Characterization of the Effects of Calcium Polyphosphate Addition to an Apatitic Calcium Phosphate Cement

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Statement of Purpose: Self-setting calcium phosphate cements (CPCs) are of great interest in bone regeneration applications because of their biocompatibility and osteoconductivity, and as delivery vehicles for several classes of therapeutics including antibiotics.[1,2] However, the relatively poor mechanical properties of CPCs limit their use for most load-bearing applications, while interactions between therapeutics and the cement setting reaction have raised some practical limitations for therapeutic delivery.[3,4] Apatitic CPCs are also minimally biodegradable.[2] Amorphous calcium polyphosphate (CPP) is a biodegradable inorganic polymer that is hygroscopic in nature.[5] These unique physical attributes and its capacity for drug delivery have led us to consider CPP incorporation in a CPC as a possible means of addressing some of the above deficiencies of CPCs.[6,7] To that end, the purpose of this work is to investigate the effects of incorporating CPP into a conventional CPC on the setting behaviour, mechanical properties and degradation behaviour of the cement.

Methods: CPP was synthesized from monobasic calcium phosphate monohydrate (MCPM) according to an established method.[5] The reference CPC consisted of an equimolar powder of dicalcium phosphate anhydrous (DCPA) and tetracalcium phosphate (TTCP) to which a 0.25M sodium phosphate solution was added.[8] Two approaches to CPP addition were considered in order to examine the role of CPP in the setting process: the CPP either replaced a fraction of the DCPA, or was added as filler while maintaining the DCPA/TTCP ratio. Five experimental groups were studied in addition to the reference CPC: 1) 5 mol% CPP (sub); 2) 5 mol% CPP (filler); 3) 15 mol% CPP (sub); 4) 15 mol% CPP (filler); and 5) 30 mol% (filler). Preliminary characterization of setting time was by the Gilmore needle method. Structure and morphology of the set CPCs were studied using powder x-ray diffraction (XRD) and scanning electron microscopy (SEM), while mechanical properties were assessed using standard compressive strength (CS) and diametral tensile strength (DTS) testing.

Results: The Gilmore needle tests did not reveal any significant differences in setting time between the reference CPC and the experimental groups. A more comprehensive study of cement setting behaviour using rheometry is planned. Mechanical testing revealed an initial increase in dry DTS with increasing CPP fraction, indicating that the added CPP may possibly act as a reinforcing phase. However, wet samples tested after ~22 hrs immersion in ddH_2O showed a significant decrease in CS for samples containing CPP compared to the reference CPC, an outcome likely tied to a degradation response. SEM imaging of set cement fracture surfaces (Figure 1) revealed a more homogeneous matrix for the reference CPC than for the 5 mol% CPP (sub) sample in which distinct particles are visible (arrows). XRD analysis of samples after immersion showed peaks consistent with hydroxyapatite (HA), DCPA and TTCP for the reference CPC. Several DCPA and TTCP peaks were much stronger in the spectrum obtained for the 5 mol% CPP (sub) sample compared to the reference CPC, while the intensity of HA peaks was reduced. These results suggest that substitution of DCPA by CPP limits conversion of the reactants, indicating that the role of CPP in setting is not equivalent to that of DCPA.

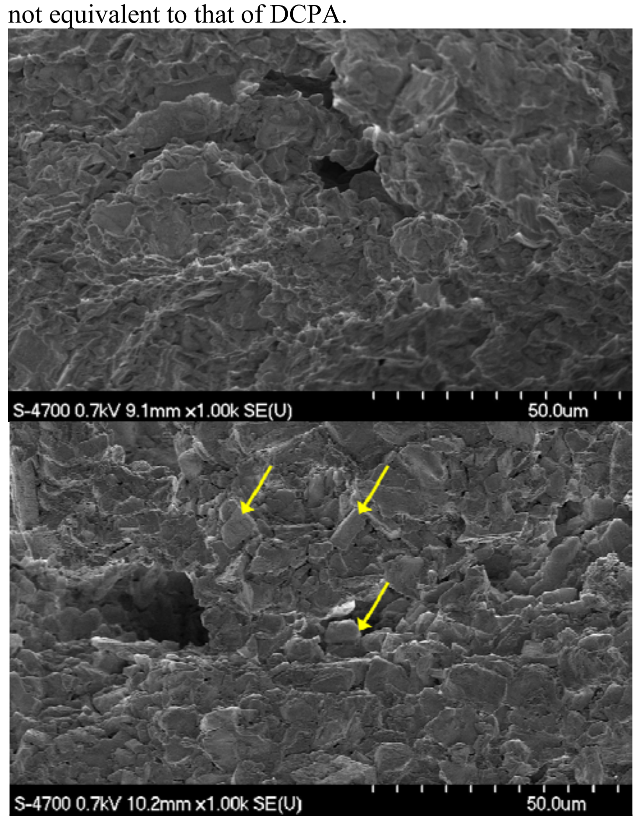

Figure 1. SEM images of fracture surfaces of (top) reference CPC and (bottom) 5 mol% CPP-CPC (sub).

Conclusions: Preliminary results indicate that the addition of CPP to an apatitic CPC improves initial mechanical strength and contributes to subsequent degradation of the cement. Future studies will more fully characterize the mechanical strength and microstructure of the cements through setting and long-term exposure to an aqueous environment. Further investigation into the role of CPP in the setting process is also required.

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