

The Effects of POSS Nanoparticles on Surface and Bulk Properties on Thiol-ene Thin Films

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Abstract: *Analysis of the physical properties of thiol-ene/POSS (PolyOligomeric Silsesquioxane) nanocomposite coatings indicates that high concentrations of POSS nanoparticles significantly affects film hardness at the surface and in the bulk of the hybrid films. The thiol-TAE (triallyl ether) films containing 0, 1, 10, 20, 50 % molar concentrations of ester vinyl POSS show increased surface hardness and decreased bulk hardness as the concentration of POSS increases. Surface and bulk properties are analyzed at depths of a few nanometers to ~1 mm by Hysitron nanoindentation, and shore A hardness test.*

Introduction

Interest in silicate-based hybrid polymeric nanocomposites for various applications has grown in which properties such as hardness, flame retardancy, scratch resistance, gas permeation, and barrier properties are important. Recent literature cite many silicate-based hybrid polymeric nanocomposites, including films incorporating ORMOSILs (organically modified silicates) and POSS (polyhedral oligomeric silsesquioxane) cages, and ceramers.¹⁻⁶ POSS cages are a unique blend of organic and inorganic characteristics in which the empirical structure of silicone cages $(\text{RSiO}_{0.5})_{n=8, 10, 12}$ varies in both the size of the cage and types of organic substituents attached to the silicone cage. Cage sizes may vary $z(n = 8, 10, 12)$ with either reactive or nonreactive organic moieties at each corner of the cage. Nonreactive organic moieties can improve the compatibility of POSS nanoparticles in organic materials thus improving the solubility.

Reactive silicate nanoparticles, including POSS cages, may be incorporated into a polymer by UV curing of its pendant organic functional groups.^{7, 9, 10} In this paper, pendant vinyl groups are chemically modified via a catalyzed Michael addition to improve the solubility of the POSS nanoparticles in thiol-ene monomer mixtures. POSS nanoparticles are subsequently incorporated into the thiol-ene polymer matrix by a thiol-ene free radical photopolymerization process (**Figure 1**).

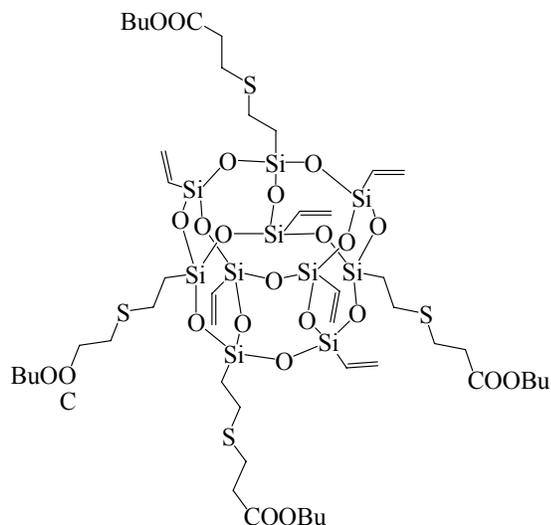


Figure 1. The chemical structure of vinyl POSS with pendant organic moieties.

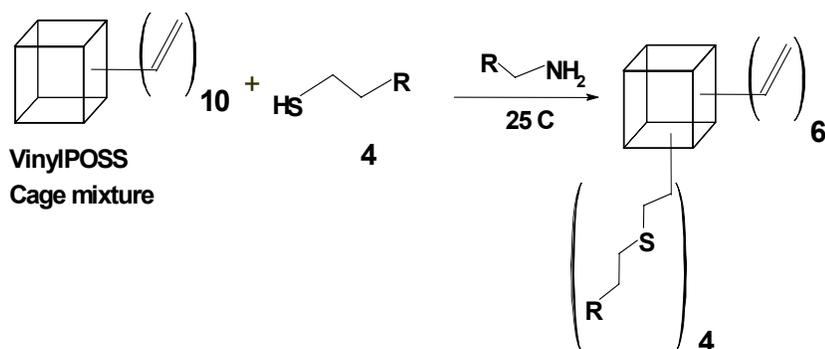
The aim of this research is to tailor polymeric materials that have improved surface hardness and fracture resistance; in addition to the traditional properties of thiol-ene films.¹² This is accomplished by incorporating chemically modified POSS nanoparticles into a series of thiol-TAE (triallyl ether) films to characterize the effects of POSS concentration on the photocured thiol-ene film properties. Nanoindentation, and other methods for evaluating hardness are used in this investigation.

Experimental

VinylPOSS-Bu, with an average cage size of ten, was obtained from Hybrid Plastics, Inc. Allyl Pentaerythritol (triallyl ether) was obtained from Perstorp Specialty Chemical Company. Photoinitiator Irgacure 651 was obtained from Ciba Specialty Chemicals, Inc. Trimethylpropane tris(3-mercaptopropionate) (trithiol), butyl mercaptopropionate, and octyl amine were purchased from Aldrich Chemical Company and used as received.

