

Comparative Study of Novel Thiol-Ene Resins and Composites

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Abstract

The kinetic, thermal, and mechanical properties of several thiol-ene resins were investigated using photo-differential scanning calorimetry (photo-DSC), thermal gravimetric analysis, real-time infrared (RTIR) spectroscopy, and tensile measurements. Photo-DSC and RTIR results show that thiol-ene systems comprised of the Triallyl-Triazine and Trithiol exhibit efficient copolymerization of the ene with the thiol. The resins exhibited high thermal stability at temperatures up to 370° C and were effective in producing photocurable composites.

Introduction

Thiol-ene resins, investigated since the 1950s,^{1,2} have distinct advantages over traditional photocured systems including low oxygen inhibition during cure. In addition, thiol-ene systems do not require a photoinitiator since the thiol undergoes a facile cleavage of the sulfur-hydrogen bond upon excitation.^{3,4} Although thiol-enes do not require a photoinitiator, the use of one dramatically increases their rate of polymerization. Additionally, they can be easily used to form thin and thick cured crosslinked networks. The cured materials are flexible and have excellent strength and abrasion resistance. Their use in coatings has been amply demonstrated. Herein we describe analysis of the thermal and physical properties of thiol-ene photocured coatings and composites. The thiol-ene systems investigated include resins comprised of a trifunctional thiol and two enes typical of those used in the past in thiol-ene investigations. First, a brief kinetic analysis via photo-DSC and real-time infrared (RTIR) spectroscopy of the base thiol-ene mixtures were conducted. Then thermal and mechanical properties of the base resins comprised of a trifunctional thiol with combinations of two enes in various concentrations were evaluated. Finally, we illustrate the use of thiol-ene curing in composite applications comprised of two thiol-ene mixtures in a carbon fiber mat.

Experimental

Materials. Trimethylolpropane tris(3-mercaptopropionate), 2,4,6-triallyloxy-1,3,5-triazine and triallyl-1,3,5-triazine-2,4,6-trione were obtained from Aldrich Chemical Co. and used as received. The photoinitiator, Irgacure 819, was obtained from Ciba Specialty Chemicals. Woven carbon fiber mats were also used as received.

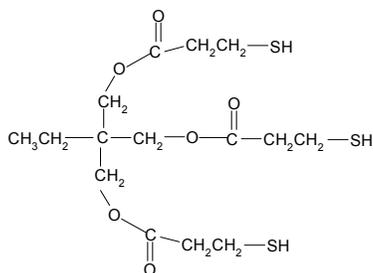
Kinetic Analysis. Polymerization rate profiles of the resins were recorded using a Perkin-Elmer differential scanning calorimeter (DSC) modified with a medium pressure UV lamp. Polymerizations were initiated in air at 25° C using 365 nm monochromatic light with an irradiance of 1.3 mW/cm². Polymerization rates were determined from the heat flow. The conversions of the ene and thiol were monitored by real-time infrared spectroscopy using a

Bruker IFS 88 IR and OPUS software. A 365 nm bandpass filter was used to provide a monochromatic light source with an irradiance of 30 mW/cm².

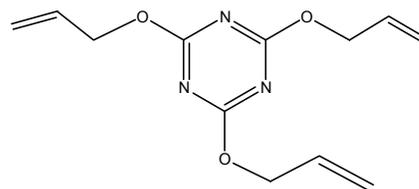
Mechanical and Thermal Analysis. Resin mixtures were prepared by adding a stoichiometric balance of thiol and total triene; however, the composition of the ene varied in 10% increments between pure Triallyl-Triazine and pure Triallyloxy-Triazine. Irgacure 819 (0.05 wt %) was added to each resin mixture. For DMA, 60 mm x 12.6 mm x 2.5 mm samples were cured under atmospheric conditions using a Fusion UV Systems, Inc. Power Cure™ 3 Ultraviolet Lamp System with a D bulb. Samples were ground before TGA analysis. Tensile measurements for composites were made on an MTS Alliance RT/10. Thermal degradation profiles of the single triene-containing resins were obtained using a TA Instruments 2960, controlled by a Thermal Analyst 2100. The temperature was increased to 700° C at 20° C/min under nitrogen and atmospheric conditions. Flexural strain profiles were obtained for the cured resins using a Perkin-Elmer dynamic mechanical analyzer (DMA). The temperature was increased from -120° C to 200° C at 4° C/min and 1Hz.

