

NEW INSIGHT INTO THE STRUCTURE-PROPERTY RELATIONSHIPS OF HYBRID (INORGANIC/ORGANIC) POSS™ THERMOPLASTICS

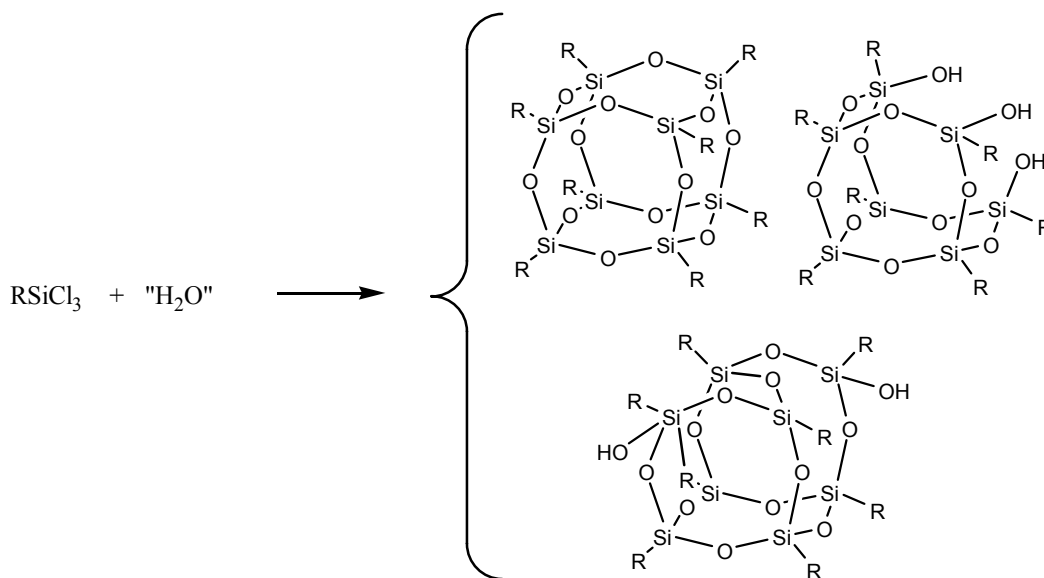
Shawn H. Phillips¹, Rusty L. Blanski, Steven A. Svejda, Air Force Research Laboratory, Edwards AFB, CA; Timothy S. Haddad, ERC Inc., Edwards AFB, CA; Andre Lee, Michigan State University, Dept. of Mat. Sci. & Mechanics, Lansing, MI; Joseph D. Lichtenhan, Hybrid Plastics², Fountain Valley, CA; Frank J. Feher, UCI, Irvine, CA; Patrick T. Mather, U of Connecticut, Inst. Mat. Sci. & Chem. Eng., Storrs, CT; Benjamin S. Hsiao, State U. of NY at Stony Brook, Stony Brook, NY.

The demand for multi-purpose, high-performance polymer systems has resulted in a need for advancing polymer properties beyond what traditional systems can offer. Only through control/alteration at the molecular level can one maximize property enhancements to meet current military and commercial needs. Over the last seven years the Air Force Research Laboratory has developed and incorporated discrete Si-O frameworks (POSS = Polyhedral Oligomeric Silsesquioxanes) into traditional organic polymer systems. This research has resulted in new hybrid inorganic-organic polymer systems with remarkable enhancements in mechanical and physical properties including dramatic increases in both glass transition and decomposition temperatures, reduced flammability, increased moduli and oxidation resistance. We have shown that these enhancements result from the chemical composition (Si-O core) and size (~15 Å in diameter) of the POSS frameworks, and can be copolymerized, grafted, or even blended using traditional processing methods. Recently, we have focused our efforts on understanding and controlling the molecular level interactions between POSS frameworks and the polymer matrix. The development of new POSS monomers has allowed us to study how functionality, size, and geometry enhances the bulk properties of these hybrid materials. For example, increasing the solubility of side groups on the POSS framework results in greater POSS-polymer matrix interactions and increased T_g and storage moduli. Recent studies with POSS blends have resulted in increases in hardness, and reductions in dielectric constants and coefficients of thermal expansion. New results in polymer synthesis, characterization, and applications will be discussed with a strong emphasis on the versatility of this new nanotechnology to many polymer systems.

