

# Aging Effects on Physical Properties of Thiol-Ene Photocured Coatings

*Junghwan Shin, Sergei Nazarenko & Charles E. Hoyle*

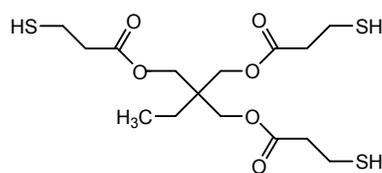
*School of Polymer Sciences and High Performance Materials  
The University of Southern Mississippi, Hattiesburg, MS 39406*

**Abstract:** *The relationships between sub- $T_g$  aging and physical/mechanical properties of Thiol-Ene photocured coatings are studied in terms of chemical structure and network density. The homogeneous network structure of thiol-enes, having narrow glass transition temperatures, showed characteristic temperature and time dependency on aging behavior which was investigated by enthalpy relaxation with a DSC. Thiol-ene films showed maximum enthalpy relaxation at  $T_g-10^\circ\text{C}$  and a linear relationship between the extent of enthalpy relaxation and log of the aging time. Physical property changes of thiol-ene films monitored by pendulum hardness changed as a function of aging time at a specific temperature, which was consistent with the temperature and time dependency of enthalpy relaxation. A multifunctional acrylate (TMPTA) being capable of homopolymerization as well as thiol-acrylate copolymerization was incorporated into the thiol-ene network structure thereby decreasing the network uniformity and affecting the aging behavior. The extent of enthalpy relaxation decreased and the distribution drastically broadened as a function of TMPTA content thus allowing unprecedented control of the sub- $T_g$  aging behavior of thiol-ene based networks by modification and manipulation of the chemical structure.*

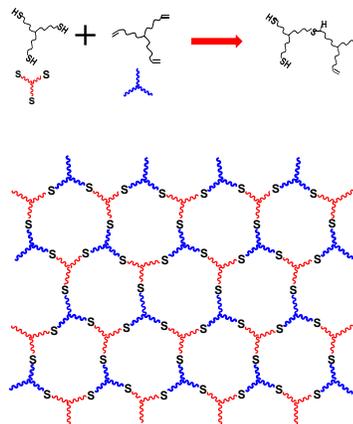
## Introduction

Thiols are relatively benign compared to many types of monomers and their odor is of little consequence as they are currently used in a large number of industrial and commercial applications including optical lenses (thiourethanes), fast cure epoxy sealants and adhesives, heat stabilizers, chain transfer agents, antioxidants, anti-bleaching reagents, and coupling agents for steel contact materials. They have also been widely used for many decades as hair perm and straightening reagents involving direct human contact. Thiols have also been successfully used to make photocurable networks produced by reactions of multifunctional thiols and enes (a typical example of which is shown in Figure 1).<sup>1</sup> Advantages of thiol-ene photocured networks include ultra-rapid polymerization in air, formation of highly uniform networks with advanced physical and mechanical properties not achievable by simple photocured acrylates, and the ability to attain very high conversions at room temperature.

Incorporating a third monomer (multifunctional acrylate) that both copolymerizes (with thiol-ene) and homopolymerizes is an approach to modify the uniform dense network structure of thiol-ene based films and alter the physical aging characteristics. Unlike single binary thiol-ene based systems, due to the faster gelation of multi-functional acrylate systems, a more inhomogeneous crosslinked network is formed.<sup>2-4</sup>



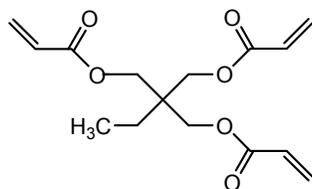
(a) Trithiol and Triallyl ether (APE)



(b) Uniform dense network structure

Figure 1. Molecular structure of trithiol, triallyl ether ene, and the resultant uniform network structure.

In Figure 2, the structure of Trimethylolpropane triacrylate (TMPTA) and corresponding matrix structure are depicted. Recently it has been reported that the energy absorbing properties of binary thiol-ene and ternary thiol-ene-(meth)acrylate networks provide the potential for a whole array of new sports and personal protection products that heretofore have not been accessible using traditional photocuring systems.<sup>3,5</sup>



(a) Trimethylolpropane triacrylate



(b) Crosslinked structure

Figure 2. Molecular structure of triacrylate and crosslinked homopolymer.

