

Enamine-based vitrimers through thiol-ene photopolymerization

Logan Dugas¹, William D. Walker¹, Rahul Shankar¹, Keely S. Hoppmeyer¹, Sarah E. Morgan¹, Robson F. Storey¹, Derek L. Patton¹, Yoan C. Simon¹

1. School of Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, MS, United States.

Associative exchange chemistries in network polymers have enabled the advent of vitrimers, a unique class of materials likened to both thermosets and thermoplastics the possess remarkable stability while displaying healability and on-demand degradability. Herein, we describe a novel thiol-ene photopolymerized vitrimer that exchanges through enamine linkages derived from cyclic triketones. Uncatalyzed enamine chemistry exhibits low energy barrier of amine exchange and the ability to rapidly depolymerize. Accordingly, we devised an alkene-functionalized triketone, 5,5-dimethyl-2-(pent-4-enoyl)cyclohexane-1,3-dione, which was reacted with 1,6-diaminohexane in a stoichiometrically imbalanced (~85:15 mol %, enamine:primary amine) fashion. We found that ester-free tetrafunctional thiols work best as they preclude transamidation. The glass transition temperatures (T_g) of the resulting network were below room temperature (~ 3-7°C) and the topology freezing temperature (T_v) was found through frequency-sweep experiments to be 90 °C. Arrhenius fitting of the stress relaxation of the networks enabled us to measure the activation energy of the exchange process (51.45 kJ/mol). The materials readily degraded upon introduction of either strong acids or excess primary amines showing the versatility of this approach. Therefore, this work opens up new avenues for the development of tailorable next-generation multifunctional and degradable materials and their implementation in a multitude of applications, such as high-performance composites or polymer upcycling.