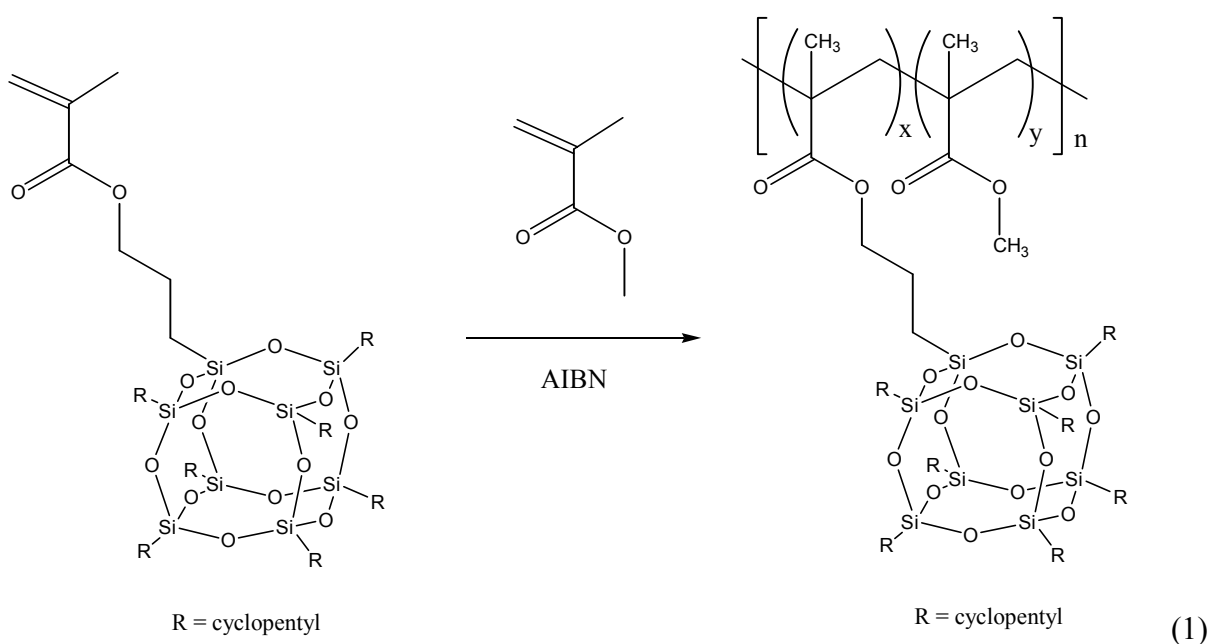
INTRODUCTION

Research efforts on hybrid inorganic/organic polymers have steadily increased as a result of both industrial and governmental demands for multi-functional, high performance polymers that are lighter weight and lower cost than their traditional counterparts. While there are numerous hybrid polymer systems, only recently have synthetic methodologies been developed to significantly increase the interfacial interactions between the inorganic and organic moieties, while also allowing for a decrease in the size of the inorganic particles. As one decreases the size of the inorganic particles, one increases the surface to volume ratio eventually leading to an aspect ratio similar to the polymer coils and resulting in the maximizing of property enhancements. Polyhedral Oligomeric Silsesquioxanes (POSS) are one of only a few nanotechnologies for hybrid polymers that is readily functionalizable and on the same length

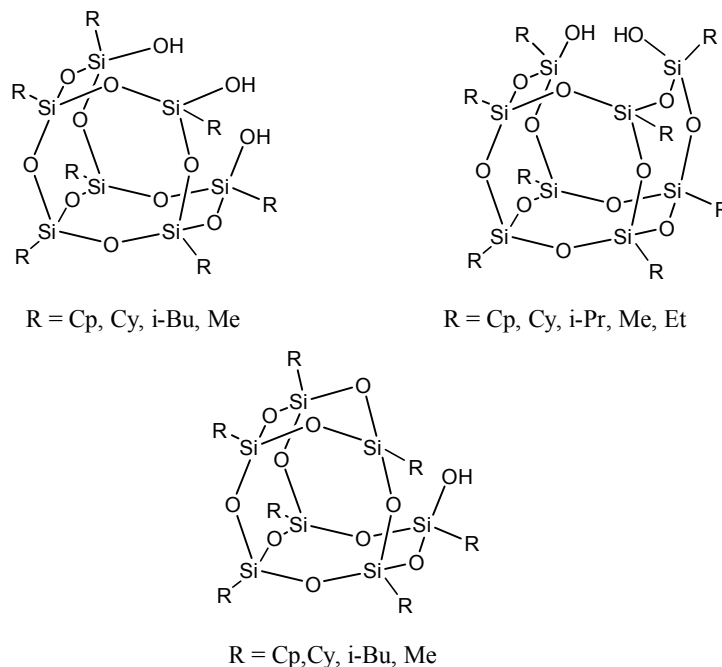
scale as the polymer coils.³ POSS frameworks are traditionally synthesized from the controlled condensation of alkyltrichlorosilanes in a solvent containing limited amounts of water (Scheme 1).⁴ Further functionalization results in polymerizable or blendable macromers, which have been incorporated into a variety of polymer systems including polyurethanes, epoxies, polystyrenes, polynorbornenes, polyimides and polyacrylics (equation 1). Physical and mechanical studies on POSS-polymers have shown significant property enhancements including increased use temperature, toughness, moduli and oxidation resistance along with decreased flammability.⁵