It is well known that chain mobility and conformational structure changes of polymer systems can occur during physical aging. This aging has been shown for linear polymers and epoxy networks to depend on molecular weight and molecular weight distribution for linear polymers, and crosslink-density and distribution of molecular weight between crosslinks for the crosslinked epoxies.<sup>6-10</sup> As suggested by the results for epoxy systems, herein we report on the physical aging behavior of thiol-ene and thiol-ene-acrylate networks monitored by enthalpy relaxation in terms of the network structural uniformity and component chemical structure in order to demonstrate how aging of thiol-ene networks occurs over a wide temperature range. It is demonstrated that the copolymerization of a multi-functional acrylate (i.e. TMPTA-trimethylolpropane triacrylate) with a traditional thiol-ene system hinders the formation of a uniform dense network structure, leading to a broader distribution of network density and retardation of the enthalpy relaxation. The rate of enthalpy relaxation as a function of TMPTA content clearly demonstrates that the sub- $T_g$  aging behavior of thiol-ene based networks can be readily controlled.

## Experimental

### Materials

All thiols (1,6-Hexanedithiol (Thiol 1), Triethylolpropane tris(3-mercaptopropionate) (Thiol 2), and Pentaerythritol tetrakis(3-mercaptopropionate) (Thiol 3)), trimethylolpropane triacrylate (TMPTA), and ene monomers (Allyl pentaerythritol (Ene 1), 2,4,6-Triallyloxy-1,3,5-triazine (Ene 2), and 1,3,5-Triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (Ene 3)) were obtained from Bruno Bock Thio-Chemicals-S and Perstorp Specialty Chemicals, respectively. The photoinitiator, 2,2-dimethoxy 2-phenyl acetophenone (DMPA), was obtained from Ciba Specialty Chemicals. All materials were used as received.

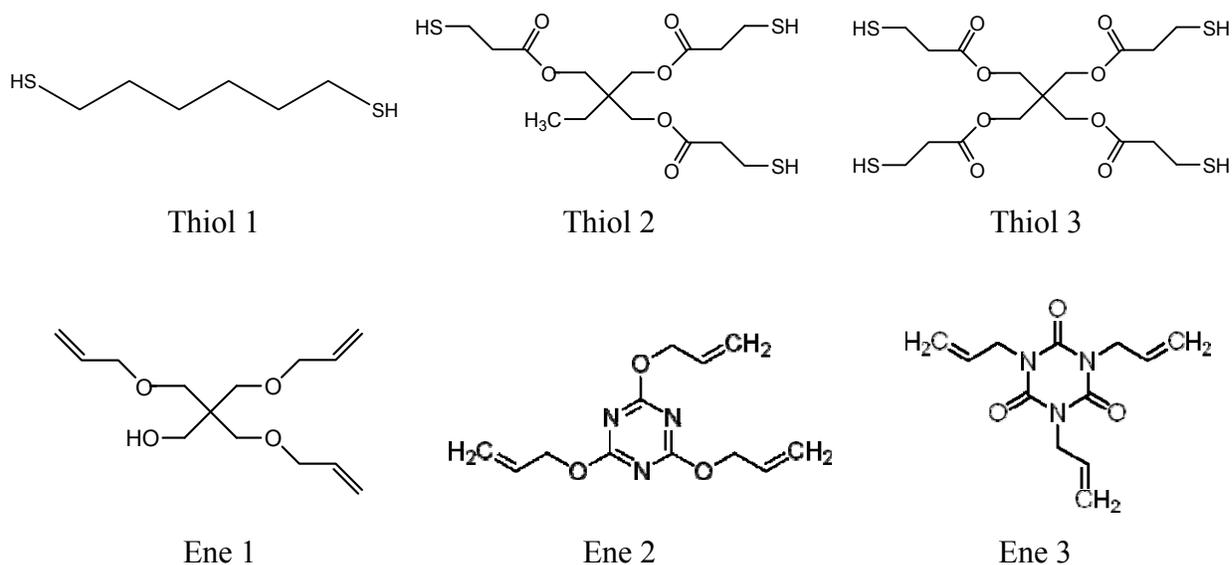


Figure 3. The structure of thiols and ene monomers.