Results and Discussion

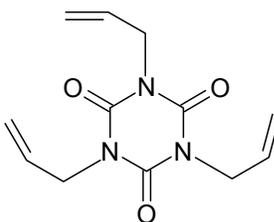
Herein, we present polymerization kinetic results and an analysis of film properties of various thiol-ene resins based upon the trithiol and two enes in Chart 1.



Trithiol
(trimethylolpropane tris (3-mercaptopropionate))



Triallyloxy-Triazine
(2,4,6-Triallyloxy-1,3,5-triazine)



Triallyl-Triazine
(triallyl-1,3,5-triazine-2,4,6 (1H,3H,5H)-trione)

Chart 1. Thiol and ene structures.

Kinetics. Photo-DSC exotherms of thiol-ene resins comprised of 1:1 molar mixtures were recorded in air at 25°C. While the thiol to ene ratio remained 1:1, the type of ene was varied incrementally from pure Triallyl-Triazine to pure Triallyloxy-Triazine. Polymerization rate maxima for each resin were recorded and plotted in Figure 1 as a function of the mol % of Triallyl-Triazine in the ene mixture. The resin based upon pure Triallyl-Triazine resin has the highest polymerization rate, but otherwise there is little variation in the rate maxima.

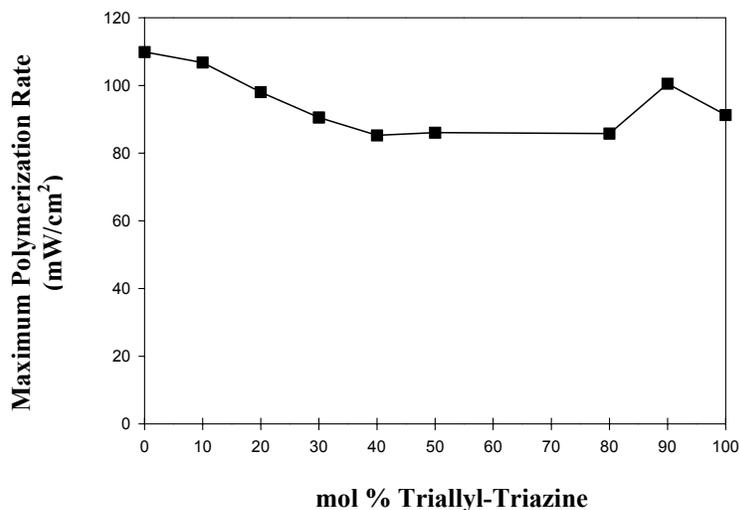


Figure 1. Photo-DSC rate maxima of thiol-ene resins, polymerized at 25°C.

IR peaks were monitored in real time at $\sim 3100\text{ cm}^{-1}$ and $\sim 2500\text{ cm}^{-1}$ corresponding to ene and thiol bands, respectively. Figure 2 shows RTIR percent conversion versus time plots for 1:1 molar mixtures of Trithiol with Triallyl-Triazine. RTIR results of percent conversion for 1:1 molar mixtures of Trithiol with Triallyloxy-Triazine were similar to those in Figure 2. From the results, it is conclusive that both enes readily copolymerize with thiol and attain high conversions, in reasonable agreement with previous reports.⁵

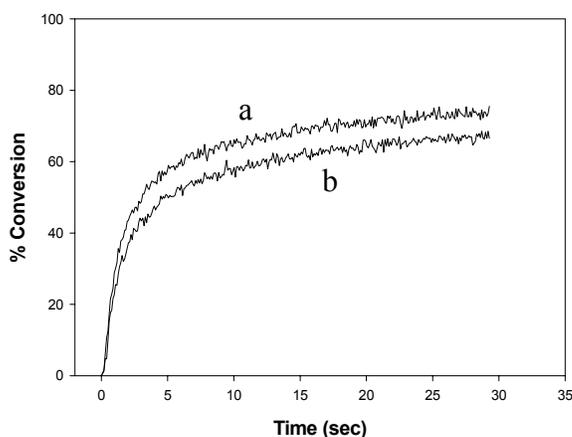


Figure 2. RTIR plot of thiol and ene conversion in 1:1 mixtures of Trithiol with Triallyl-Triazine at 25°C. (a) ene conversion, (b) thiol conversion.

