

# Photocurable Thiol-Ene Thermosets for Sports Applications

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**Abstract:** *Photocurable multifunctional thiol-ene and acrylate based monomer mixtures of varying compositions were photopolymerized, and the inhomogeneity of the final films was investigated. The mechanical and impact properties of the films were measured by dynamic mechanical analysis (DMA) and a modified Tinius Olsen testing instrument. Also, the morphology was probed by atomic force microscopy (AFM). Nano-structure formation in the crosslinked networks was correlated with the improved mechanical properties of these hybrid systems.*

## Introduction

Without exception, photocuring is the fastest, environmentally friendly methodology for creating films that can be applied to virtually any type of substrate including wood, plastic, glass, or metal. For over three decades, photocuring of acrylates to produce highly crosslinked matrices has been the primary focus of UV-curing. This technology has been successfully applied to applications that range from coatings on furniture and floors to compact discs and microelectronics.<sup>1</sup> The photopolymerization of multifunctional acrylates is unique in that it is very fast compared to monofunctional counterparts. Basically, early gelation in multifunctional acrylate polymerization forms inhomogeneous high density regions that are characterized by very rapid rates of polymerization due to a combination of reduced termination and high concentrations of reactive acrylate groups in the proximity of propagating chain ends.<sup>2-5</sup> It has been assumed that these high density “ball” type structures coalesce to some degree at

high conversions, however, the final matrices generated with respect to free-volume distribution are still very inhomogeneous.<sup>2,4-6</sup> This inhomogeneity results in networks that have broad glass transition regions that can range up to 200 °C.

Recently, there has been considerable interest in thiol-ene systems, which were used many years ago in some of the first large scale industrial applications of photocuring.<sup>7,8</sup> Multifunctional thiol-ene mixtures undergo polymerization by a free-radical step-growth process that forms a highly uniform crosslinked network with a very narrow glass transition region.<sup>9</sup> Since the shrinkage that results from the addition of thiols across the ene double bonds takes place in the liquid phase up to the point of gelation, there is a reduction in stress in the final cured materials. This can be quite important when considering the impact of low shrinkage on adhesion, scratch resistance and other physical phenomenon inherent to the crosslinked networks formed. Bowman et al. have reported that polymerization of thiol-enes results in the production of networks with very low stresses due to low volume shrinkages and delayed gelation.<sup>10</sup> Finally, it is important to note that thiol-ene polymerization is essentially uninhibited by oxygen.

We ask the simple question, what types of photopolymerization processes occur and what types of networks are formed by combining a thiol-ene system with a multifunctional acrylate. Indeed Bowman et al. have indicated very recently that photopolymerization of thiol-ene/acrylate ternary systems can lead to some exceptional polymerization kinetics.<sup>11</sup> Herein, we report the photopolymerization of a combination of a 1:1 thiol-ene monomer mixture with varying molar percentages of a trifunctional acrylate. In addition to measuring physical and mechanical properties of thiol-ene/acrylate hybrid systems, a morphological investigation of the networks was conducted by atomic force microscopy (AFM), and a modified Tinius Olsen Testing instrument was used to determine the amount of energy absorbed by thick (4 mm or greater) plates of thiol-ene/acrylates. It was found that optically clear matrices with energy absorbing properties tunable to a particular performance temperature can be fabricated, suggesting applications for sports equipment. The mechanical properties of these thiol-ene/acrylate based systems have been interpreted in the context of the nano-scale phase-separated morphology that develops upon curing.