### Preparation of thiol-ene films

The photoinitiator (DMPA, 1 wt%) was dissolved in the thiol, TMPTA, and ene monomer mixtures by sonication for 10-20 min. All thiol-ene and thiol-ene-(TMPTA) films were cast on glass plates (using 200  $\mu\text{m}$  draw down bar) and cured on a Fusion UV curing line system via a D bulb (belt speed of 10 feet/min and 3.1  $\text{W}/\text{cm}^2$  irradiance).

### Characterization

Glass transition temperatures and thermal properties were measured with a TA Q1000 differential scanning calorimeter (DSC) from -80 to 200  $^{\circ}\text{C}$  at a 10  $^{\circ}\text{C}/\text{min}$  heating and cooling rate. The enthalpy relaxation was characterized by (a) differential cooling rate, (b) isochronal, and (c) isothermal methods. BYK Gardner pendulum hardness tester was used for measuring Persoz pendulum hardness. Thiol 3-Ene 2 ( $T_g=34$   $^{\circ}\text{C}$ ) and Thiol 3-Ene 3 ( $T_g=53$   $^{\circ}\text{C}$ ) systems were aged at room temperature ( $T_g-14$   $^{\circ}\text{C}$ , 20  $^{\circ}\text{C}$ ) and  $T_g-10$   $^{\circ}\text{C}$  (43  $^{\circ}\text{C}$ ), respectively. Measurement was conducted at room temperature with three different thiol-ene films for each system coated on glass plates at least 10 times for each sample and the five median results were averaged.

## Results and discussion

### Thiol-Ene Binary Systems

In this section we provide a brief summary of representative results that have been obtained for all of the combinations of thiols and enes in Figure 3: accordingly conclusions reflect our observations of the data presented as well as similar data obtained (not shown) for the other systems. Thiol-ene films were aged every 10 °C from  $T_g+5$  to  $T_g-45$  °C to investigate the temperature dependency of enthalpy relaxation. For each scan, the sample was cooled and heated at 10 °C/min from  $T_g-50$  to  $T_g+50$  °C which is high enough to remove the previous thermal history of each sample. Figure 4a shows DSC heating scans of a typical thiol-ene film (Thiol 2 + Ene 1) after aging at different temperatures. Normalized curves were obtained by subtracting from each curve the reference curves generated by heating without aging. The largest enthalpy relaxation peak was observed at  $T_g-10$  °C: the enthalpy relaxation peak becomes smaller as the difference in the aging temperature and  $T_g$  becomes larger (Figure 4b).

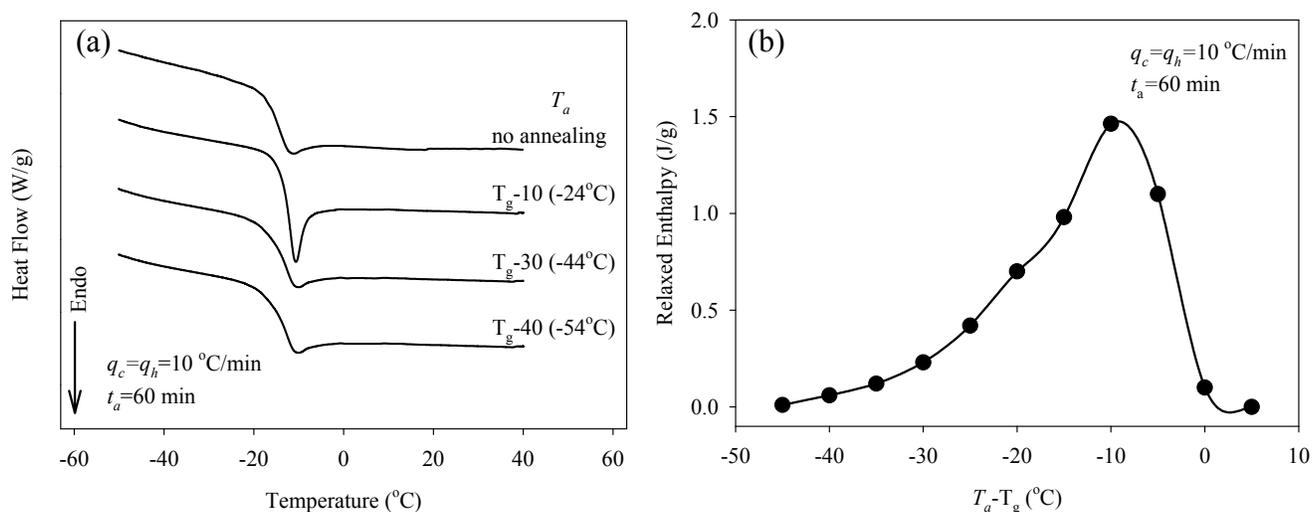


Figure 4. Temperature dependency of Thiol 2 + Ene 1 film on enthalpy relaxation; (a) DSC heating scans after aging at different temperature, (b) The area of enthalpy relaxation peaks ( $t_a=60$ min,  $q_h=q_c=10$  °C/min).

