Reinforced Magnesium Phosphate Cement with Wet-spun PCL Fibers

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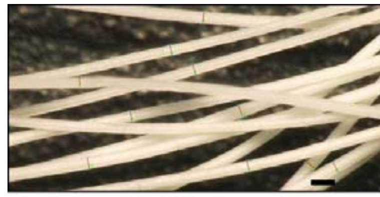
Statement of Purpose: The concept of reinforcement through fibrous inclusions is widely utilized in the commercial cement industry to improve the fracture toughness and reduce catastrophic brittle failure of concrete. The same principle, only at a smaller scale, is under exploration for ceramic bone cements. Use of polymer fibers may improve the toughness, decrease brittle fracture and improve the ability of the cement systems to withstand drilling stresses [1.2]. While current studies have focused on calcium phosphate bone cements, in this study a magnesium phosphate cement system is explored because recent studies have shown magnesium phosphates may have higher initial strengths and faster resorption rates than the calcium counterparts [3,4]. In this study, biodegradable polycaprolactone (PCL) fibers are created and utilized. The inclusion of degradable fibers serves dual purposes: reinforcement of the cement when first implanted and the generation of interconnected porosity to promote cellular infiltration during fiber degradation. Additionally, the use of degradable, in-house generated fibers may permit the further development of a complex cement system, wherein the fibers also serve as a delivery system for DNA, nanoparticles, genes or drugs such as BMP-2 and gentamycin [5].

Methods: PCL fiber solution was composed of a 50:50 mixture of acetone and THF with PCL(mw:70-90K) loaded at 2grams/10mL solution. The dissolved polymer solution was mixed for 48hours, then injected into dual ethanol coagulation baths at 5 mL/h from a 16g needle with a linear collection rate of 250cm/min. Fibers were dried in a desiccator following collection, and then cut into 1.5mm long strips for use in cements. Fibers were imaged using digital optical microscopy and the elongation to break of individual fibers was measured using a UTS. Commercial tri-magnesium phosphate hydrate (TMP) was thermally treated (1000°C, 6h) to reduce the surface area. Series of cements were created by gently mixing TMP powder with varying weight percentage additions of PCL fiber in a random, non-aligned fashion, followed by the addition of ammonium phosphate reacting solution of 3.0M at pH 7.0 to create cements. Setting time measurements (1st and 2nd) setting times (ST) were determined using a Gillmore needle apparatus. Handling characteristics were qualitatively assessed based on consistency and injectability. Resulting cements were incubated in PBS at 37°C and mechanical evaluation was completed through compression testing.

Results: The use of a dual ethanol coagulation bath wet spinning system to create PCL fibers reliably generated opaque fibers of 100μm in diameter under the conditions stated above, as seen in **Figure 1**. Altering a variety of the parameters (concentration, MW, solvent and coagulant solutions, collection rate) yielded a wide variety of fiber diameters and morphologies (not presented). The fibers were able to undergo a large amount of plastic elongation prior to rupture, on average more than 600%. This level of deformation is expected to improve the flexibility and toughness of cement while reducing the ultimate strength of the cement.



Wet Spun PCL Fibers	
Length (μm)	1446.2 ± 238.4
Diameter (μm)	101.6 ± 15.5
Elongation (%)	637.30± 119.0

***Figure 1**. Example image of PCL fibers (Scale: 200μm) and fiber properties.*

Cements generated with up to 15 weight % PCL fiber resulted in setting times of 6:30-9:00 minutes first ST and 12:30-15:00 minutes second ST. Up to 10% fiber results in a putty which is moldable but not flowable at P:L of 7:5. At 15% fiber, the cement consistency during mixing is more sponge-like and difficult to handle. After setting, all embodiments resulted in cement bodies which were durable to the touch. **Figure 2** shows compressive strengths and representative macroscopic failure images of fiber reinforced cement samples. The addition of 5 weight % PCL fibers increased the compressive strength of the cement, followed by a sharp decrease at 10 weight % fiber. Visually, the improvement in catastrophic brittle failure is evident in the fiber containing samples, which remain bound together, retaining incremental levels of strength after the initial fracture which the unreinforced sample are unable to retain. Although compressive strength is a benchmark indicator of the fibrous cement performance, ongoing studies will assess the flexural strength and fracture toughness of the cements, both of which are better determinants of the cement performance, while continuing to test additional levels of fiber addition in the 5-10% range to assess the turning point in compressive strength.

Cements	Strength (MPa)
0 wt% Fiber	33.56 ± 0.74
5 wt% Fiber	39.90 ± 2.61
10 wt% Fiber	18.24 ± 1.64
15 wt% Fiber	14.61 ± 3.67

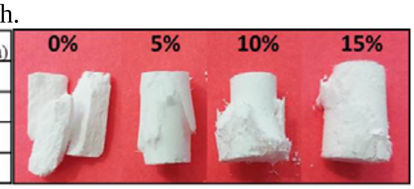


***Figure 2**: Cement strength and macro images of failure.*

Conclusions: Wet spinning of high molecular weight polycaprolactone solution through a dual ethanol coagulation bath system results in reliably produced, 100μm diameter PCL fibers. These fibers were introduced into a model magnesium ammonium phosphate cement system to test the handling and mechanical resilience of the resulting cement. In particular, the 5weight% fiber system resulted in higher strengths than the baseline system which retaining good workability and set times.

References: [1]Vasconcellos LA. Mat. Sci Engr C. 2013; 33:1032-1040. [2] Xu HHK. J. Biomed Mater Res. 2001; 57:457-466. [3]Mestres G. Acta Bio. 2011; 7:1853-1861. [4] Klammert U. J. Mater Sci: Mater Med. 2010; 21:2947-2953. [5] Lavin DM. Acta Bio. 2013; 9:4569-4578