

Shape Memory Polymer Networks With Tailorable Toughness Under Physiological Conditions

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Statement of Purpose: Shape memory polymers (SMPs) represent a class of smart biomaterials that are used for their ability to change shape under a predetermined stimulus.¹ The stimulus usually involves increasing temperature beyond a specific activation temperature, the glass transition temperature (T_g), but SMPs can also activate upon exposure to moisture.² To extend the use of SMPs to other biomedical applications, particularly orthopaedic, an SMP must have a T_g that is tailored to achieve activation under physiological conditions (i.e. water) as well as exhibit the appropriate mechanical properties or durability to be implemented long term in load-bearing environments. The *objective* of this work is to assess the effect of phosphate buffered saline (PBS) on the T_g and toughness of a SMP copolymer network.¹ Toughness as a function of immersion time was also evaluated for various SMP compositions and compared to other biomedical polymers to demonstrate their potential use in minimally invasive load-bearing applications.

Methods: Copolymer networks consisting of methyl acrylate (MA), methyl methacrylate (MMA) and poly(ethylene glycol) dimethacrylate (PEGDMA $M_n \sim 750$) were polymerized under 365nm UV light using 2,2 dimethoxy-2-phenyl acetophenone as a photoinitiator. The ratio of MA to MMA was varied while holding the PEGDMA crosslinker constant at 10 wt%. 1 mm thick sheets of poly(methyl methacrylate) (PMMA) and ultra-high molecular weight polyethylene (UHMWPE) were obtained from McMaster-Carr, Inc. (Atlanta, GA).

Samples of each composition were soaked in PBS for 1 week and 9 months and then subjected to the following regime of testing. To determine T_g , differential scanning calorimetry (DSC) was performed where samples were subjected to a heating ramp of 5°C/minute from -75°C to 200°C. The T_g was defined as the second order step change in heat flow on the DSC thermogram ($n=3$). To assess mechanical properties, ASTM D638 dogbone samples were strained to failure in tension mode at a strain rate of 5% strain/sec at 37°C under dry conditions or in an environmental bath filled with PBS. Toughness was calculated as the area under the stress-strain curve ($n=4$). Mean +/- standard deviation was calculated and statistical significance determined by ANOVA with post-hoc Student's t-test.

Results: As MA concentration increased (18wt.%MA to 72wt.%MA), the mean T_g of the network decreased from $49.5 \pm 0.5^\circ\text{C}$ to $21.5 \pm 4.3^\circ\text{C}$ and $48.9 \pm 3.1^\circ\text{C}$ to $5.3 \pm 2.8^\circ\text{C}$ in air and PBS, respectively (Figure 1a). The T_g of each composition also decreased upon 1 week exposure to PBS to a greater extent as MA concentration increased. From Figure 1b, mean toughness of the network was highest in the composition whose T_g aligned with 37°C. As seen in Figure 1c, the toughness of the copolymer containing

18% MA significantly increased after 1 week immersion in PBS and then significantly decreased after 9 months. 29%MA significantly increased after 1 week immersion but did not significantly change after 9 months. The toughness of 36%MA was not significantly affected by immersion in PBS.

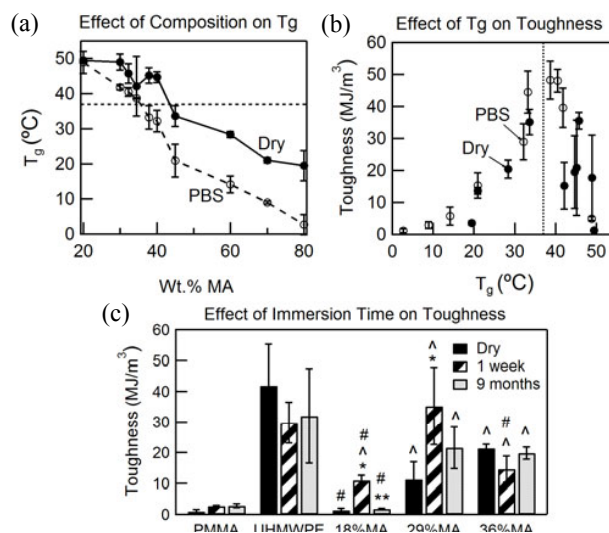


Figure 1. (a) Effect of MA concentration and PBS on T_g . (b) Effect of T_g on toughness in air and PBS. Dotted line denotes 37°C. (c) Effect of immersion time in PBS on toughness of MA-MMA networks, PMMA, and UHMWPE. * $p < 0.05$ vs. dry for that material; ^ $p < 0.05$ vs. PMMA at that time point; # $p < 0.05$ vs. UHMWPE at that time point.

Conclusions: Toughness and T_g of MA-co-MMA-co-PEGDMA networks are both affected by exposure to PBS in a manner dependent upon copolymer composition. By varying the ratio of linear monomers (MA to MMA), T_g can effectively be tailored to achieve activation at body temperature in the presence of PBS. Furthermore, toughness reaches a maxima in the composition whose T_g falls close to 37°C, independent of hydration conditions. This T_g -toughness relationship provides additional benefits for SMPs by allowing for enhanced durability during the packaging and recovery process. The decrease in toughness of 18%MA after 9 months immersion indicates that long term toughness in PBS is dependent upon composition, perhaps with regard to the copolymer's initial viscoelastic state as signified by the location of its T_g in relation to environmental temperature. The comparable toughness levels of 29%MA and 36%MA to UHMWPE, a common orthopedic polymer, after 9 months immersion demonstrate the long term use of these SMPs for load-bearing applications.

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References: ¹Lendlein A. Science. 2002; 296(5573): 1673; ²Huang WM. Appl Phys Lett 2005, 86(11).