

New Generation Calcium Phosphate Bone Cement

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Statement of Purpose: Calcium phosphate (CaP) cements (CPCs) were discovered two decades ago and generally based on a combination of two or more calcium salt reacted together in an aqueous media to form a putty-like paste consistency. Based on the type of chemical reaction, three major types of cement are identified [1]: acid-base cements, monocomponent cements, and hydrolysable cements.

The purpose of this paper is to report a new generation of monocomponent CPCs (based on amorphous calcium phosphate) which were prepared by using a high energy milling process, and to compare physico-chemical and mechanical characteristics of this CPC with commercially available cements.

Methods: An amorphous calcium phosphate (ACP) (with $\text{Ca/P} < 1.5$) and dicalcium phosphate dihydrate (DCPD) seeded with apatite (10-25% w/w) were prepared using a low temperature double decomposition technique. Two powders (at a 1:1 ratio) were high energy ball milled from 1 to 24 hours. The process is performed in a rotating ceramic jar that agitates the media (high density ZrO_2 balls, with $\text{Ø} = 10$ mm) into a random state of motion of internal porosity called kinematic porosity [2]. The physico-chemical and mechanical performance of 3 hours milling CPC (referred as γ -BSM) was investigated, and compared with some existing CPC in the current market.

Results: The high energy mechano-chemical process first reduces the particle size of bulk CaP (mixture of ACP and DCPD) powder (initially less than $50 \mu\text{m}$) and then compacts them together to form agglomerates. In longer residence time (over 10 hours) the materials are partially or completely amorphized as confirmed by FTIR and XRD. The tap density of CPC powder increases rapidly (about 45%) during the first hours of milling, and then slowly increases to a steady value after three hours of milling (Figure 1). The liquid to powder ratio (L/P) that forms a putty-like paste consistency decreases dramatically (about 62%) after 1h milling and slowly decreases to a steady value after 3 hours to reach $0.4 \text{ cm}^3/\text{g}$ confirming the affect of powder densification. The paste density follows a trend similar to tap density, but a drop observed beyond 10 h milling could be related to amorphization of CaP. The total porosity of hardened cement decreases from 61 to 30%, confirming also powder inter-granule compacting. The cement chosen in this study underwent 3 hours of milling (γ -BSM), had a L/P ratio of $0.4 \text{ cm}^3/\text{g}$, hardened in less than 3 minutes (at 37°C), and reached a peak compressive strength of about 50 MPa after 2 hours of incubation. The final product (after hydration, incubation and fully conversion) was low

crystalline carbonated calcium deficient ($\text{Ca/P} = 1.45$) apatite, with a specific surface area range of $180\text{-}200 \text{ m}^2/\text{g}$ and having nano-sized crystal (Length = 26 nm, and Width-Thickness = 8 nm). These crystal sizes are analogue to human bone mineral crystal which was reported to be: $L = 23\text{-}32$ and $\text{Th} = 6.7\text{-}8.0$ [3].

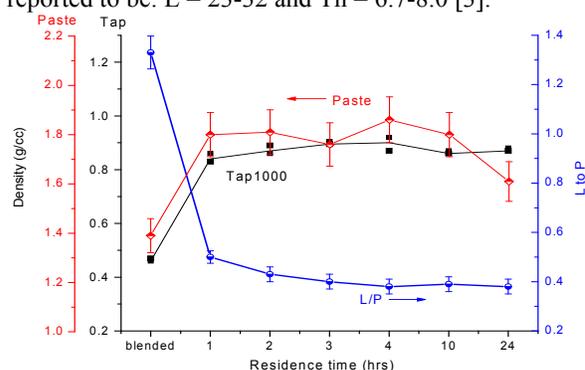


Fig 1: Tap and paste density and L/P ratio vs. time Comparative performance of γ -BSM with some commercially available CPC showed that this new cement had a longer working time (10-15 min vs. 2-6 min) at room temperature, and was fast setting (2-3 min vs. 8-12 min) at body temperature.

Conclusion: In the high energy dry mechano-chemical technique, the media and CaP powder are free to move, collide, impinge upon each other and generates shear. The simultaneous media-powder collision and friction, generating (local) heat to hygroscopic CaP, causes an inter-diffusion of particles, and produces structural (amorphization) and chemical changes. After 3h milling, new nano-crystalline CPC with faster setting and greater strength was produced. The fast-hardening reaction could be related to the rapid hydrolysis (about 1 hr) of unstable ACP into apatite [3]. DCPD plays as a template and hydrolysis lasts longer (over 10 hrs). The existence of an epitaxial relationship [4] between DCPD and apatite probably favors nucleation of apatite.

References: [1] Rey C., Tofighi A. et al., *Actualites en Biomateriaux* 2002 ;VI:27-37, Ed. Romillat, Paris. [2] Just A., *Union Process Inc.*, 1997, Akron, Ohio. [3] Tofighi A. et al., *Key Engineering Materials* 2001;192-195:769-772. [4] Francis MD. et al. *Calcif. Tissue, Res.* 1971;6:335.