Photopolymerizations are of great interest to the material science community because of their low energy requirements; solvent-free resins; and spatial and temporal control over polymerizations. As a result, UV-initiated polymerizations have been utilized in several industrial applications, such as coatings, adhesives and inks.\(^1\)

Thiol-ene polymerizations have recently become of interest because of their nearly perfect crosslinked network formation, resulting in well-defined properties.\(^2-4\) The work by Hoyle \(et\ al.\)^\(^2-7\) and Bowman \(et\ al.\)^\(^8-11\) have highlighted the utility of the thiol-ene reaction in the formation of crosslinked polymer networks. Free radical thiol-ene photopolymerizations proceed by a chain transfer process where oxygen inhibition is negligible. Gelation occurs at high functional group conversion, resulting in low stress levels and reduced shrinkage upon network formation. These homogenous networks are characterized by narrow glass transition temperatures, which can be tuned by monomer functionality\(^7\) or the incorporation of inorganic monomers resulting in hybrid thiol-ene materials.\(^11-14\) Hybrid polymer materials incorporate both inorganic and organic moieties in an effort to combine the thermal and oxidative properties of inorganic materials with the processability and toughness of organic materials.

In our work, cyclic tetravinylsiloxanetetraol ([Vi(OH)SiO]\(_4\)) is incorporated into two different thiol-ene resin systems.\(^15\) [Vi(OH)SiO]\(_4\) is an eight-membered ring made up of alternating siloxane bonds with vinyl and hydroxyl functionalities. The inorganic moiety was loaded into thiol-ene resins at varying concentrations (0, 10, 25 and 50 mol%). The kinetics of the network formation was followed using Real-time Fourier Transform Infrared spectroscopy (FTIR), where conversion values were determined by the change in the area under peaks corresponding to the thiol and alkene functionalities. Thermomechanical properties were measured using dynamic mechanical analysis.
Synthesis of Thiol-ene Networks

Hybrid thiol-ene networks were prepared using allyl isocyanurate (TTT) or pentaerythritol triallyl ether (APE) with pentaerythritol tetra(3-mercaptopropionate) (PETMP), shown in Figure 1. Cyclic tetravinylsiloxanetetraol ([Vi(OH)SiO4]), synthesized according to a modified literature procedure16 was added to the thiol-ene formulations at various concentrations (0, 10, 25 and 50 mol%) while maintaining a one-to-one ratio of thiol to alkene. Irgacure 184 was incorporated at 1 mol % as a photoinitiator. Irgacure and [Vi(OH)SiO]4 were dissolved in the alkene monomer (TTT/APE) using a small amount (no more than 400 µL) of N,N’-dimethyl formamide (DMF). Once completely dissolved, PETMP was added and mixed thoroughly. The resin was loaded into a silicone mold and cured under a medium-pressure mercury UV lamp at an irradiance of 16 mW cm⁻² for 30 minutes. The resulting crosslinked polymers were soaked in deionized water for 12 to 15 hours to remove residual DMF and, subsequently, dried overnight under vacuum at 100°C.

Polymerization Kinetics

Polymerization kinetics was monitored using real-time FTIR, where samples were sandwiched between NaCl plates. A series of spectra were taken as the sample was cured using UV radiation with an irradiance of approximately 20 mW cm⁻². Conversion values were determined by the change in the area under peaks corresponding to the thiol and alkene moieties at approximately 2570 cm⁻¹ and 3080 cm⁻¹, respectively. In the TTT/[Vi(OH)SiO]₄-PETMP networks, 1-to-1 conversion of both thiol and alkene functionalities with values greater than 90% were observed in the neat system, shown in Figure 2 (■ = Ene functionality, ○ = Thiol functionality with 0% [Vi(OH)SiO]₄).

Upon the incorporation of 10% of the inorganic moiety, a slight decrease in the thiol conversion was observed, while the ene conversion remained relatively unchanged. A gradual decrease in thiol conversion was observed as the concentration increased to 50 mol% of [Vi(OH)SiO]₄ (△ = Thiol functionality with 50% [Vi(OH)SiO]₄). The deviations of the conversion values for the thiol and alkene functionalities from 1-to-1 are due to homopolymerization events between the alkene functionalities, leading to a decrease in the overall thiol conversion. In the APE-PETMP formulation, nearly quantitative conversion values (>99%) were observed. One-to-one conversions of the thiol and alkene groups were observed in the conversion versus time plots of APE-PETMP with increasing concentration of [Vi(OH)SiO]₄. Slight decreases in overall conversion values were observed at higher concentrations of the inorganic moiety due to the increase in crosslink density of the material, which could limit the diffusion of reactive groups.

Thermomechanical Properties

The thermomechanical properties of the hybrid thiol-ene networks were investigated using dynamic mechanical analysis. The glass transition temperature of the materials was determined from the peak maximum of the Tan δ curves. In the APE-PETMP samples, nearly a 30°C increase in glass transition temperature was observed as the concentration of the inorganic moiety increased to 50 mol%. The increase in glass transition temperature is attributed to an overall increase in the crosslink density of the material, as indicated by the increase in rubbery storage modulus.

In contrast to the APE-PETMP results, the glass transition temperature of the TTT-PETMP decreased approximately 20°C as the concentration of [Vi(OH)SiO]₄
was increased to 50 mol%, despite an obvious increase in the crosslink density and the decrease in the calculated values of the molecular weight between crosslinks (M_c). The decrease in glass transition temperature can be explained in the context of monomer rigidity, where a more rigid monomer (TTT) is being replaced by a more flexible monomer, [Vi(OH)SiO_4]. As the concentration of the more flexible inorganic moiety increased, the overall rigidity of the network decreased, resulting in the observed decrease in glass transition temperature.

**Conclusion**

In conclusion, hybrid thiol-ene networks were synthesized by incorporating varying concentrations of [Vi(OH)SiO_4]. The inorganic moiety was incorporated into two different thiol-ene resins, APE-PETMP and TTT-PETMP, at 10%, 25% and 50% loading while keeping a 1-to-1 stoichiometric ratio of enes to thiols. Polymerization kinetics of the network formations was followed using real-time FTIR techniques, where the conversion values were determined by the change in the areas of the peaks corresponding to the thiol and ene functionalities. The APE-PETMP systems showed nearly quantitative conversion values at low loading percentages, while slight deviations were observed at higher loading.

However, 1-to-1 conversion values of enes to thiols was observed at each concentration of [Vi(OH)SiO_4]. The polymerization kinetics of TTT-PETMP system showed deviations of the thiol conversion as the concentration of [Vi(OH)SiO_4] increased due to homopolymerization occurring during the photopolymerization. The thermomechanical properties of the thiol-ene systems are unique in that the inorganic additive affects each formulation differently. An increase in glass transition temperature was observed in the APE-PETMP system as the concentration of [Vi(OH)SiO_4] increased due to an increase in crosslink density and a decrease in the molecular weight between crosslinks. In contrast, the glass transition temperature of the TTT-PETMP system showed a decrease in glass transition temperature with higher concentrations of [Vi(OH)SiO_4], despite an obvious increase in crosslink density. We attribute the decrease in glass transition temperature to monomer structure, where TTT is replaced with a much less rigid [Vi(OH)SiO_4] monomer resulting in a decrease in glass transition temperature.

**References**


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