As shown in Figure 4 for the representative Thiol 2+Ene 1 film, all of the thiol-ene films, enthalpy relaxation shows a maximum in the relaxation process near  $T_g-10$  °C as a result of the competition between chain mobility and the thermodynamic relaxation force. Chain mobility decreases with temperature below  $T_g$  while the relaxation thermodynamic driving force increases as temperature decreases. Finally, although not all of the data is shown, it can be concluded from a similar examination of all possible combinations of the thiols and enes in Figure 3 that monomer combinations having higher thiol functionalities (Thiol 3 > Thiol 2 > Thiol 1) and enes with more rigid structure (Ene 3 > Ene 2 > Ene 1) have lower enthalpy relaxation due to decreased chain mobility.

The structural effects also have a significant effect on the relaxation time ( $t_\infty$ ) as calculated by the Struik equation below for establishment of thermodynamic equilibrium at a given temperature ( $T_a$ ) below the  $T_g$ <sup>11</sup>

$$t_{\infty} = 100 \times 10^{(T_g - T_a)/3} = 100 \times e^{0.77(T_g - T_a)}$$

where  $t_{\infty}$  is in seconds and  $T_g - T_a$  is in  $^{\circ}\text{C}$ . Figure 5a shows DSC heating scans of Thiol 2+Ene 2 after aging for different annealing time at  $T_g - 10^{\circ}\text{C}$  where enthalpy relaxation has a maximum in the Isochronal experiment. The enthalpy relaxation peak is significantly dependent on the aging time ( $t_a$ ): the extent of enthalpy for the Thiol 2 + Ene 2 film was calculated and plotted in Figure 5b. Enthalpy relaxation for all combinations of Thiol 2 and the enes in Figure 3 approach equilibrium with increasing aging time at different rates. Linear plots of enthalpy relaxation versus  $\log t_a$  clearly show that the relaxation rate (Figure 5b), which is simply the slope of the plots, is also highly dependent on the flexibility of the monomer units comprising the network.

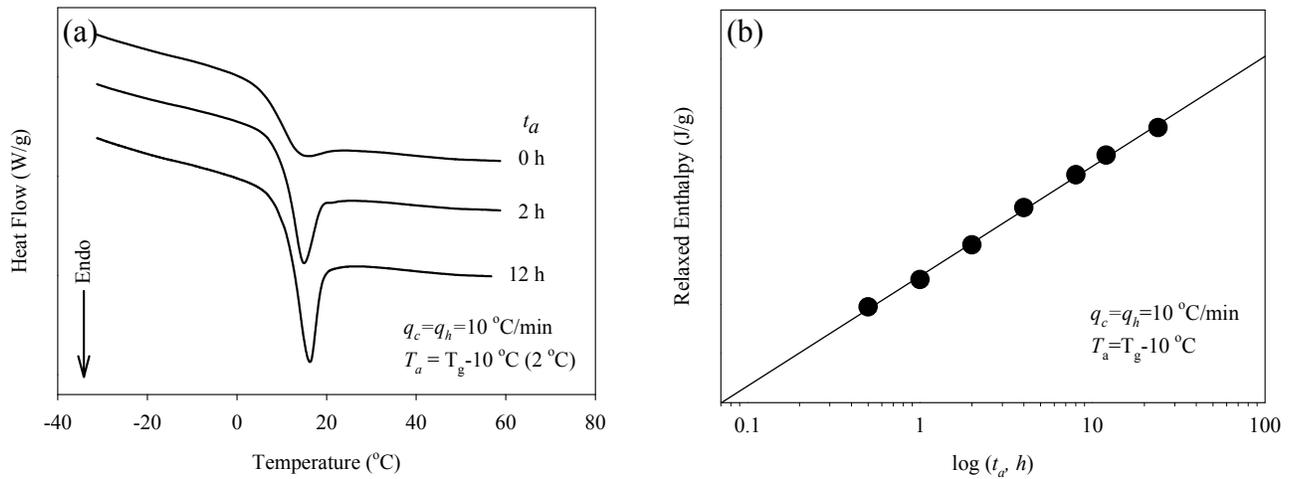


Figure 5. Time dependency of Thiol 2 + Ene 2 film on enthalpy relaxation; (a) DSC heating scans after aging for different time, (b) The area of enthalpy relaxation peaks ( $T_a = T_g - 10^{\circ}\text{C}$ ,  $q_h = q_c = 10^{\circ}\text{C}/\text{min}$ ).

