SHAPE MEMORY-ASSISTED SELF-HEALING (SMASH) OF THIOL-ENE NETWORKS

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Shape memory-assisted self-healing is a promising concept to improve the self-healing performance of vitrimeric networks. With the help of the entropic recoil coming from the shape memory functionality of thiol-ene vitrimers, we achieved high healing efficiency, following a close-then-heal strategy for a scratch of a size in the range of several hundred micrometers. The networks were prepared out of a trifunctional thiol crosslinker, functional acrylates bearing aromatic rings for stiffness and -OH groups for transesterification, an organic phosphonate as catalyst and a photo-initiator for photo-curing. Organic phosphonates were used as transesterification catalysts, which proved to show catalytic effects on transesterification of thiol-ene networks in another study by our group [1]. Herein, we continue the study by varying the molar content of the thiol compound to produce several networks with varying glass transition temperatures (Tg) and stiffness. The performance of the selected networks was examined by carrying out FTIR, DMA, stress-relaxation tests, TGA and tensile testing for determining the healing efficiency. The results showed that Tg and storage modulus (E') in the rubbery region increase with decreasing thiol content. Based on the network structure and mobility, we expect a difference in the efficiency of the scratch closure induced by shape recovery (affected by rigidity) and healing efficiency (influenced mostly by network mobility and availability of –OH and ester moieties). Stress relaxation indicates a topology freezing transition temperature (Tv) between 74 °C and 137 °C. The general trend is that a decreased thiol content produces stiffer networks with higher Tg that are slower in shape recovery and take longer time for relaxing stresses, therefore needing an extended thermal treatment to successfully induce healing.

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[1] Rossegger, Elisabeth, et al. "Digital light processing 3D printing with thiol–acrylate vitrimers." *Polymer Chemistry* (2020).