## Experimental

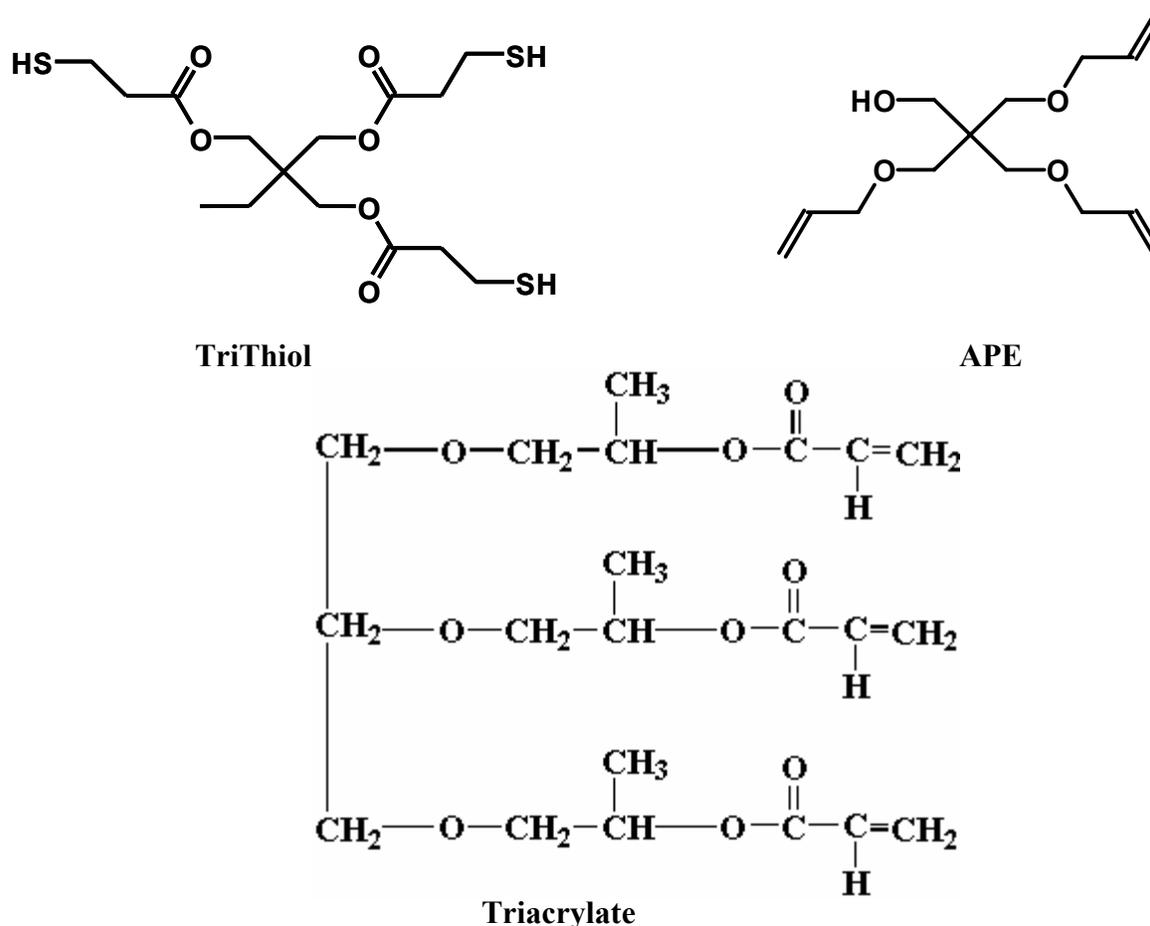
All reagents were used without further purification. Allyl pentaerythritol (APE) was obtained by Perstop Specialty Chemicals. Trimethylolpropane tri(3-mercaptopropionate) (TriThiol) was obtained from Bruno Bock Thio-Chemical-S. Propoxylated glycerol triacrylate (Ebecryl 53) was from Cytec Surface Specialties and 2,2-dimethoxy 2-phenyl acetophenone (DMPA) from Ciba Specialty Chemicals.

Mechanical transitions of the films were recorded using a TA Q800 dynamic mechanical analysis (DMA) by heating the samples from -50 to 200 °C at a rate of 3 °C/min and at a frequency of 1 Hz in air. DMA was conducted under the shear sandwich mode for 10 x 10 mm square size samples with thicknesses of 150-200 µm. A modified Tinius Olsen impact tester (Model 92T) was used to record energy absorption by the samples. Samples were subjected to a given impact (1.13 Joules). Surface topography studies were conducted using a MultiMode<sup>TM</sup> scanning probe microscope from Veeco Instruments, Inc. (Santa Barbara, CA). A silicon probe (RTESP) with nominal resonance frequency of 275 KHz was used in the tapping mode.

