**α-TRICALCIUM PHOSPHATE- AND TETRACALCIUM PHOSPHATE/DICALCIIUM PHOSPHATE-BASED DUAL SETTING CEMENTS**


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Abstract—“Dual-setting” calcium phosphate cements (DS-CPCs), characterized by a polymerization reaction that proceeds along with the conventional hydraulic setting, were prepared and studied. Acrylamide (AA), 2-hydroxyethyl methacrylate (HEMA), and N-vinyl-2-pyrroldone (VP) in 5, 10, and 20 wt./vol.-% were added to the liquid of α-tricalcium phosphate (α-TCP) and tetracalcium phosphate/dicalcium phosphate anhydrous (TTCP/DCPA) conventional cements. N,N′-methylenebisacrylamide was used as cross linking agent. N,N,N′,N′-tetramethylethylenediamine in the liquid, and ammonium persulfate in the powder, were employed as polymerization catalyst and initiator, respectively. Diametral tensile strength (DTS), setting time, phase composition, conversion rate, and microstructure of the DS-CPC were compared with those of non-added cements. The DTS increased 22 % for α-TCP and 85 % for TTCP/DCPA DS-CPCs by adding 20 wt./vol.-% AA. The HEMA and VP had no positive effect on DTS. The extent of the hydraulic setting reaction for α-TCP DS-CPC was only slightly decreased by the addition of 20 wt./vol.-% of AA to the mixing liquid.

Keywords—calcium phosphate cement, dual-setting, α-tricalcium phosphate, tetracalcium phosphate, hydroxyapatite.

1. INTRODUCTION

Calcium phosphate cements (CPC) are very promising materials for dental, orthopedic, and maxillo-facial applications because of their excellent biocompatibility and injectability. CPC based on α-Ca₃(PO₄)₂ (α-TCP) sets as the result of the precipitation of an entanglement of apatite crystals according to Eq. 1 (Driessens et al., 1993).

$$3\alpha\text{-Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{O} \rightarrow \text{Ca}_9(\text{HPO}_4)(\text{PO}_4)_5(\text{OH})$$ (1)

The resulting apatite is similar to bone mineral, and has excellent biocompatibility, bioactivity and osteointegability (Driessens et al., 1997).

However, the low strength of α-TCP CPC, especially shortly after initial setting, is a handicap that restricts its clinical applications (Ginebra et al., 1997).

On the other hand, a water-soluble “in situ” polymerizing system based on acrylamide (AA), N,N′-methylenebisacrylamide (MBAA), ammonium persulfate (AP, initiator), and N,N,N′,N′-tetramethylmethylenediamine (TEMED, accelerator) was first employed in gel-casting technology to bind together the particles of an aqueous slurry of ceramic powder. When polymerization is conducted a cross-linked polyacrylamide hydrogel is formed that binds and immobilizes the powder and provides with strength the resulting green body. Gel-casting technology has been successfully employed to manufacture hydroxyapatite ceramics (Padilla et al., 2004).

In addition, the gel casting approach has been proposed to reinforce α-TCP-based CPC during the first stage of setting (Garcia Carrodeguas et al., 1999; Santos et al., 1999; Davidenko et al., 2002). The polyacrylamide network formed in the so-called “dual-setting” CPC effectively reinforced the material and is non toxic; however, residual acrylamide monomer may be released from the polyacrylamide hydrogel. Neurotoxic effects in humans, and carcinogenicity and reproductive disorders in rodents have been associated to exposure to acrylamide monomer. Also, abnormal transformations in S Rican hamster embryo cells cultured in presence of this monomer have been observed (Park et al., 2002).

The gel casting approach has not been used to modify and improve the short term strength of other than α-TCP CPC. However, tetracalcium phosphate/dicalcium phosphate anhydrous (TTCP/DCPA) CPC produces also apatite by setting according to Eq. 2 (Brown and Chow, 1983) and has been extensively studied in *vitro* and *in vivo* with remarkable results. It also has low strength during the first stages after initial setting (Chow et al., 1994).

$$2\text{Ca}_9(\text{PO}_4)_2\text{O} + 2\text{CaHPO}_4 + \text{H}_2\text{O} \rightarrow \text{Ca}_10(\text{PO}_4)_3(\text{OH})_2$$ (2)

Accordingly, this work was aimed to evaluate other non toxic monomers, like 2-hydroxyethyl methacrylate