Examination of Radio-opacity Enhancing Additives in Shape Memory Polyurethane Foams

Andrew C. Weems[a], Jeffery E. Raymond[b], Kevin T Wacker[c], Tiffany P. Gustafson[b], Brandis Keller[a], Karen L. Wooley[b,c], Duncan J. Maitland[a]

[a]Biomedical Device Laboratory, Department of Biomedical Engineering, Texas A&M University,
[b]Laboratory for Synthetic-Biologic Interactions, Department of Chemistry, Texas A&M University,
[c]Departments of Chemistry, Chemical Engineering, Materials Science & Engineering, Texas A&M University.

Statement of Purpose: The high recovery strain and large reversible changes in elastic moduli during the transition between glassy and rubbery phases have made shape memory polymers (SMPs) appealing for a wide variety of medical devices; SMP foams particularly have gained interest for aneurysm filling and stents.[1,2] A major limitation for implantable device application of SMPs is insufficient radio-opacity for visualization using clinical fluoroscopic imaging equipment.[3] We examine the use of radio-opacity enhancing additives in SMP foam to evaluate their use as medical materials. In this study, the radio-opacity enhancing moieties tungsten (W), barium sulfate ($BaSO_4$), and zirconium oxide (ZrO_2) were physically added to SMP foams. The effects that these additives have on physical properties, thermal transitions, shape recovery behavior, and radio-opacity were characterized and compared.

Methods: N,N,N',N'-Tetrakis(2-hydroxypropyl) ethylenediamine (HPED, 99%, Sigma Aldrich), triethanolamine (TEA, 98%, Sigma Aldrich) and 2,2,4-trimethyl hexamethylene diisocyanate (TMHDI, TCI America, a mixture of 2,2,4 and 2,4,4 monomers) along with $BaSO_4$ (particle size of 3 µm, 99%, Sigma Aldrich), ZrO_2 (particle size of 5 µm, 99%, Sigma Aldrich) and W (particle size > 1 µm, 99.95%, Alfa Aesar) were used without modification. SMP thermoset foams were made using the procedures reported by Wilson and Singhal.[1,2] Density measurements were taken following ASTM standard D-3574-08 procedure. Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and thermogravimetric analysis (TGA) were used to determine thermal transitions (glass transition (T_g) and degradation temperature (T_d)). Pore sizes were compared using confocal microscopy. Shape recovery was measured using samples submerged in water at 50°C and 70°C after shape setting into a compressed cylinder over a wire; total recovery as well as the recovery kinetics were determined. Corresponding kinetic measurements were taken using an environmental DMA. Changes in radio-opacity were quantified using a Bruker In-Vivo Xtreme multimodal preclinical imaging system (Bruker BioSpin Corp.), comparing the background corrected X-ray density (X.D.) of compressed SMP foams over a monofilament line with a commercially available platinum (Pt) embolization coil and a custom Pt coil.

Results: The SMP foams demonstrated decreasing T_gs as filler concentration increased (dry samples with approximately 74°C for unfilled to 65°C for 4%W, with plasticized T_g between 48-44°C) with densities ranging from 0.012 g/cc to 0.076 g/cc. TGA examinations revealed T_d of approximately 230°C for all samples. Pore size decreased with increasing additive concentration. Total strain recovery decreased, in addition to the rate of recovery decreasing with addition of filler. Changes in strain recovery were quantified using the immersion DMA, demonstrating additives increasing the time to initiation of shape recovery. Figure 1 shows an X-ray image of the examined samples, with distinct enhancement of X.D. shown with increasing additive concentrations.

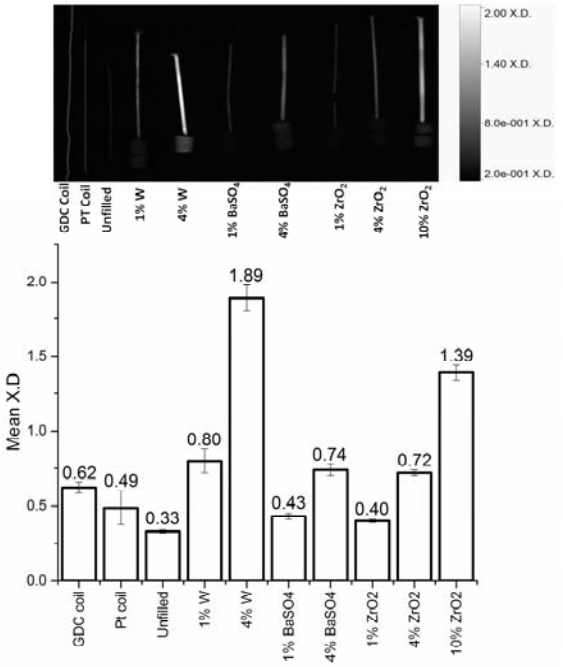

Figure 1. Qualitative (above) and quantitative (below) comparison of mean X.Ds of compressed SMPs and coils.

Conclusions: The use of radio-opacity additives showed drastic enhancements to the optical properties of SMP foams, with X.D. values exceeding those of a commercially available device. This finding, in addition to the changes in physical properties and shape recovery kinetics, could be used to develop a range of medical devices from these materials that possess varied pore sizes and recovery times. While *in vivo* degradation is not yet known, this material platform hold promise as a device scaffold for a variety of applications, where tailoring the additives used without altering the bulk chemistry provides a means for dramatically changing shape recovery time and optical properties.

References: 1.T.Wilson, J.App.Polym.Sci., 2007, 106, 540-551. 2. P Singhal, J.Polym.Sci.Pol.Phys. 2012, 50, 724-737. 3. J. Cui, Smart Mater. Struct. 2010, 19, 1-10.