Scheme I



While general trends in property enhancements have been observed there is a growing need to tailor POSS monomers (size, shape, functionality) in order to study the structure/property relationships of POSS-polymers (Scheme II). With such an understanding one can control/alter the properties of POSS-polymers. In this paper we describe our collaborative strategy for such an ambitious project, the early successful experimental data obtained from our investigations and the future direction of POSS-polymer research.

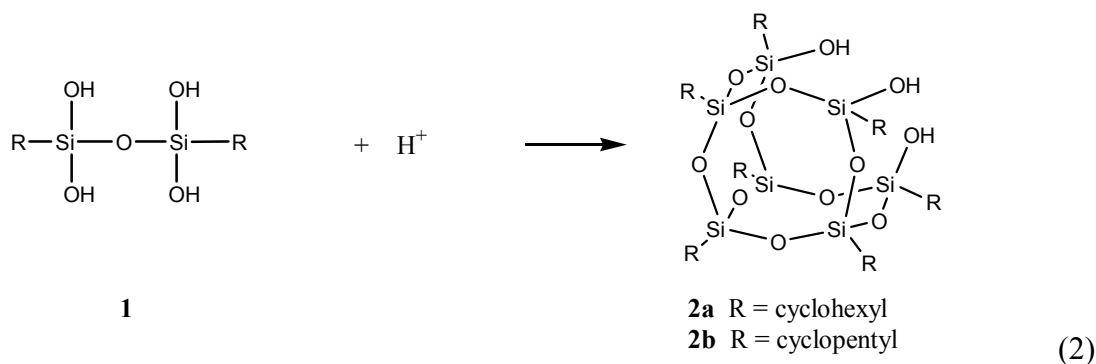


Scheme II: Varying Size, Shape and Functionality of POSS monomers

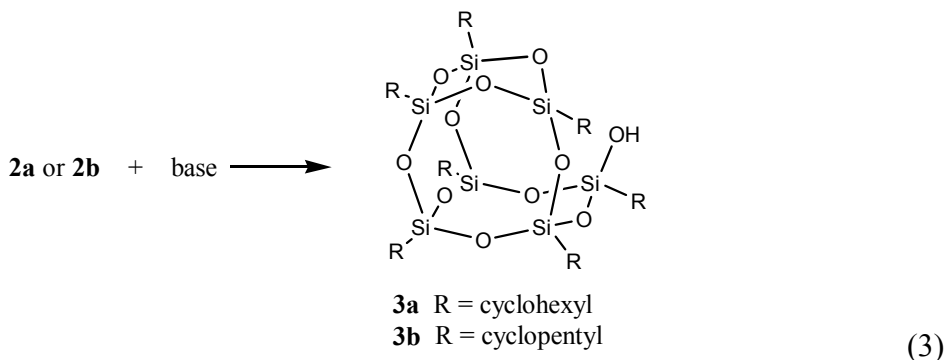
RESULTS AND DISCUSSION

POSS Monomers

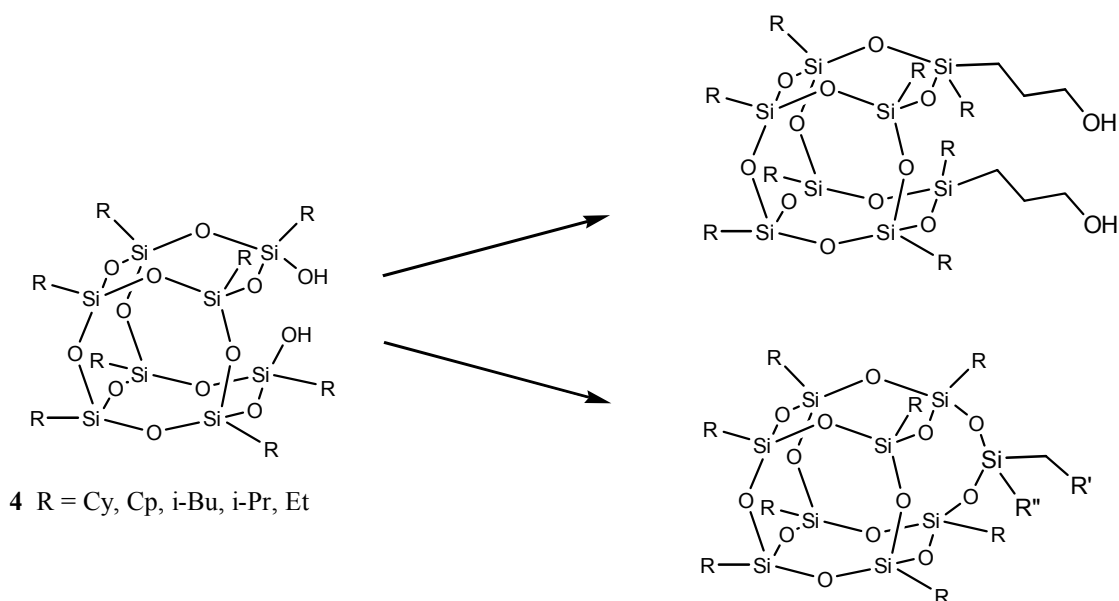
The majority of POSS-polymers contain either the cyclohexyl (**2a**) or cyclopentyl (**2b**) POSS frameworks. Long reaction times of 3-36 months limited the available quantities of **2a**, prompting the production of the less soluble, but readily produced (1-2 weeks) **2b**. The need for more soluble POSS monomers prompted the development of alternative synthetic techniques for producing **2a**. The starting alkyltrichlorosilane was added and precipitated from a 90:10 water/acetone solution to yield **1**,⁶ followed by reactions with various acids to produce cyclohexylPOSS monomers in less than three weeks (equation 2). Variations in reaction parameters results in the synthesis of different POSS structures. CyclopentylPOSS monomers can also be made from this method.