Hysitron TriboIndenter was used in a closed loop/feedback displacement method to measure surface hardness. A Berkovich diamond tip with an included angle of 142.3° having an average radius curvature of 100-200 nm was used. μ N. Shore A hardness tests were performed using ASTM method.¹¹ Persoz pendulum hardness test were performed on a BYK-Gardner pendulum hardness tester.

POSS monomer (**vPOSS-Bu**) with both vinyl and carboxylate groups available was synthesized by an amine-catalyzed thiol Michael addition of thiol and ene groups (**Scheme 1**).



Scheme 1. Synthesis of hexavinyl POSS with pendant organic groups that solubilize the nanoparticle in coatings formulations. R= -COOBu.

Thiol-ene films containing 0 mol%, 1 mol%, 10 mol%, 20 mol%, and 50 mol% vPOSS-Bu nanoparticles were photocured on a Fusion 6000 UV cure line. Reaction mixtures contained equal molars of thiol to ene in addition to 1 wt% photoinitiator. Throughout the series of films, reaction mixtures were maintained at 50:50 thiol:ene molar ratios as the concentration of each ene was varied. A 400-W Fusion D-bulb lamp was used as the light source, and each film was cured on 1 pass at a light intensity of 2.29 W/cm². Each film had a film thickness of 6 mils.

All vPOSS-Bu films prepared cured rapidly upon exposure to a single pass on the UV curing line to give hard, optically clear, defect free films.

Results and Discussion

Surface hardness, as well as other measures of hardness, were analyzed with respect to increasing vPOSS-Bu concentration using nanoindentation, shore A hardness, pencil hardness, and Persoz hardness tests. Surface hardness, as measured by nanoindentation, increased with increasing molar concentration of vPOSS-Bu (**Table 1**). Increased hardness of the film is inherent since POSS nanoparticles act as hard beadlike structures distributed throughout the surface. Conversely, shore A hardness values attained a maximum for the sample with 10 mol% vPOSS-Bu, with failure occurring for samples with molar concentrations greater than 10 mol% vPOSS-Bu (**Table 2**). High concentrations of POSS nanoparticles form brittle materials that readily fracture. It is possible that coatings containing high POSS concentrations may result from phase separation of POSS particles within the film.

Mol% POSS	Force (μN)
50	550
20	375
10	320
1	300
0	250

Table 1. Nanoindentation studies. Surface hardness was determined with respect to maximum force applied to indent the film surface at maximum depths of 2.5 μ .

Mol% POSS	Hardness
50	38
20	51
10	54
1	34
0	26

Table 2. Shore hardness test. Resistance to fracture failure was determined by the relative hardness of the film as measured by the durometer (type A).

Persoz and pencil hardness tests exhibited similar trends to the shore A hardness with POSS incorporation. Finally, burn tests indicated that film samples with PSS content of 10 mol% or greater exhibited significantly reduced burn rates, an important advantage for POSS-containing systems.

Conclusion

Various molar concentrations of POSS nanoparticles were added to a thiol-TAE polymer matrix to improve surface hardness, and fracture resistance of the films. Results show that surface hardness

improve considerably as the POSS concentration increases from 0 to 50 mol%. Fracture resistance optimizes at a concentration of 10 mol% POSS, and steadily declines at higher concentrations.

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References

1. Peterson, K. A.; Conley, W. R. In *US Patent 6335224 B1*, **2002**.
2. Hendrick, J. L.; Miller, R. D.; Yoon, D.; Cha, H. J.; Brown, H. R. Srinivasan, A. A.; Di Peitro, R.; Flores, V. *Polym. Prepr.* **1997**, 38,558.
3. Vorotilov, K. A.; Petrovsky, V. I.; Vasiljev, V. A.; Sobolesvsky, M. V. *Journal of Sol-Gel Sci. And Tech.* **1997**, 8, 581-584.
4. Miller, R. D.; Hedrick, J. L.; Yoon, D. Y.; Cook, R. F.; Hummel, J. P. *MRS Bull.* **1997**, 22, 44-48.
5. Scott, D. W. *J. Am. Chem. Soc.* **1946** 68 (3), 356-358.
6. Chisholm, B.; Resue, J. *Proceedings of the International Waterborne, High-Solids, and Powder Coatings Symposium*, **2003**, 30, 261-281.
7. Wilkes, G. L.; Orler, B.; Huang, H. H. *Polym. Prepr.* **1985**, 26, 300-302.
8. Vreugdenhil, A. J.; Balbyshev, V. N.; Donley, M. S.; *J. Coatings Tech.* **2001**, 73, 35-43.
9. Ravaine, D.; Seminel, A.; Charbouillot, Y., Vincens, M. *Journal of Non-Crystalline Solids*, **1986**, 82, 210-219.
10. Mackenzie, J. D. *Journal of Sol-Gel Sci. and Tech.* **1994**, 2, 81-86.
11. *ASTM 1956*, D 568-56 T.
12. Jacobine, A. F., *Thiol-ene Photopolymers in Radiation Curing*; Elsevier Science Publishers Ltd.: New York, **1993**.