

# The Effect of POSS Compatibility on the Morphology of Thiol-ene Polymer Nanocomposites

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## Abstract

The changes in physical properties of trithiol-TAE (triallyl ether) films were measured with respect to increasing POSS concentrations in order to understand how POSS compatibility affects film morphologies of a nanocomposite series. Compatibilization of POSS particles improves the solubility of the silicate particles in the organic medium. POSS monomers (vPOSS-Bu and vPOSS-E2MP) with both vinyl and carboxylate pendant groups were synthesized by an amine-catalyzed thiol Michael addition reaction. Chemically modified POSS particles were incorporated into the trithiol-TAE polymer networks by a thiol-ene free radical photopolymerization at ene molar concentrations of 0 mol%, 5 mol%, 10 mol%, 20 mol%, and 50 mol%. Surface hardness and scratch resistance were measured by Persoz pendulum and pencil hardness tests. Surface properties decreased appreciably with decreased compatibility of vPOSS nanoparticles at high concentrations of the silicate particles. The presence of large aggregates at the surface contributed to the decrease in surface hardness and scratch resistance.

## Introduction

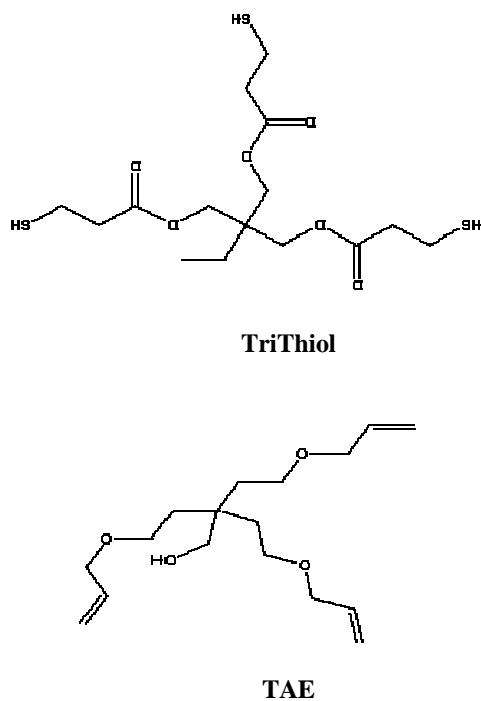
Thiol-ene photopolymers, which are formed by a photoinduced, stoichiometric reaction of thiol and ene (C=C) groups, are a unique and versatile class of polymers.<sup>1,2</sup> Thiol-ene polymers are highly flexible materials that exhibit superb mechanical and physical properties, which are attributed to the formation of thioether bonds and the uniformity of the crosslink density of the polymer network. Traditionally, thiol-ene photopolymers have been used in applications of adhesives, wood and floor coatings, and optical and circuit board coatings. The thioether bond contributes to the flexibility and antioxidant properties of the material. Also, the low glass transition temperature ( $T_g$ ) of the material is directly related to the presence of the thioether bond.

Photopolymerization of this system involves a free radical reaction of thiol and ene groups that builds high-molecular weight polymers by a step-growth mechanism<sup>1,2</sup>. The reaction mechanism is initiated by the photoinduced formation of a thiyl radical that subsequently attacks a double bond to form a carbon-centered  $\beta$ -radical.

Next, the  $\beta$ -radical abstracts hydrogen from a thiol in a chain transfer reaction to form a thiyl radical that initiates polymerization. The polymerization is unaffected by the presence of oxygen since oxygen inhibition is retarded by the chain transfer reaction between the peroxy radical and thiol monomer. Since the thiol-ene polymerization can occur with any available ene monomer, the properties of the thiol-ene polymers may be tailored by ene selection. By ene selection, the properties of the polymers may range from being soft, flexible coatings to hard, scratch resistant films. Thiol-ene films have been formulated using various ene structures, including vinyl ethers, allyl ethers, and acrylates.<sup>1,2</sup> Additionally, siloxane-based thermosets and ceramics have been formulated using thiols with siloxane enes and vinyl silane groups.

Generally, polyhedral oligomeric silsesquioxane (POSS) particles improve thermal, mechanical, and physical properties when added to a polymer matrix.<sup>3</sup> Previous publications cite that incorporated POSS particles significantly improve surface hardness, use temperature, oxidation and fracture resistance, and flammability, as well as thermomechanical properties.<sup>3-5</sup> POSS nanoparticles have chemical structures that consist of an inorganic core surrounded by organic pendant groups ( $R_n(\text{SiO}_{1.5})_n$ ). The organic pendant groups may be reactive or nonreactive, and, thus, POSS particles are easily added into a polymer backbone via copolymerization by the reactive pendant groups, whereas the solubility of the POSS particles is improved by the presence of nonreactive organic pendants. Selection of a nonreactive pendant group is critical for the dispersion of POSS particles in an organic medium since these pendant groups improve the compatibilization of the inorganic particles with an organic medium.