Thermal Properties. Thermal gravimetric analysis (TGA) is used to analyze the thermal stability of polymer films under a variety of conditions. Mixtures of Trithiol and Triallyloxy-Triazine and Triallyl-Triazine were photocured as described in the Experimental section. Figure 3 shows the TGA profiles of the resins cured in nitrogen and air, respectively. Both resins show high thermal stability with the onset of bulk degradation starting at 381° C in nitrogen and at 385° C in air for the Triallyloxy-Triazine based film, and at 371° C in nitrogen and 369° C in air for the Triallyl-Triazine based film. The cured matrix based upon Trithiol and Triallyloxy-Triazine shows a higher thermal stability than films formed by copolymerization of Trithiol and Triallyl-Triazine in both air and nitrogen.

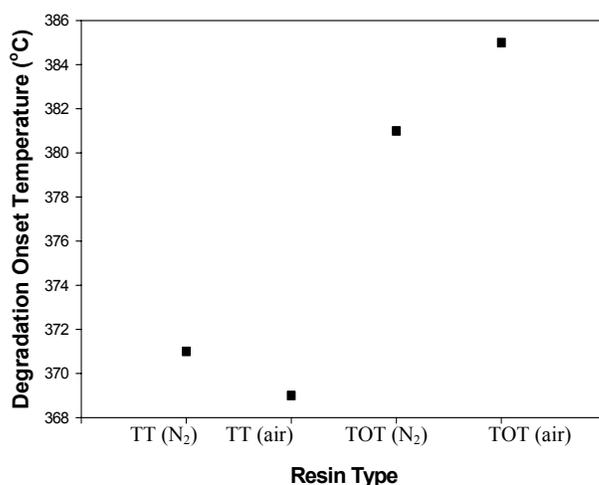


Figure 3. TGA profiles of thiol-ene resins, showing onset of degradation in nitrogen and air. The abbreviations TT and TOT are for 1:1 Trithiol:Triallyl-Triazine based films and 1:1 Trithiol:Triallyloxy-Triazine based films, respectively.

Mechanical Properties. Dynamic mechanical analysis (DMA), a useful tool for measuring polymer physical properties such as modulus and glass transitions, was performed on the cured resins. The DMA samples were prepared by pouring resin mixtures into 60 mm x 12.75 mm molds, and curing was conducted using 365 nm light illumination for 30 minutes: sample thicknesses were 3.5 ± 0.2 mm. DMA plots of $\tan \delta$ versus temperature, given in Figure 4 for samples made from cured films of Trithiol with pure Triallyl-Triazine and Triallyloxy-Triazine as well as a mixture of 50 mol % Trithiol and 25 mol % of each ene, were used to obtain film glass transition temperatures, T_g s. The T_g s calculated for the three plots in Figure 4 and similar T_g s obtained for other cured films made from different mixtures of each ene with Trithiol are given in Figure 5 as a function of concentration of Triallyl-Triazine. As expected from the structures of the two monomers, the higher the Triallyl-Triazine content, the higher the glass transition of the film. The allyloxy moiety in the Triallyloxy-Triazine no doubt adds flexibility to the final cured film.