In Figure 6, Persoz pendulum and pencil hardness data for Thiol 3+Ene 2 as a function of aging time ( $t_a$ ) are shown. A film of Thiol 3 + Ene 2 coated onto a glass plate was isothermally aged at room temperature ( $20^{\circ}\text{C}$ ,  $T_g - 14^{\circ}\text{C}$ ) before measurements were made. A linear relationship between hardness and  $\log$  aging time ( $t_a$ ) was obtained consistent with the time dependency of the enthalpy relaxation.

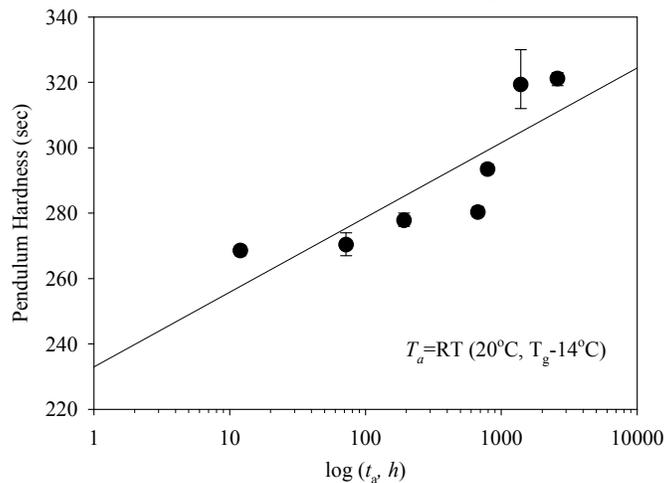


Figure 6. Persoz pendulum hardness for Thiol 3-Ene 2 as a function of aging time ( $t_a$ ).

In addition, the pencil hardness value also increased from 1H (initial) to 4H after annealing for four months. Both hardness went back to the initial value when samples were reheated to  $T_g+50$  °C, showing that the physical property changes are consistent with physical aging.

### Thiol-Ene-Acrylate Ternary Systems

In order to determine how acrylates added to thiol-ene networks can affect the sub- $T_g$  relaxation, thiol-ene-acrylate ternary films were prepared by mixing Thiol 2 + Ene 1 with different molar concentrations of TMPTA (10, 20, 30, 40, 50, 60, and 100 mole %). The glass transition temperature increases continuously and broadens as a function of TMPTA content, and the enthalpy relaxation peak observed in the neat Thiol 2 + Ene 1 network also disappears for samples with > 20% TMPTA (actual relaxation peaks not shown). It is clear that incorporating TMPTA into thiol-ene network successfully decreases the network uniformity and corresponding enthalpy relaxation.

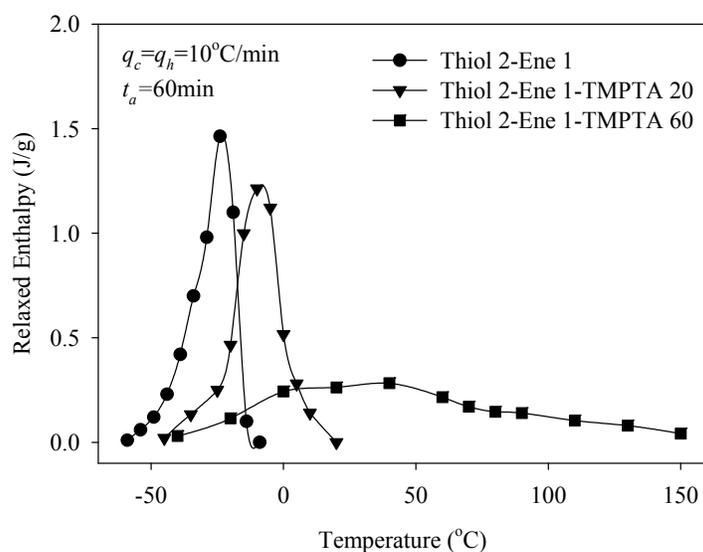


Figure 7. Temperature dependency of enthalpy relaxation of Thiol 2 + Ene 1 + TMPTA ternary system ( $t_a=60$ min,  $q_c=q_h=10$  °C/min)

