Effect of Chemistry and Crosslinking Density on Thermo-Mechanical Properties of (Meth)acrylate Shape-Memory Polymer Networks

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Statement of Purpose: The purpose of this study is to determine the effect of (meth)acrylate monomer structure and crosslinking density on the thermal and mechanical properties of networks intended for use in biomedical applications. A series of networks composed of a constant crosslinker and varying mono-functional monomer are used to establish the relationship between mono-functional monomer structure and thermo-mechanical properties. Failure strain and toughness are highlighted due to their significance for shape-memory polymers. High strain capacity is required for devices to undergo large and complex geometry changes. Toughness is needed to allow for both high strain capacity and large recovery forces. Mechanical properties of thermoplastics have been predicted using the characteristic ratio (C_∞) and cohesive energy density (CED)[1,2]. These parameters will be examined to reveal any relationship to these thermoset networks.

Methods: Networks of varying mol% Poly(ethylene glycol) dimethacrylate Mn~550 (PEGDMA550) with five different mono-functional (meth)acrylates were created. The mono-functional monomers were benzyl methacrylate (BMA), tert-butyl acrylate (TBA), 2-Ethoxyethyl methacrylate (2EEM), ethylene glycol phenyl ether methacrylate (EGPEM), and benzyl acrylate (BZA). Ternary networks were made with a constant amount of PEGDMA550 while varying the composition of BMA with TBA, EGPEM, or BZA. 1 mm thick sheets were created through free radical polymerization under a 365 nm UV source. Thermo-mechanical characterization was performed by a TA800 DMA. The temperature range was from -50°C to 200°C at a rate of 5°C/min with a strain of .2%. A MTS Insight and Thermcraft thermal chamber were used to perform the isothermal tensile tests. Half-sized ASTM type IV dog-bones were the specimen geometry. The crosshead displacement was 1mm/min. C_∞ and CED were calculated using the group contribution method.

Results: C_∞ showed no correlation to failure strain, while monomers with higher CED values had higher failure strains at equivalent crosslink density. The failure strain and toughness diverged at a rubbery modulus (Er) of 10 MPa for networks composed of varying concentrations of PEGDMA550 and five different mono-functional monomers. Failure strain as a function of relative temperature from glass transition temperature (Tg) found a higher and broader peak for a network with phenyl ring side groups as compared to a branched side groups. There was an increase in failure strain as the concentration of BMA was increased in ternary networks.

Conclusions. A divergence point separates the mono-functional monomer and crosslinker dominated regions. Below the divergence point, the mono-functional

monomer, governs the large strain mechanical properties. From the ternary networks, increasing the concentration of α-methyl group and moving the phenyl ring closer to the backbone increases the failure strain and toughness of these networks. C_∞ held no relationship, but CED allowed for general comparisons. This work provides a basis for relating chemical structure to mechanical properties of (meth)acrylate networks.

References:

1. Wu, S.. Polym. Eng. and Sci., 1992. 32: 823-830.
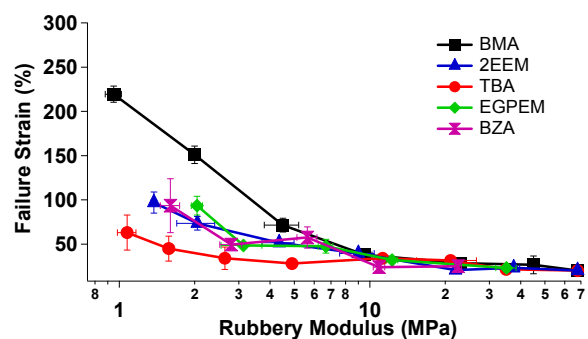2. Van Krevelen, D. W., P.J.H., *Prop. of Polym*. 1972, Amsterdam: Elsevier.

Figure 1. Failure Strain as a function of Er for five mono-functional monomers
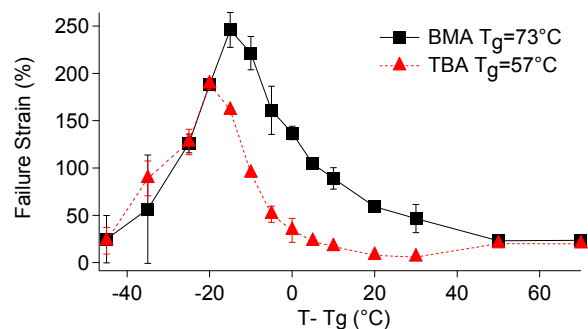

Figure 2. Failure strain as a function of relative temperature from Tg of phenyl ring and branched network
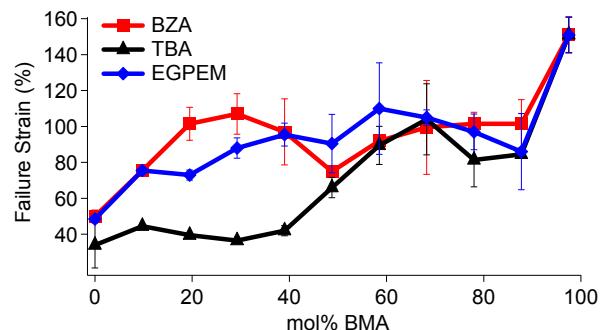

Figure 3. Failure strain as a function of mol% BMA-co-3rd monomer.