Thiol-ene mixtures were prepared by blending TriThiol with APE based on equal molar functional groups. Ebecryl 53 was then added to the TriThiol-APE mixture by 10 mole% increments to prepare eleven different TriThiol-APE/Ebecryl 53 mixtures: each mixture contained 1 wt % DMPA photoinitiator. Samples for DMA analysis were cured under a UV Fusion EPIQ 6000 lamp system (D bulb; 3.15 W/cm<sup>2</sup> at a line speed of 10 ft/min). Thick samples for impact testing contained 0.02 wt % DMPA initiator and were cured with a low pressure mercury lamp (254 nm) over an extended time (4 hours). In the case of the pure acrylate, an oxygen scavenger was added to ensure complete cure. Surface topography studies were performed on the cross-section of the samples.

## Results and Discussion

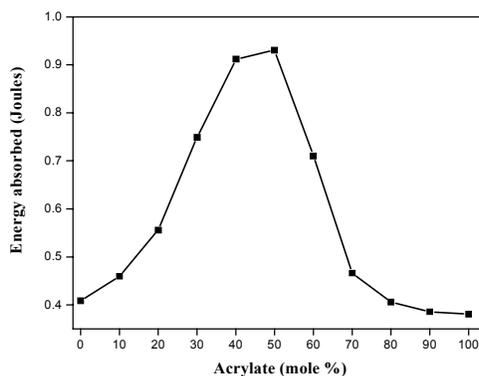
The chemical structures of each of the components that comprise the ternary thiol-ene/acrylate mixtures are shown in Figure 1 along with their corresponding acronyms. Plates prepared from mixtures of these three monomers were investigated with respect to their propensity for absorbing an impact that is commensurate with the type of impact energy that an athlete might receive to the cranium in a sporting event.



**Figure 1.** Structures of monomers in the thiol-ene/acrylate systems.

Samples were prepared by mixing various mole percentages of Triacrylate with a base 1:1 molar mixture of Trithiol and APE. Samples with a very small concentration of photoinitiator were placed in a

mold of 4 mm thick and subjected to the output of a 254-nm low-pressure mercury lamp in intervals that allowed for control over the sample temperature, i. e., this reduced the tendency of some samples to attain high temperatures and thereby generate optical and mechanical aberrations in the final cured plates. The plates produced were fairly optically clear with little visible variation in surface topology. Impact absorbance of the cured samples was measured with a Tinius Olsen instrument modified to measure the energy absorbed by thick samples, in our case 4-mm plates. As shown in Figure 2, the samples containing 40-50 mole % Triacrylate were the most effective at dissipating energy at room temperature ( $\sim 24^\circ\text{C}$ ), as evidenced by the peak maximum of the energy absorbed versus the mole percent acrylate plot: note that an energy of 1.13 Joules was delivered to each 4 mm plate. Thus, the sample with 50 mole percent Triacrylate absorbed 86 % of the impact energy.



**Figure 2.** The energy absorption plot of thiol-ene/acrylate hybrid systems as a function of acrylate mole percent.

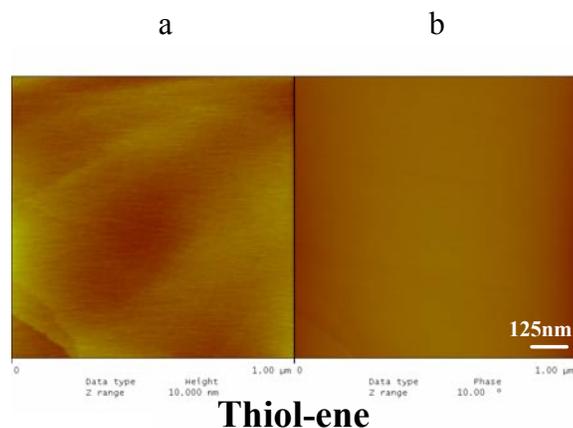
Table 1 lists the temperatures corresponding to the maxima in the  $\tan \delta$  versus temperature plots obtained by dynamic mechanical analysis (DMA) at an oscillation frequency of 1 Hz. Interestingly, the peak temperatures in the  $\tan \delta$  plots that are closest to room temperature (i. e. those samples with peak  $\tan \delta$  maxima from 18 to  $42^\circ\text{C}$ ) have the highest energy absorbance. Hence, a rough guide to fabricating thiol-ene/acrylate based energy absorbing materials is to choose mixtures such that their photopolymerization will produce crosslinked matrices that have  $\tan \delta$  peak maximum temperatures that are near the temperature at which impact energy absorbance is desired. For example, since the application temperatures of mouthguards used in sports applications is roughly between  $30\text{-}35^\circ\text{C}$ , our results would suggest that it is desirable to fabricate thiol-ene/acrylate crosslinked networks whose peak  $\tan \delta$  maxima are near that temperature range.