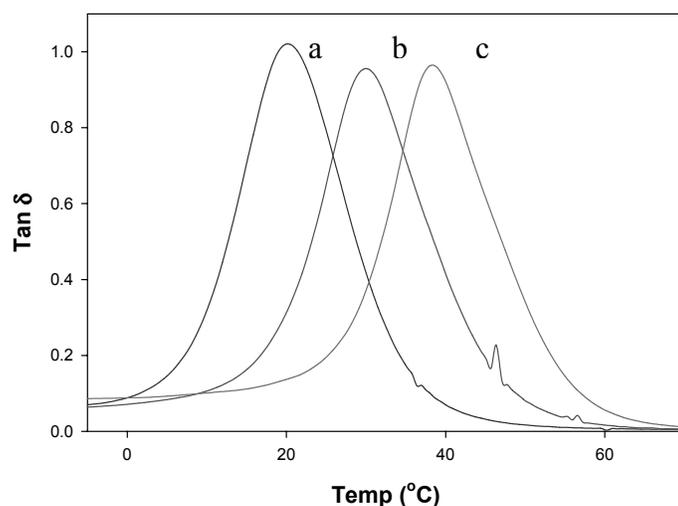


Figure 4. $\text{Tan } \delta$ versus temperature DMA plots derived for 1:1 thiol:ene molar mixtures of various combinations of Triallyl-Triazine and Triallyloxy-Triazine. (a) 0% Triallyl-Triazine, (b) 50% Triallyl-Triazine, (c) 100% Triallyl-Triazine.

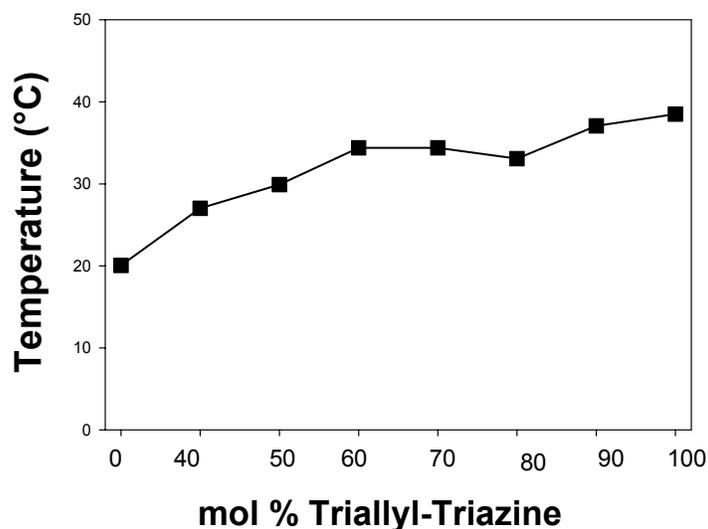


Figure 5. T_g of cured thiol-enes obtained using DMA.

Finally, filled and unfilled 1:1 molar mixtures of photocured samples of trithiol and either Triallyl-Triazine or Triallyloxy-Triazine were evaluated by tensile measurements. As shown in Figure 6, the modulus of the carbon fiber is greatly improved with addition of the resins, and

the moduli of the cured composites were much greater than the corresponding cured unfilled resins.

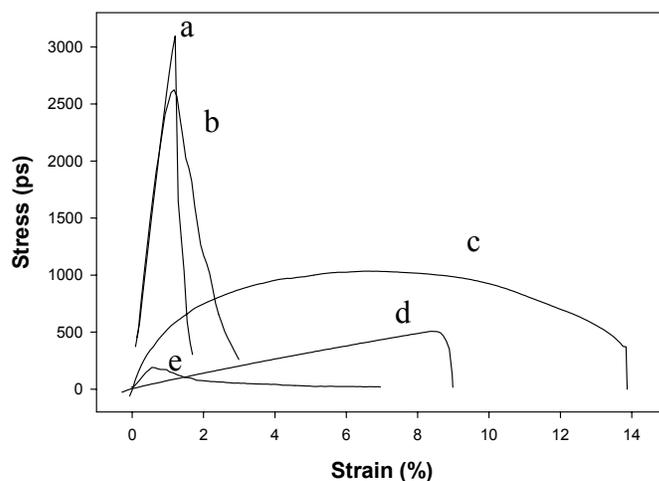


Figure 6. Tensile testing results of filled and unfilled resins. (a) Triallyloxy-Triazine composite, (b) Triallyl-Triazine composite, (c) Triallyl-Triazine resin, (d) Triallyloxy-Triazine resin (e) carbon fiber mat.

Conclusions

Thiol-ene mixture based on a Trithiol and Triallyloxy-Triazine produced films with low glass transition and high thermal stability. Photocured composites were readily made from photocuring resins in carbon fiber mats.

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