In addition, new POSS monomers were synthesized from the readily available **2a** and **2b**, in an affordable and efficient process. Previous literature on the functionalization of **2a** and **2b** for surface modeling and ligand synthesis reported the facile cyclodehydration to produce **3a** or **3b** (equation 3).⁷ However, isolation and purification of the soluble product was not pursued. The stability, solubility and further functionalization for studies as a pendant group for polymer systems have been explored. The product is unstable under reaction conditions from which it is formed, being subject to rehydration and polymerization. Once isolated, the soluble cyclodehydrated monomer can revert back to the starting triol only under forcing conditions, and is readily reacted to form polymerizable macromers (acrylates, hydrides, alcohols). The change in solubility from the starting triol is most likely to result from reducing the 3-fold symmetry of **2a** and **2b**.

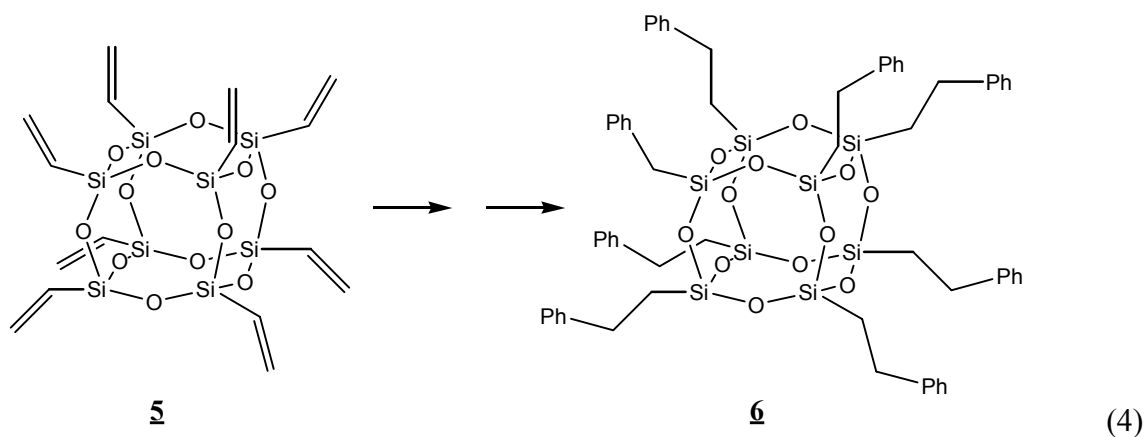


Collaborative efforts with Professor Frank Feher have allowed us to exploit new breakthroughs in POSS cage-opening reactions.⁸ Completely condensed POSS monomers containing a variety of organic side groups can be side-opened (**4**) to form difunctional species, or the subsequent reaction with a dialkyldichlorosilane can lead to the formation of new POSS frameworks containing nine silicon atoms. New monomers for polyurethanes, polyimides and polymethacrylates have been synthesized (Scheme III).



