Mechanical Properties of Poly(propylene fumarate) Reinforced Brushite Cement: Effects of Cement Composition and Powder to Liquid Ratio

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Statement of Purpose: Calcium phosphate cements are prepared by mixing calcium phosphate powder with a liquid component to form a paste that hardens over time via a dissolution-precipitation reaction. Thus, in addition to being osteoconductive and resorbable, these biomaterials have the advantageous property of being injectable. This property can be leveraged for casting-based approaches to scaffold fabrication. While brittleness has previously limited the use of calcium phosphate cements as bone tissue engineering scaffolds, it is possible to reinforce these biomaterials by infiltrating them with a polymer and then cross-linking the polymer *in situ*. Our lab is interested in developing a poly(propylene fumarate) (PPF) reinforced brushite cement scaffold. PPF is an unsaturated polyester that has previously been used in bone tissue engineering. Brushite cement, on the other hand, is of interest because it has shown excellent resorbability and enhanced bone formation *in vivo* compared to hydroxyapatite cements. One variable that will affect the mechanical properties of the reinforced composite is the cement composition. Brushite cement is typically prepared by mixing monocalcium phosphate monohydrate (MCPM) and β-tricalcium phosphate (β-TCP) with water, and the MCPM:β-TCP molar ratio is known to affect the mechanical properties as well as the acidity of the cement. The powder to liquid mass ratio (P/L) used during cement preparation is another important variable, as it controls the cement porosity, and consequently how much polymer can be incorporated into the cement. Thus, the objective of this study was to characterize the effects of these two variables on the mechanical properties of PPF reinforced brushite composites.

Methods: A 2x2 design was used to investigated the effects of MCPM:β-TCP molar ratio and P/L. MCPM and β-TCP were dry mixed in 1:1 and 1:3 molar ratios, and then mixed with deionized water in P/L of 1.0 and 1.5. Bar-shaped specimens (2 mm x 2 mm x 25 mm) were prepared by pressing the unhardened cement paste into a stainless steel mold. After setting, the cements were removed from the mold and dried thoroughly under vacuum in a dessicator chamber. Powder x-ray diffraction was used to characterize compositional differences between the 1:1 and 1:3 treatments. Specimens were scanned from 5 to 40 degrees 2θ at 1 degree/min. Reinforcement was achieved by submerging the samples in a 4:3 mass ratio mixture of PPF (M_n = 1,700 g/mol) and N-vinyl pyrrolidinone with 5 wt % benzoyl peroxide and 0.1 wt % butylated hydroxytoluene and applying vacuum. The specimens were at 80°C for 24 hours under vacuum. Mechanical properties were characterized by three point bending. Flexural strength, flexural modulus, maximum displacement during testing and work of fracture were calculated. The trends were correlated to the mass of polymer incorporated.

Results: Powder x-ray diffraction showed that while the 1:1 MCPM:β-TCP molar ratio consisted of predominantly brushite, the 1:3 MCPM:β-TCP cements contained a mixture of brushite and unreacted β-TCP. This difference had an interesting effect on the extent of polymer incorporation. For the 1:1 cements polymer incorporation was 0.38 ± 0.02 mg/mm^3 and 0.20 ± 0.02 mg/mm^3 at P/L of 1.0 and 1.5 respectively, while for the 1:3 cements polymer incorporation was increased to 0.58 ± 0.03 mg/mm^3 and 0.41 ± 0.04 mg/mm^3 at P/L of 1.0 and 1.5 respectively. This trend was likely due to porosity differences, as β-TCP is more dense than brushite, and it resulted in differences in the mechanical properties of the composite (Figure 1). For the 1:1 cements with P/L of 1.0, reinforcement greatly increased the flexural strength, maximum displacement and work of fracture compared to non-reinforced controls. However, due to the reduced polymer incorporation, only small increases were seen at P/L of 1.5. In contrast, because polymer incorporation was increased in the 1:3 cements, large increases were seen for both P/L of 1.0 and 1.5. Interestingly, the modulus appeared to be dominated by the polymer phase. This result was possibly due to cement microcracking, which we previously correlated to polymerization shrinkage.

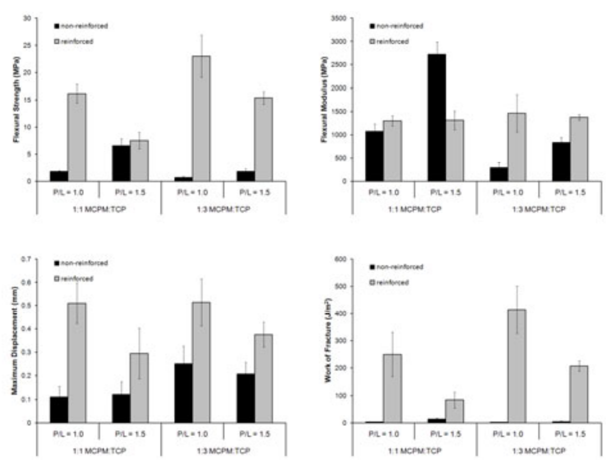

Figure 1. Results from three point bending.

Conclusions: PPF reinforcement greatly improves the mechanical properties of brushite cement. However, the efficacy is directly related to the extent of polymer incorporation, which can be controlled by adjusting the MCPM:β-TCP ratio and the P/L. Future studies should seek to tune these parameters to develop an optimized bone substitute.