Radiation Crosslinked Shape Memory Polymers for Biomedical Applications

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Statement of Purpose: Shape-memory polymers (SMP's) exhibit tunable stiffness changes at specific temperatures, making them ideal smart materials for a variety of biomedical applications. In the past, thermoset SMP's have not been used is many cost-competitive biomedical devices such as orthopedic casts and custom prosthetics, because common low-cost plastics processing techniques are difficult or infeasible with network polymers. A novel manufacturing process called *Mnemosynation*, named for the Greek goddess of memory, Mnemosyne[1], is described. In a similar vein to *Vulcanization*, which imparts recoverable elastomeric behavior on natural rubber using sulfur crosslinks, *Mnemosynation* crosslinks polymers, but by combining advances in radiation grafting[2,3] and advances in tuning thermomechanical properties of SMP's[4]. *Mnemosynation* enables traditional plastics processing (blow molding, injection molding, transfer molding, etc.) and allows thermoset SMP properties in complex geometries for cost-competitive biomedical device manufacture.

Methods: *Materials*: Methyl acrylate (MA), isobornyl acrylate (IBoA), Triallylisocyanurate (TAIC®), Trimethylolpropane triacrylate (TMPTA), *n*-isoproyl acrylamide (NiPAAm), Acryloyl morpholine (AMO), 4-*tert*-Butylcyclohexyl acrylate (tBCHA), 2-Carboxyethyl acrylate oligomers (Mn ~ 170) (CXEA) and photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) were all ordered from Sigma Aldrich, unless otherwise noted and used in their as received conditions without further purification. *Synthesis of Polymer Networks*: Copolymers were synthesized by free radical polymerization using 0.1 wt% DMPA. Samples were blended with unreacted crosslinker (TMPTA or TAIC®) in a Brabender PlastiCorder. 35 g thermoplastic copolymer batches were pelletized and fed into the mixer and heated to between 150 ˚C and 220 ˚C. The liquid crosslinking agent was dripped into the mixing chamber. *Radiation Crosslinking*: Samples blended with unreacted crosslinker (TMPTA or TAIC®) were injection molded or heated and pressed with a 12-Tonne Carver Press into their desired shapes. Samples were packaged in air into sealed polyethylene specimen bags and crosslinked at Sterigenics' electron beam facility in San Diego, CA. Samples were exposed to 5, 10, 20, 33, 50, 66, 100, 200 or 300 KGy as denoted. Samples were tested as received from Sterigenics using dynamic mechanical analysis, differential scanning calorimetry, uniaxial tensile tests, and sol-gel tests.

Results: In this study of thermoset SMP's, we adjust the glass transition temperature (T_g) between 25 and 75 °C and tune rubbery modulus between 0.5 and 13 MPa. T_g can be manipulated independently by altering the ratio of linear builders in radiation crosslinked SMP systems. Large scale tunability of rubbery modulus is demonstrated in **Figure 1**. Copolymers made from MA and IBoA at a 94 to 6 ratio are blended with increasing concentrations of radiation sensitizer from 6.25 wt% TMPTA to 25.0 wt% TMPTA. A greater than order of magnitude increase in rubbery modulus from 1.09 to 13.13 MPa is observed in samples irradiated at 50 kGy. A recoverable shape memory cycle on MA-IBoA copolymers blended with 3.00 wt% and 12.5 wt% TMPTA is presented. When strained to 50%, the 3.00 wt% TMPTA samples shows residual strains of 3.00% while the 12.5 wt% sample fully recovers.

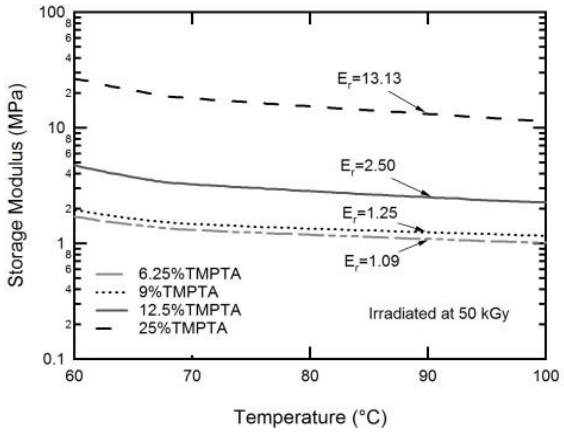

Fig. 1. The effect on rubbery modulus of changing the concentration of TMPTA in 94:6 MA:IBoA copolymers, irradiated at 50 kGy.

Conclusions: A new method has been proposed and validated for accurately tuning the thermomechanical properties of network acrylates with shape-memory properties. Adjustment of rubbery modulus in the range from below 1 MPa to above 13 MPa was demonstrated. Rubbery moduli were tailored by varying both radiation dose between 5 and 300 kGy and crosslinker concentration between 1.00 and 25.0 wt%. T_g manipulation was independently shown between 23 ˚C and 70 ˚C in copolymers of MA and various other linear acrylates and acrylamides. Shape memory behavior was demonstrated by free strain recovery tests with recovered strains above 90% for all samples. *Mnemosynation* makes possible the low cost mass-manufacture of custom biomedical devices in complex shapes with tunable thermomechanical and shape-memory properties.

References:

[1] Hesiod. Theogony, 700 B.C.
[2] Charlesby A. Nature 1953;4343:167.
[3] Vijayabaskar V, Bhattacharya S, Tikku VK, and Bhowmick AK. Radiation Physics and Chemistry 2004;71(5):1045-1058.
[4] Yakacki CM, Willis S, Luders C, and Gall K. Advanced Engineering Materials 2008;10(1-2):112-119.