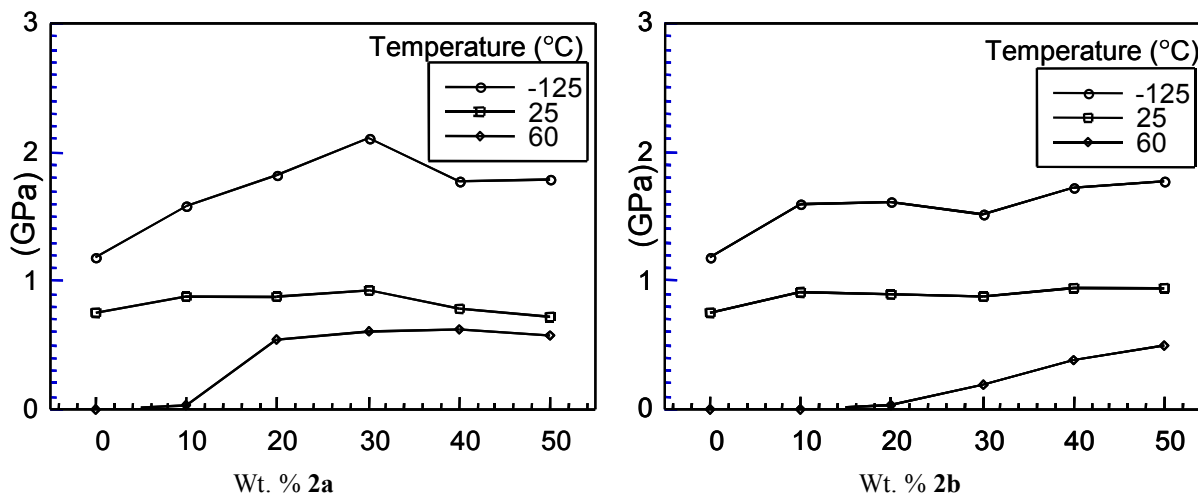
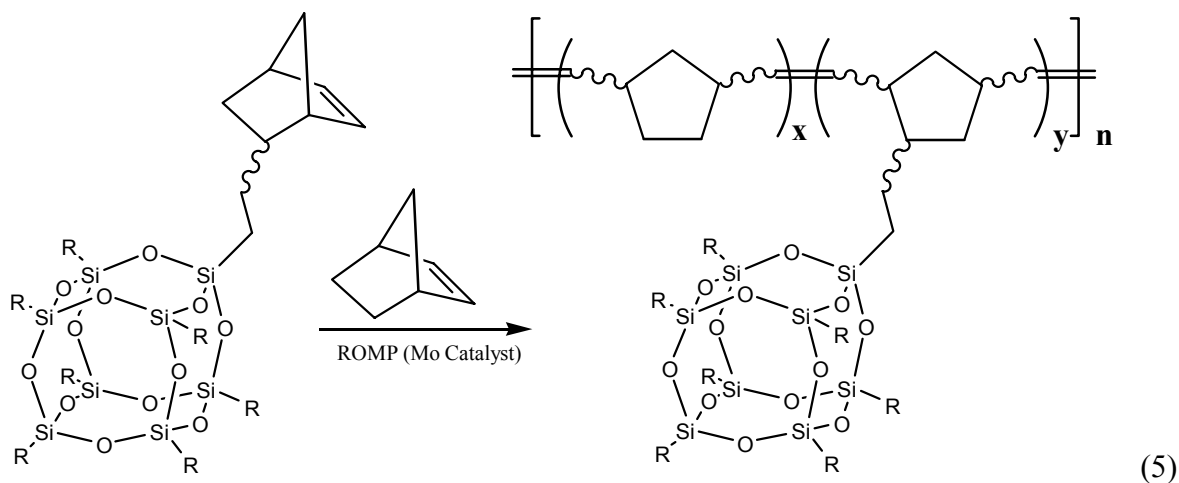
Scheme III

