Surface modification optimization of poly(methyl methacrylate) microspheres for use in two-solution bone cements

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Statement of Purpose: Two-solution bone cements have been developed as an alternative to powder-liquid bone cements, in order to reduce the porosity[1]. Nevertheless, these cements have a relatively low polymer-to-monomer ratio (P:M 0.9:1). We have developed two-solution bone cements in our laboratory, comprised of cross-linked Poly(methyl methacrylate) (PMMA) microspheres and linear PMMA in methyl methacrylate (MMA) monomer. These cements are composites with cross-linked PMMA microspheres and polymerized PMMA matrix phase. The surface of the PMMA microspheres have been modified with ethanolamine followed by acryloyl chloride to attach reactive carbon-carbon double bonds (C=C) on the surface[2], for use in two-solution bone cements[3]. The C=C on the surface of the microspheres are hypothesized to form covalent bonds between the surface of the beads and the matrix. The goals of this study were to evaluate the effect of modification on viscosity and optimize the surface modification of PMMA microspheres in order to increase the reactive groups on the surface and hence improve the mechanical properties by promoting better interfacial adhesion between the microspheres and the PMMA matrix.

Methods: Surface modification: A two stage modification reaction was adopted from Jayachandran et al.,[3] to add C=C on the surface of the microspheres. Cross-linked PMMA microspheres were modified to add hydroxyl terminal groups on the surface by varying the ethanolamine-PMMA molar ratios. An ethanolamine concentration of 2.013 ml/g PMMA was chosen for further modification by varying the molar ratios of acryloyl chloride to ethanolamine from 0.8:1 to 1.4:1. FTIR spectroscopy was used to estimate the concentration of amide and C=C groups on the surface of the beads.
Mechanical Testing: Cement samples with modified and unmodified PMMA microspheres were prepared at a P:M ratio of 1:1 and cross-linked polymer to linear polymer ratio (P_b:P_l) of 2:1. Fracture toughness and three point flexural tests were performed on two-solution bone cement samples with unmodified PMMA microspheres and modified PMMA microspheres with varying acryloyl chloride concentrations, as per ASTM standards.

Results: FTIR analysis of ratios of characteristic peak areas showed an increase in amide groups with an increasing molar ratio of ethanolamine to PMMA, with the degree of functionalization saturating at a ratio of 3.077. An increase in the C=C concentration was also observed with increasing acryloyl chloride to ethanolamine molar ratios, with a maximum at 1:1. Surface modification of PMMA microspheres significantly affected the properties of two-solution bone cements. Cements prepared with surface modified PMMA microspheres exhibited significantly higher fracture toughness values versus cements with unmodified microspheres at the same P:M ratio and P_b:P_l ratio ($p<0.05$). There was also a significant difference in fracture toughness values for cements containing modified microspheres with 1:1 and 1.2:1 molar ratios of acryloyl chloride:ethanolamine versus the other molar ratios ($p<0.05$) as shown in Figure1. Micrographs of fracture surfaces of cements with these compositions showed better interfacial adhesion between the microspheres and the cement matrix as opposed to cements with unmodified microspheres as indicated in Figure 2. The surface of the cement sample with modified microspheres appeared rougher indicating a higher degree of matrix deformation and energy dissipation at the crack tip. Furthermore, the viscosity of cement solutions with modified microspheres was significantly lower than cement solutions with unmodified microspheres, due to a lower degree of swelling of modified microspheres in monomer.

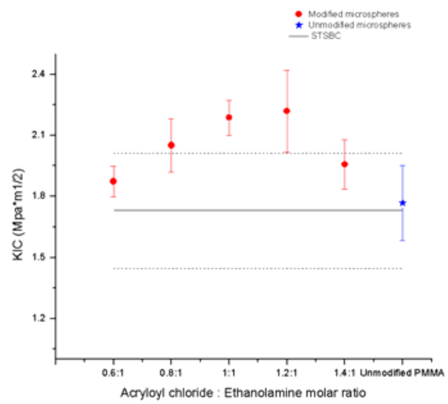

Figure 1. Fracture toughness versus acryloyl chloride concentrations.

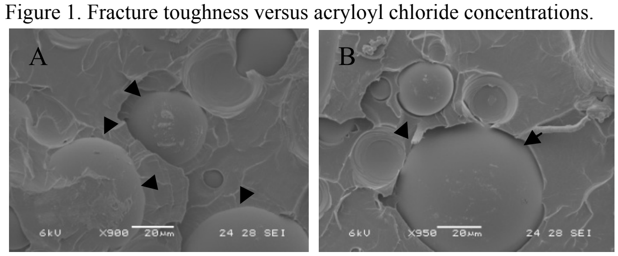

Figure 2. SEM micrographs of fracture surface of samples with (A) modified and (B) unmodified microspheres.

Conclusions: The results confirmed that increasing the concentration of ethanolamine and acryloyl chloride results in an increase in the concentration of reactive sites formed on the surface of the microspheres. The modification of the microspheres resulted in a lower degree of swelling of these microspheres in monomer, hence decreasing the solution viscosity of two-solution bone cements and allowing for a potential increase in the P:M ratio of these cements. Further the modification of microspheres results in an increased fracture toughness of cements when compared to unmodified microspheres.

References:

1. Hasenwinkel JM et al. J Biomed Mater Res 1999;47(1):36-45
2. Merkhan I.K. PhD Dissertation; Syracuse University.
2. Jayachandran et al. European Polymer Journal 2000;36(4),743-9