Fiber Reinforced Calcium Silicate Phosphate Bone Cements

Azadeh Goudarzi[1], Tom Troczynski[1], N. Dorin Ruse[2]
[1] Materials Engineering, Faculty of Applied Science, University of British Columbia, Vancouver, Canada
[2] Biomaterials, Faculty of Dentistry, University of British Columbia, Vancouver, Canada

Statement of Purpose: Tricalcium silicate (C_3S) based cements have higher strength than calcium phosphate cements and better biological properties that PMMA based bone cements. C_3S cement is self-setting, hydraulic, bioactive and osteoconductive [1,2]. It hydrates to calcium silicate hydrate (CSH) gel and calcium hydroxide (CH). In vivo study has shown its ability to regenerate bone; ~50% resorption of the cement was measured after 12 months [3]. However, setting C_3S has high pH (~11), long setting time (~3 h) and relatively low fracture toughness (~0.1 MPa√m). Addition of monocalcium phosphate monohydrate (MCPM) decreases pH and enhances bioactivity of the cement [4], by reacting with CH to precipitate amorphous and crystalline phosphates. We hypothesize that cement toughness can be increased by micro-fiber reinforcement. Due to the slow rate of cement resorption, it is anticipated that the fibers will be embedded within the newly grown bone.

Methods: Tetraethyl orthosilicate and calcium nitrate tetra hydrate aqueous solution were used in a sol-gel synthesis followed by firing at high temperature to obtain C_3S powder. All chemicals were reagent grade. Four groups were prepared: (C) is C_3S; (C-10M) is C_3S with 10 wt% MCPM; (C-3CF) is C_3S with 3 wt% of 7 μm diameter/3 mm long carbon fibers; and (C-10M-3CF) is C_3S with both 10 wt% MCPM and 3 wt% of the same carbon fibers. After mixing (at water/powder ratio ~0.4), the cements set for 10 days at 37˚C. Fracture toughness (K_{IC}) was measured using the notchless triangular prism (NTP) specimen test [5]. Compressive strength was determined on 12mm tall by 6mm diameter cylindrical samples. At least three samples were tested to determine the average strength and toughness. The samples were further characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and densitometry.

Results: The presence of un-reacted C_3S was determined in all samples by XRD phase analysis. Portlandite (CH) represents the degree of the hydration reaction of calcium silicate, as CSH gel is amorphous and thus does not have distinctive XRD pattern. In set C-10M samples, the relative intensity of the C_3S to CH peaks was lower than in pure C_3S, which could be attributed to the reaction of CH with MCPM. There were also monetite peaks in C-10M pattern, which could be an intermediate phase before formation of hydroxyapatite, the most thermodynamically stable phase in this system. Table-1 shows that significant improvement in the compressive strength and K_{IC} was obtained after addition of carbon fibers to both C and C-10M samples. Addition of CF has not considerably affected the porosity of C_3S, but MCMP has increased the porosity in C_3S. Reaction of the CH and MCPM results in formation of water [4], which may lead to increased porosity.

Table-1- Compressive strength and K_{IC} of C_3S with MCPM and carbon fibers

Sample Name	Strength (MPa)	K_{IC} (MPa√m)	Porosity (%)
C	54.8±0.60	0.120±0.017	37.7±0.1
C-10M	50.9±4.63	0.197±0.020	45.4±0.6
C-3CF	88.3±5.90	0.487±0.025	37.3±0.9
C-10M-3CF	80.2±6.28	0.398±0.054	41.8±0.4

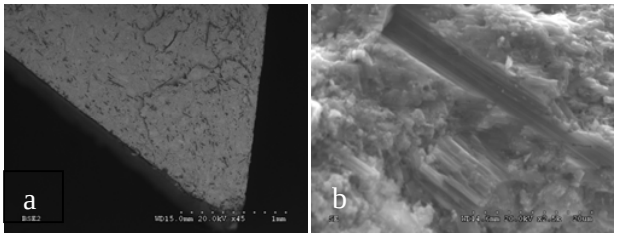

Fig. 1- SEM of fractured surface of C-10M-3CF sample

SEM images of the fractured surfaces suggest that the mechanism for toughening was mainly fiber pull out. The pull-out grooves can be seen in Fig.1b. Figure 1a shows the macro image of the triangular prism fractured surface and the distribution of the fiber in the matrix.

Conclusions: Carbon fiber reinforced calcium silicate phosphate cements were processed and evaluated. Compressive strength increased by factor 1.5-1.7 and K_{IC} increased by factor 2.0-2.5 upon addition of 3 wt% of the fibers. The dominating toughening mechanism appears to be fiber pullout, in which the energy is dissipated by the frictional work done in the fiber-matrix interface during the pull-out [6]. To our knowledge, this is the first time that the fiber reinforced calcium silicate phosphate composite cement have been processed and characterized. We believe that the C-10M-3CF cements, with relatively good mechanical properties (~80 MPa compressive strength and K_{IC}≈0.4 MPa√m) could be applied as bone cements. The follow-up of this research will include biocompatibility and osteoconductivity evaluations by *in vitro* tests, resorption rate determination *in vitro* and *in vivo*, and the use of accelerators to control the cements' setting time.

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