Polymer blends using POSS-macromers have been of great interest to both the Air Force and commercial sectors. Processing is often more costly than any other part of part fabrication, and interest will increase if significant property enhancements are observed from a drop-in additive which does not negatively affect processing conditions. The addition of $\text{Me}_8\text{Si}_8\text{O}_{12}$ to polypropylene resulted in over a 30°C increase in the heat distortion temperature as observed by DMTA. $\text{Me}_8\text{Si}_8\text{O}_{12}$ is insoluble in most polymer system except polypropylene. Based on such a promising result a stronger focus on POSS blends is being pursued. The enhanced miscibility of aromatic containing silsesquioxanes with polystyrene and other aromatic polymers has been studied by Prof. Chujo's group at Kyoto University, Japan.⁹ Following this research effort, we decided to prepare OctaphenethylPOSS (**6**). OctaphenethylPOSS (**6**) was made by the catalytic metathesis of **5** and subsequent hydrogenation (equation 4). As reported, the monomer displays remarkable solubility in many polymer systems, prompting alternative synthesis optimization via the self-condensation of phenethyltrichlorosilane.



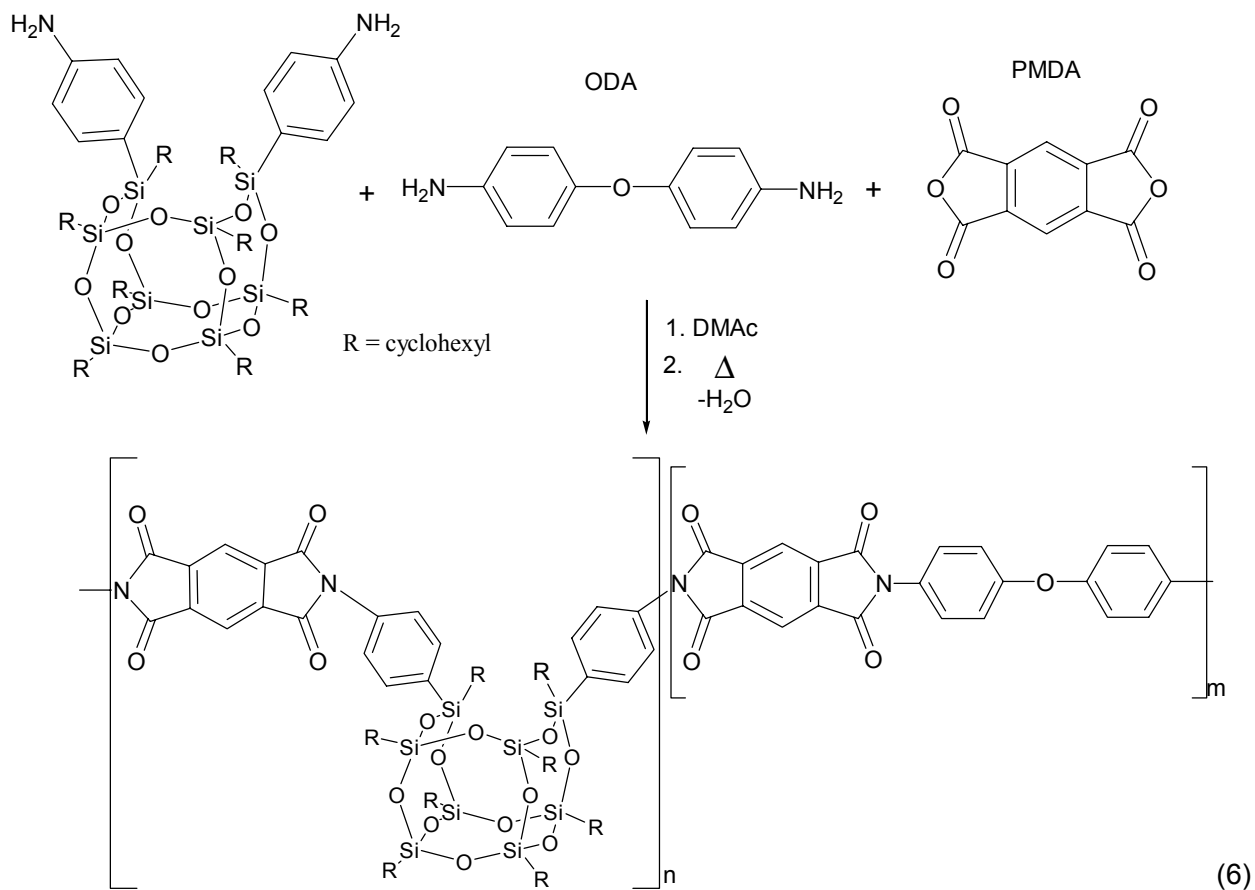
POSS Polymers and Characterization

While incorporation of the newly developed POSS monomers is ongoing, preliminary results show significant improvements in polymer properties with increasing solubility of the POSS framework. For POSS-polynorbornene polymers (equation 5), changing of the R groups from cyclohexyl to cyclopentyl results in greater interaction with the polymer matrix and a more dramatic increase in the tensile moduli both at $-120\text{ }^{\circ}\text{C}$ and $60\text{ }^{\circ}\text{C}$ (Figures 1 and 2). The drastic difference in the moduli can be attributed to the degree of interaction between the POSS framework and the polymer matrix.¹⁰