Herein we show that vinyl POSS (vPOSS) particles modified with ester tails by an amine-catalyzed thiol-Michael addition reaction can be photochemically incorporated into a trithiol-triallyl ether (TriThiol-TAE—Structures given in Figure 1) polymer network via copolymerization of thiol with vinyl and allyl ether groups, are. This study reports how the morphology and physical properties of a TriThiol-TAE polymer network are affected by the compatibility of the POSS particles with trithiol and triallyl ether comonomers at various concentrations of vPOSS particles.



**Figure 1.** The chemical structures of TriThiol, and triallyl ether (TAE).

## 1. Experimental

Trimethylolpropane tris(3-mercaptopropionate) (TriThiol), butyl 3-mercaptopropionate (Bu), ethyl 2-mercaptopropionate (E2MP), and diethyl amine were purchased from Aldrich Chemical Company and used as received. Allyl pentaerythritol (TAE) was obtained from Perstorp Specialty Chemical Company, and vinyl POSS was donated by Hybrid Plastics, Inc. The photoinitiator Darocur 1173 was obtained from Ciba Specialty Chemicals, Inc.

### 1.2 Monomer Synthesis

The POSS monomers (vPOSS-Bu and vPOSS-E2MP) with both vinyl and ester tails were modified by an amine-catalyzed Michael addition of two aliphatic thiols (butyl 3-mercaptopropionate and ethyl 2-mercaptopropionate) to the electron-deficient vinyl groups of the vinyl POSS (vPOSS) cage. A 20-g sample of POSS ( $f_{\text{avg}} = 10$ ) and 2 wt% diethyl amine catalyst were dissolved in 25 ml THF. The solution was slowly added to each thiol in 3-4 ml aliquots every 10 minutes while continuously stirring. The solution was stirred for at least 6 hours before THF was removed by rotovaporization. Oil containing the product remained after the complete evaporation of THF. Proton NMR analysis indicated that the reaction contained no

unreacted thiol since the thiol peak (1.6 ppm) was undetected. The average vinyl functionalities were  $f_{\text{vinyl}} = 6$  and  $f_{\text{vinyl}} = 4$  for the vPOSS-Bu and vPOSS-E2MP nanoparticles, respectively.

### 1.3 Polymer Synthesis

TriThiol-TAE films containing 0 mol%, 5 mol%, 10 mol%, 20 mol%, and 50 mol% of vPOSS particles were photocured on a Fusion Epiq 6000 UV cure line. A 400-W D bulb was used as the light source. Each film, having a thickness of 150-300 microns, was cured at a light intensity of 3.1 W/cm<sup>2</sup> and at a line speed of 12.2 m/min. Each reaction mixture contained equal molars of thiol and ene functional groups in addition to 2 wt% photoinitiator. The reaction mixtures were maintained at 50:50 thiol:ene molar ratio while the concentration of each ene was varied.

### 1.4 Physical Property Analysis

Scratch resistance of the TriThiol-TAE/vPOSS nanocomposite series was determined by a pencil hardness test using a series of pencils of varying hardness. The range of pencil lead hardness is ordered from softest (9B-B) to mid-grade (F, HB) to hardest (H-9H). Film hardness was also determined by a Persoz pendulum hardness test. The degree of hardness is directly related to the number of oscillations required for the pendulum to dampen on the polymer surface.

### 1.5 Instrumentation

Dynamic light scattering analysis was performed on a Nanotracc NPA 252 analyzer to measure silicate particle sizes in the prepolymer mixtures.

## 2. Results and Discussion

The efficiency of POSS copolymerization with the thiol and ene comonomers depends greatly on the nanoparticles compatibility with the organic phase. Compatibilization of the silicate particles prevents phase separation of the inorganic and organic phases, thus improving the solubility of the silicate cages within the organic medium. POSS compatibilization is achieved by selection of type and quantity of nonreactive pendant groups attached to the cage structure. In this study, the type and number of pendant organic groups added to the vPOSS particles are varied in order to understand the relationship between POSS compatibility and the film morphologies of the TriThiol-TAE/vPOSS nanocomposite series. Specifically, the changes in the physical properties of TriThiol-TAE films are analyzed with respect to vPOSS concentrations in order to illustrate the effects of compatibilization on film properties. The vPOSS particles used in this study were modified with butyl 3-mercaptopropionate (Bu) and ethyl 2-mercaptopropionate

(E2MP) having vinyl functionalities of  $f_{\text{vinyl}} = 6$  and  $f_{\text{vinyl}} = 4$ , respectively (Figures 2 and 3).

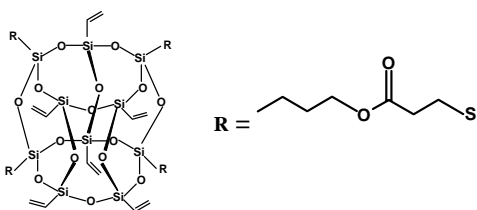


Figure 2. The chemical structure of vPOSS modified with butyl-3-mercaptopropionate (vPOSS-Bu).

