Shape Memory Polymers with Novel Processing Capabilities for Biomedical Device Applications

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Statement of Purpose: Shape memory polymers (SMPs) are advanced smart materials that have the ability to actuate from a metastable geometry or geometries to a primary geometry when introduced to a stimulus such as heat or moisture. Because SMP-based biomedical implant devices can change their geometries after insertion in the body, SMPs are being considered for numerous biomedical applications.[1] Although covalently crosslinked SMPs have excellent thermo-mechanical properties, these thermoset materials cannot be mass-manufactured into complex geometries by thermoplastic processing methods such as injection molding or solution casting.[2] Consequently, the mass-manufacture of complex thermoset SMP-based medical devices is neither economically favorable nor time-efficient.[3] Our goal was to synthesize polyurethane SMPs with tunable mechanical properties that could be made into thermoplastic polymers, processed into complex thermoplastic precursors, and later crosslinked in a final curing step using electron beam irradiation to fix a permanent primary geometry.

Methods: We hypothesized that a thermoplastic polyurethane SMP series based on 2-butene-1,4-diol would be susceptible to radiation crosslinking because of the resonance stabilization of e-beam-induced α-carbamate radicals by adjacent unsaturated groups in the polymer backbone. We investigated the effects of radiation dose and radiation sensitizer composition on the crosslink density (and corresponding rubbery moduli) of the irradiated SMPs. Tris[2-(acryloyloxy)ethyl] isocyanurate (TAcIC), pentaerythritol triacrylate (PETA), and diurethane dimethacrylate (DUMA) were solution blended in THF in 2.5-25 mole % ratios with thermoplastic polyurethanes synthesized from equimolar ratios of 2-butene-1,4-diol and trimethylhexamethylene diisocyanate (TMHDI). 300 μm films were solution cast by dissolving the thermoplastic urethane and radiation sensitizer monomers in THF, pouring the mixtures in polypropylene dishes, and evaporating the THF at 1 torr at 40 °C for 72 h. Samples were then irradiated at 5, 10, 20, 50, and 100 kGy. Sol/gel analysis and dynamic mechanical analysis (DMA) were run to determine if covalent crosslinking occurred during irradiation. Differential scanning calorimetry (DSC), tensile testing, and various shape recovery experiments were run to evaluate the biomedical relevance of the new SMPs.

Results: Sol/gel analysis and DMA results provided concrete evidence that covalent crosslinking occurred during irradiation. Gel fractions approaching 100% were achievable with doses as low as 5 kGy. Rubbery moduli were tailorable between 0.1 and 72.0 MPa and could be controlled by varying both radiation dose and radiation sensitizer composition, as Figure 1 demonstrates. Further mechanical characterization demonstrated other outstanding mechanical properties, including tailorable glass transitions between 25 and 80°C, cyclic recoverable strains approaching 100%, failure strains of over 500% at T_g, toughness values as high as 50.2 MJ/m^3, and qualitative shape-recovery times of less than 12 s at body temperature for certain samples.

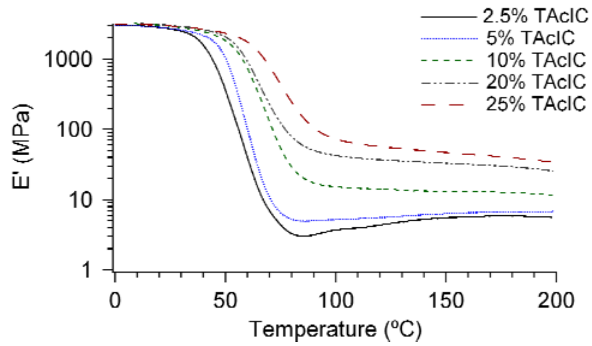

Figure 1: Plots of storage modulus versus temperature for samples irradiated at 50 kGy.

Conclusions: We developed novel polyurethane SMPs that can be first made into thermoplastic precursors and later crosslinked using electron beam irradiation. Consequently, the mass-manufacture of complex SMP-based biomedical implant devices may become more economically feasible. Furthermore, mechanical characterization of this new SMP system demonstrated that high crosslink densities and correspondingly high rubbery moduli are achievable upon irradiation. Since the recovery stress of SMPs is proportional to rubbery modulus, it is believed that this SMP system will be potentially useful in applications that demand high recovery stresses, such as self-deploying cardiovascular stents. To demonstrate the processability of this new SMP system, we molded a thermoplastic urethane into a complex medical device, an artificial oropharyngeal airway device, pictured in Figure 2.

Figure 2: Oropharyngeal airway device molded from novel urethane SMP

References:
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