was measured continually until the cement was too viscous to be extruded from the syringe, i.e. the piston folded at $F=240$ N. The time between measuring points was different for varying water contents in order to get approximately the same amount of measuring points for all cements.

2.3. Injectability

Injectability of the cements was evaluated with the use of a universal testing machine (Shimadzu AGS-H). The force needed to extrude the paste from a 3 ml disposable syringe with a barrel diameter of 8.55 mm and an outlet diameter of 1.90 mm at a cross-head speed of 60 mm/min was measured. The value obtained was the mean force between 10 and 30 mm displacement. From each batch three measurements were performed, the first starting 5 min after finishing mixing and the last starting 9 min after finishing mixing, resulting in a total of 12 measurements per group.

2.4. Setting time (ST)

Five cylindrical molds, ∅ 6 mm, height 3 mm, were filled with cement. The filled molds were immersed in 37 °C phosphate buffered saline solution (PBS, pH 7.4, Sigma) 5 min after finishing mixing. Setting time was measured from the immersion in PBS. The cement was considered to have set when the sample could support a 453.5 g Gillmore needle with a tip diameter of 1.06 mm without breaking. The five samples were tested consecutively every 3 min. The mean between the time when the sample supported the weight and the previous time where the sample broke under the load was regarded as the setting time. A total of 8 measurements were made per group.

2.5. Compressive strength

Cylindrical molds, Ø 6 mm and height 12 mm were filled with cement and immersed in 50 ml PBS at 37 °C in a sealed beaker. After 24 h the samples were removed from the molds and carefully polished to make the sample sides parallel and obtain uniform height. The maximum compressive stress until failure was measured using a universal testing machine (Shimadzu AGS-H), with a cross-head speed of 1 mm/min. A thin plastic film was placed between the sample and the cross-head in order to reduce the effect of potential surface defects. A total of 12 samples were made for each group.

2.6. SEM

To study the pore structure of the set cements, the cross-sections were investigated with scanning electron microscopy (SEM, LEO 1550, Zeiss). The samples were polished using 1200 grit SiC paper. A thin gold/palladium coating was sputtered onto the surface before analysis to avoid charging of the surface.

2.7. X-ray diffraction (XRD)

The resulting phase composition of the cements after setting was analyzed using XRD (diffractometer, Siemens). Diffraction angles (2θ) 20–40 were analyzed at 0.45°/min. The set samples were crushed using a mortar prior to analysis.

3. Results

3.1. Working time

The working time was clearly altered with the change in water content. As can be seen in Fig. 1, the force needed to extrude the 3.4 wt.% paste increased much faster than the force needed for 1.7 wt.% paste. In addition, the extrusion force of the cement with no water only increased slightly during the first 6 h. Furthermore, the cement containing 3.4 wt.% water was ejectable for 2–2.5 h, the cement with 1.7 wt.% water for 5–6 h, while the cement containing no water could be stored at room temperature up to 2 weeks before it could no longer be ejected from the syringe.

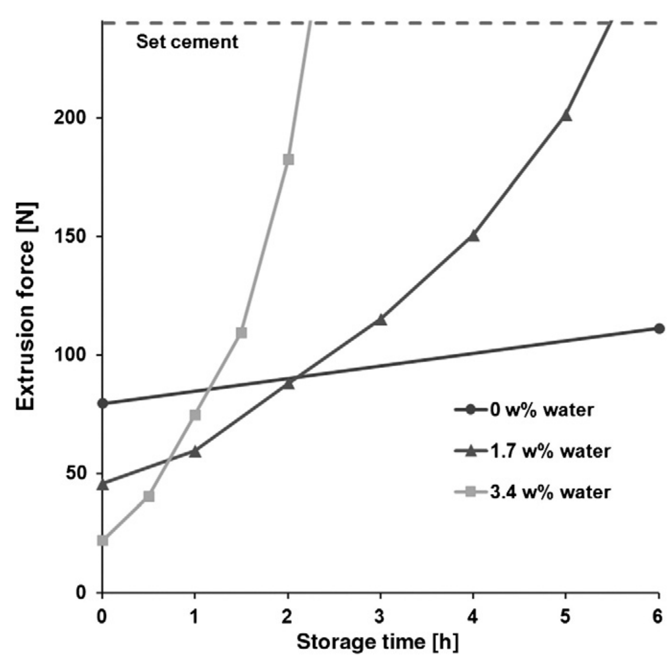

Fig. 1. Working time test for 0 wt.%, 1.7 wt.% and 3.4 wt.% water. ($n=2$).