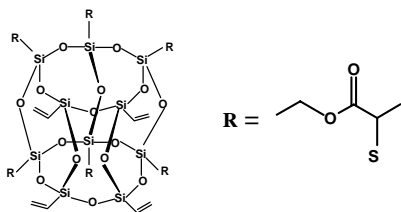


Figure 3. The chemical structure of vPOSS modified with ethyl-2-mercaptopropionate (vPOSS-E2MP).

Surface hardness and scratch resistance values (Table 1) determined for a series of TriThiol-TAE/vPOSS-Bu films containing 0 mol%, 10 mol%, and 50 mol% of vPOSS-Bu were found to be strongly influenced by compatibilization of vPOSS-Bu. The physical properties significantly improve as vPOSS-Bu concentrations increased to 10 mol% of the ene concentrations then begin to decrease at higher concentrations. Analysis of the prepolymer mixtures by dynamic light scattering (DLS) show that vPOSS-Bu aggregates are detectable at high vPOSS-Bu concentrations of 20 mol% or greater. Phase separation between the thiol and allyl ether comonomers and the silicate particles occurs producing large POSS aggregates. At low concentrations, vPOSS-Bu particles are miscible with the thiol and allyl ether comonomers, which results in good dispersion of vPOSS-Bu throughout the polymer matrix. Since the silicate particles are well dispersed throughout the polymer, the hard POSS particles reinforce the soft TriThiol-TAE network, and the surface hardness and fracture resistance increase appreciably. By contrast, decreased surface properties are observed at high vPOSS-Bu concentrations resulting from the presence of aggregates as identified by TEM and AFM (actual data not given herein). The distribution of large aggregates contributes to the brittleness of the polymer surface, thus causing the material to readily fracture. Also, poor dispersion of the vPOSS-Bu particles within the polymer network results in a decrease in the hardness of the material. Consequently, the poor dispersion of the vPOSS-Bu indicates that the silicate particle is incompatible with the trithiol comonomer at high concentrations.

In an effort to reduce aggregation in the prepolymer mixture, vPOSS was modified with an ethyl-2-mercaptopropionate (E2MP) pendant group (Figure 2). Additionally, the number of pendant groups was increased to improve miscibility of the modified POSS particles at high concentrations. A series of Trithiol-TAE/vPOSS-E2MP films containing 0 mol%, 10 mol%, and 50 mol% vPOSS-E2MP were tested to determine how surface hardness and fracture resistance changed with respect to the vPOSS-Bu concentration. Analysis of the prepolymer mixtures by DLS shows no presence of detectable POSS aggregates for all ene concentrations of vPOSS-E2MP, indicating that the vPOSS-E2MP nanoparticles are miscible in trithiol even at high concentrations of POSS. The vPOSS-E2MP particles are compatible with the thiol and allyl ether comonomers, thereby resulting in good dispersion of vPOSS-E2MP particles throughout the polymer network. The hardness measurements in Table 1 show an initial increase with increased vPOSS-E2MP concentrations (10 mol%), and no substantial decrease at the higher vPOSS-E2MP concentration (50 mol%) apparently vPOSS-E2MP particles are not excluded from the basic softer trithiol-TAE network. Consequently, fewer POSS particles are located at the surface of the material since the improved compatibility allows for the POSS particles to be easily incorporated into the polymer network. Further study of the film morphologies via TEM and AFM microscopy will be presented at the meeting.

	[vPOSS-R] (mol%)	Particle size (nm)	Perso2 (seconds)	Pencil (lead grade)
<b>R = Bu</b>	0	0	184	2H
	10	1	255	6H
	50	725	79	2H
<b>R = E2MP</b>	0	0	184	2H
	10	1.21	252	2H
	50	7.28	230	2H

Table 1. Particle sizes of vPOSS particles as measured by dynamic light scattering (DLS). Surface properties of trithiol-TAE/vPOSS nanocomposites as measured by Persoz and pencil hardness tests.

## Conclusion

The physical properties of thiol-ene networks are strongly influenced by the compatibility of the inorganic POSS particle incorporated into the thiol-ene polymer matrix. At high vPOSS-Bu concentrations, the presence of large silicate aggregates result in a decrease in physical properties, i.e. the surface hardness and scratch resistance

decrease significantly with a higher concentration of vPOSS-Bu ([vPOSS-Bu = 50 mol%]). Selection of the type and number of nonreactive pendant group contributes to the solubility of the inorganic silicate particle in the thiol and allyl ether prepolymer mixture. At high vPOSS-E2MP concentrations, aggregation of silicate particles is inhibited and the particles are dispersed well throughout the photocured polymer network.

## References

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