The effect of structure modification on aging obtained by incorporating TMPTA into the thiol-ene network is more readily observed by temperature (Figure 7) and time dependency measurements (Figure 8). The peak of enthalpy relaxation distribution of Thiol 2 + Ene 1 + TMPTA films obtained from Isochronal analysis drastically decreases as a function of TMPTA content, and the peaks broaden implying that enthalpy relaxation is not concentrated in a narrow temperature range (Figure 7).

The extent and time of enthalpy relaxation evaluated at  $-24$  °C in Figure 8 shows that the rate of enthalpy relaxation of the Thiol 2 + Ene 1+TMPTA ternary systems decreases with increasing TMPTA content. Consequently, it is concluded that sub- $T_g$  aging of a base Thiol 2-Ene 1 network as monitored by enthalpy relaxation is successfully controlled by incorporating TMPTA. This has far reaching implications for controlling the relaxation process, and as will be shown in the presentation, it has implications for controlling changes in physical properties such as Persoz hardness, pencil hardness and scratch resistance when thiol-ene-acrylate systems are aged at temperatures below their glass transition.

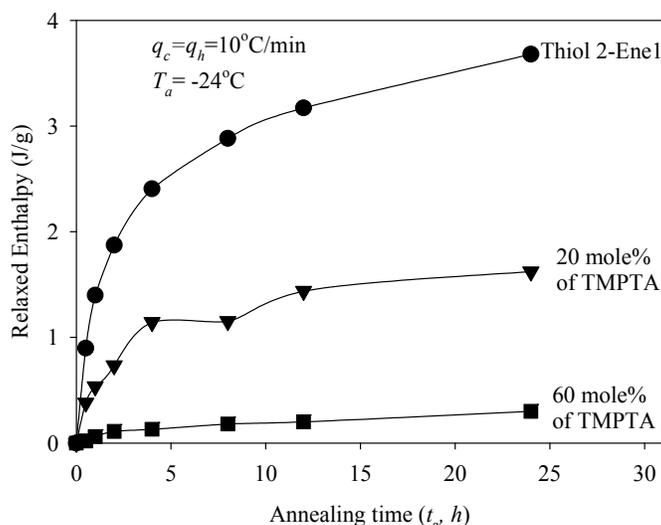


Figure 8. Time dependency of enthalpy relaxation of Thiol 2 + Ene 1 + TMPTA ternary system ( $T_a = -24$  °C,  $q_c = q_h = 10$  °C/min).

## Conclusions

Photopolymerized thiol-ene and thiol-ene-acrylate ternary films were studied in terms of aging and its effect on enthalpy relaxation and physical properties. Maximum enthalpy relaxation was observed at  $T_g - 10$  °C for all thiol-ene films investigated. The extent of the enthalpy relaxation showed a linear logarithmic dependence on the aging time. The temperature and time dependency of the enthalpy relaxation process is directly related to the flexibility of the units comprising the network. Physical property changes monitored by Persoz and pencil hardness increased as a function of aging time and also showed temperature dependent behavior which was coincident with the enthalpy relaxation of thiol-ene films. When a multifunctional acrylate was incorporated into the thiol-ene network, it was observed that the extent of enthalpy relaxation decreased and broadened as a function of TMPTA content thus allowing direct control of the enthalpy relaxation behavior of thiol-ene based networks. The enthalpy relaxation is a guide for changes in other physical and mechanical properties which are subjected to sub- $T_g$  aging. In the presentation the importance of sub- $T_g$  aging of a wide variety of mechanical/physical properties (hardness, abrasion resistance, and adhesion) of thiol-ene and thiol-ene-acrylates will be discussed with emphasis on how to formulate such resin systems with the goal of minimizing harmful changes in film-performance parameters. Also, implications of sub- $T_g$  physical property changes for coatings produced from traditional acrylic formulations will be contrasted with results obtained from the thiol-ene and thiol-ene-acrylate system.

## Acknowledgements

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