Figures 1 and 2: Moduli of cyclohexyl and cyclopentyl POSS

The condensation polymerization of POSS-dianiline with 4,4'-Oxydianiline and pyromellitic dianhydride to form POSS-Kapton™ (equation 6) results in a material that has increased moduli beyond the T_g of the material (Figure 3). Kapton™ with no POSS loses almost all mechanic properties prior to reaction(s) occurring at 435 °C. Increasing the wt. % of incorporated POSS results in an improvement in the rubber regime of the polymer. Mechanical tests over the last year have shown that such improvements in the modulus of the polymer system is typical of POSS polymers, but has never before been observed for a high-temperature polymer system.



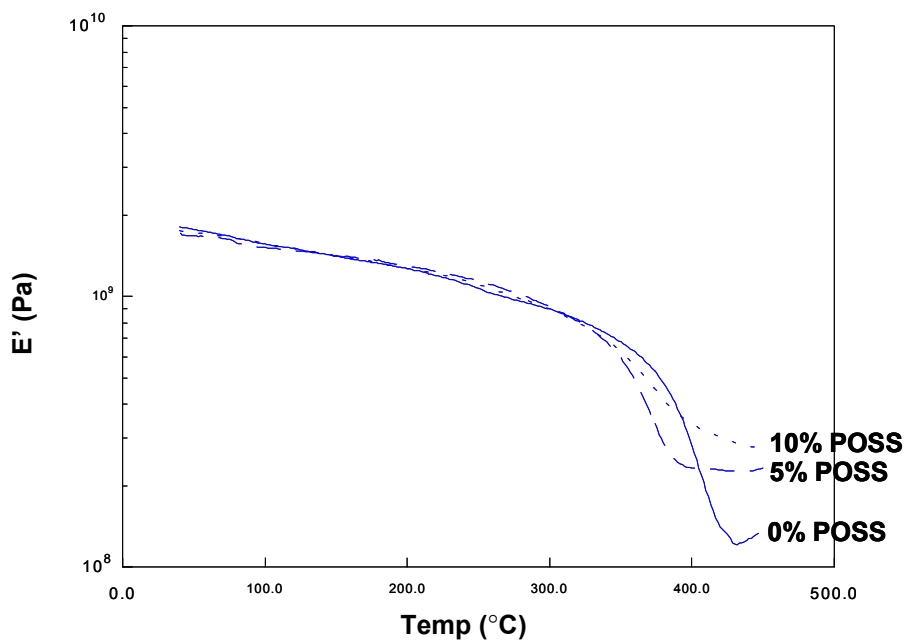
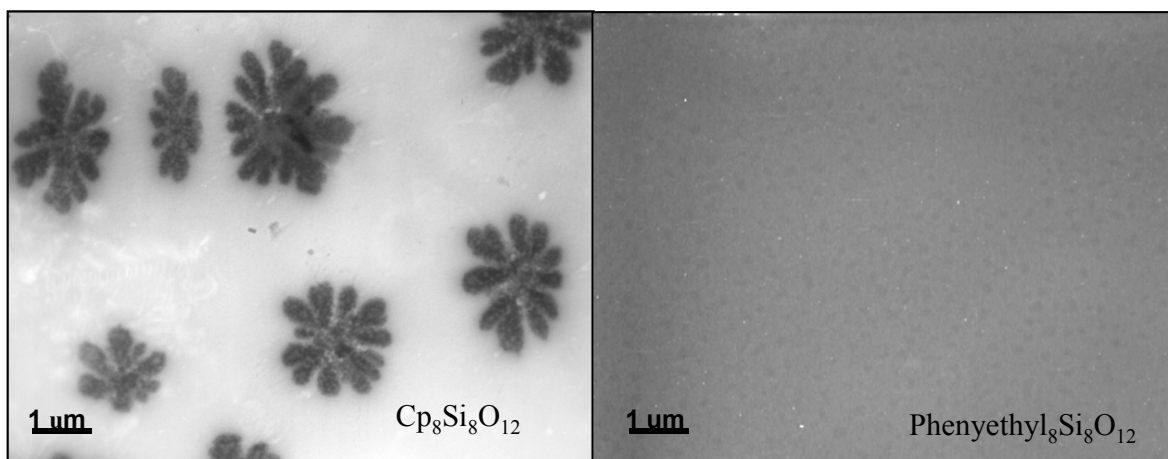