An interesting aspect of the photocured thiol-ene/acrylate systems deserves additional attention. While the initial mixture of thiol, ene and acrylate in this report are thoroughly and thermodynamically mixed and represent a single phase, this is not true for the photopolymerized networks. First, let us consider the phases of pure TriThiol-APE and Triacrylate networks on a nanoscopic level, i.e., for

Mole % Acrylate	Temperature (°C tan $\delta$ peak maximum)	Mole % Acrylate	Temperature ( °C tan $\delta$ peak maximum)
0	8	50	36
10	14	60	42
20	15	70	58
30	18	80	80
40	26	100	117

**Table 1.** Peak maxima of tan  $\delta$  vs temperature plots for samples with increasing mole percent of acrylate in thiol-ene/acrylate systems.

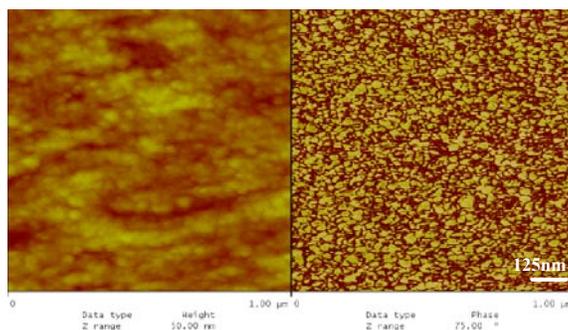
dimensions between 1 and 100 nanometers. Figure 3 shows the resulting AFM height and phase images. Obviously, there is little surface roughness, no any phase separated morphology can be detected on the nanoscopic level for the TriThiol-APE based films.



**Figure 3.** (a) Height and (b) phase images of film cross section of photocured 1:1 molar TriThiol-APE.

By contrast, AFM results in films produced by photopolymerization of mixtures of 0 to 90 mole % Triacrylate in 1:1 molar mixtures of TriThiol-APE clearly show nanostructure development and phase separated film morphology depending upon the concentration of Triacrylate. The AFM micrograph of the sample made from 50 mole % Triacrylate shown in Figure 4 indicates a clear phase separated morphology in the range of 20 to 80 nm. It is reasonable to suspect that the hard phase (light regions in Figure 4) have an excess of polymerized acrylate. The AFM image of the film formed from pure Triacrylate, like that from the 1:1 TriThiol-APE system, shows essentially no such distinct nanophase separated morphology. Our initial results using a nanoprobe force field technique, indicates that the differences in moduli between the dark and light regions, while there, are small. This accounts for the macroscopic observation of a narrow, single tan  $\delta$  versus temperature plot and the absence of multiple glass transitions by DSC (actual scans not shown here). This tailoring of the single tan  $\delta$  peak maximum to occur at a particular temperature by simply selecting the correct concentration of acrylate

allows for the fabrication of an energy absorbing material that is tuned for a given application temperature.



**Figure 4.** Height and phase images of film cross section of photocured 50 mole% Trithiol-APE and 50 mole% acrylate.

## Conclusions

The morphology development and the mechanical properties of thiol-ene/acrylate based crosslinked networks were studied. The addition of acrylate into the thiol-ene mixture results in the formation of a phase separated nano-structured morphology. The ability of thick plates to absorb high impacts is related to the temperature corresponding to the maximum in the  $\tan \delta$  versus temperature plots and the temperature of the impact measurement.

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