Figure 3: DMTA of Kapton™ with varying wt.% POSS incorporation

Cyclopentyl and cyclohexyl POSS cages are often insoluble as blending agents (Figure 4), however the OctaphenethylPOSS monomer (**6**) is highly soluble in many polymer systems, including greater than 50 wt % in 2 million mol. wt. polystyrene as observed by TEM (Figure 5) and the loss of the crystal peak by wide-angle diffraction. Nano-indentation of the sample showed a 30% increase in the hardness of the material.



Figures 4 & 5: TEM of $Cp_8Si_8O_{12}$ (Figure 4, left) and TEM of OctaphenethylPOSS (**6**) (Figure 5, right) in 2 million mol. wt. polystyrene.

CONCLUSION

POSS incorporation into polymer systems has resulted in significant improvements in both physical and mechanical properties. While over sixty POSS monomers have been made to date, almost all stem from 4 starting precursors. In order to study how the size, shape, and functionality of the frameworks affect POSS-polymer and POSS-POSS interactions a variety of new POSS monomers were targeted for synthesis. These monomers were incorporated into various polymers with preliminary results showing increases in use temperature, oxidation resistance, and moduli. Decreased solubility of POSS frameworks in the polymer matrix resulted in increased aggregation and reduction in physical and mechanical properties of the system. More importantly, improved POSS-polymer interactions lead to increases in T_g , HDT, and T_{dec} along with the expected improvements in oxidation resistance and flammability reduction. Future work on controlled variations within specific polymer systems are ongoing and should yield further insights into POSS-polymer fundamentals.

ACKNOWLEDGMENTS

The authors would like to thank the Air Force Office of Scientific Research (AFOSR) for the continued support to advance the understanding of how POSS incorporation enhances the physical and mechanical properties of polymers. Also, the SERDP Green Missile Program for funding of the POSS-norbornene research.

REFERENCES/LITERATURE CITED

1. Author to whom correspondence should be sent, shawn.phillips@ple.af.mil.
2. Hybrid Plastics is the company that the POSS nanotechnology was transferred to with a goal of increasing production and decreasing the price of POSS monomers and polymers.
3. F.J. Feher, T.A. Budzichowski, *Polyhedron*, **14**, 3239 (1995).
4. (a) J.D. Lichtenhan, J.J. Schwab, F.J. Feher, D. Soulivong, U.S. Pat. 5,942,638 (August 24, 1999) (to the United States of America). (b) J.D. Lichtenhan, J.W. Gilman, F.J. Feher, U.S. Pat. 5,484,867 (January 16, 1996) (to the University of Dayton, Regents of the University of California, and United State of America).
5. (a) R.A., Mantz, P.F. Jones, K.P. Chaffee, J.D. Lichtenhan, J.W. Gilman *Chem. Mater.*, **8**, 1250 (1996); (b) A. Lee, J.D. Lichtenhan *Macromolecules*, **31**, 4970, (1998); (c) B.S. Hsiao, X. Fu, et. al. *Poly. Mat. Sci. Eng.* **79**, 389 (1998).
6. J.F. Brown, L.H. Vogt Jr, *J. Am. Chem. Soc.*, **87**, 4313, 1965.

7. F.J. Feher, T.A., Budzichowski, K. Rahimian, J. W. Ziller, *J. Am. Chem. Soc.*, **114**, 3859 (1992).
8. Organic/Inorganic Hybrid Materials II, *MRS Symposium Proceedings*, ed. L. C. Klein, L. F. Francis, M. R. De Guire, J. E. Mark, **576**, 111 (1999).
9. (a) Tamaki, Ryo; Samura, Ken; Chujo, Yoshiki. *Chem. Commun.* 1131 (1998). (b) Chujo, Yoshiki; Naka, Kensuke; Tamaki, Ryo; Kamada, Yutaka; Nakamura, Shoukichi; Matsuo, Takashi. *PCT Int. Appl. WO 9914274*, 32 (1999). (c) Chujo, Yoshiki; Naka, Kensuke; Tamaki, Ryo; Kobayashi, Masaaki. *Jpn. Kokai Tokkyo Koho JP 11109153*, 10 (1999).
- 10 P.T. Mather, H.G. Jeon, A. Romo-Uribe, T.S. Haddad, J.D. Lichtenhan, *Macromolecules*, **32**, 1194 (1999).