

Developments in Nanoscience: Polyhedral Oligomeric
Silsesquioxane (POSS)-Polymers

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Report Documentation Page			Form Approved OMB No. 0704-0188		
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1. REPORT DATE 08 MAR 2004		2. REPORT TYPE		3. DATES COVERED -	
4. TITLE AND SUBTITLE Developments in Nanoscience: Polyhedral Oligomeric Silsesquioxane (POSS) - Polymers			5a. CONTRACT NUMBER F04611-99-C-0025		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Shawn Phillips; Timothy Haddad; Sandra Tomczak			5d. PROJECT NUMBER 2303		
			5e. TASK NUMBER M1A3		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) ERC Incorporated,555 Sparkman Drive,Huntsville,AL,35816-0000			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT This review is intended to cover the more recent advances in both structure-property relationships of polymers incorporating Polyhedral Oligomeric Silsesquioxane(s) (POSS) nanostructured chemicals as well as space-survivability testing of POSS-polymers. The strategy employed for using POSS as building blocks is discussed in addition to current models and predictions pertaining to the ideal crystallite/aggregate size of the nanocomposite within the polymer matrix to provide maximum mechanical improvements. The oxidation and rapid formation of SiO2 during atomic oxygen testing leads to a passivating layer, and conclusive proof of these phenomena is presented. Also, a brief history of POSS is outlined to help readers understand how they relate to the recent boom in nanotechnology and their position in nanomaterials R&D.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES 37	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

Abstract

This review is intended to cover the more recent advances in both structure-property relationships of polymers incorporating Polyhedral Oligomeric Silsesquioxane(s) (POSS) nanostructured chemicals as well as space-survivability testing of POSS-polymers. The strategy employed for using POSS as building blocks is discussed in addition to current models and predictions pertaining to the ideal crystallite/aggregate size of the nanocomposite within the polymer matrix to provide maximum mechanical improvements. The oxidation and rapid formation of SiO₂ during atomic oxygen testing leads to a passivating layer, and conclusive proof of these phenomena is presented. Also, a brief history of POSS is outlined to help readers understand how they relate to the recent boom in nanotechnology and their position in nanomaterials R&D.

Background and Introduction

The recent nanotechnology surge, both in funding and interest, has provided for a potential user-wide understanding of the meaning behind this buzzword. The general public hears of nanotechnology in TV commercials such as BASF's advertisement explaining how nanotechnology benefits them or in Hewlett Packard's claim during Sunday

NFL games of the almost limitless possibilities that nanotechnology offers [1]. In the scientific community there have been heated exchanges between rational scientists and paranoid futurists [2]. However in most cases one can safely assert that we are not yet at a nanotechnology stage but rather at an earlier research and development stage called nanoscience.

This is evident within the nanomaterials reinforced polymers realm, where only a handful of small-niche successful technology transfers have occurred (e.g., clay nanocomposites for packaging, POSS for dental adhesives) despite the large dollar investment in nanomaterials science. While nanomaterials are still in a fledging phase, the dramatic increase in R&D funding has already resulted in a shift away from monomer/feedstock developments and a movement towards structure/property relationship studies of the nanomaterials incorporated into polymer systems. When these nanomaterials are well dispersed in a polymer matrix, they are often described as nanocomposites, with the most successful structure-property studies having started with the idea of developing a model for the nanofiller-polymer interaction [3]. Such models start with an established polymer system model and an assignment of dimensionality to the nanofiller. The most

promising nanofillers and their dimensionality include clay layered silicates (2-D), single & multi-walled nanotubes (1-D), carbon nanofibers (1-D), and POSS Nanostructured Chemicals (0-D).

Once the nanofiller is successfully compatibilized within the polymer matrix to make a nanocomposite, then mechanical testing (e.g., DMTA, Rheology) combined with physical property spectroscopy (SEM, TEM, AFM) is needed in order to correlate molecular level structuring with macroscopic property enhancements. Models are developed and are then further refined in an iterative fashion both within polymer classes and across polymer systems, with the ultimate goal of predicting and controlling property enhancements of polymers reinforced with nanofillers.

Polyhedral Oligomeric Silsesquioxanes (POSS) are a class of nanofillers for polymers where such a program exists. An ongoing concerted multi-team effort is focused on studying the structure-property relationships of POSS-polymers. As a starting point, a recent nanocomposite review classified POSS as having zero-dimensionality or a sphere-like structure [3]. While this is a good initial assignment, the ability to higher dimensionality through aggregation or crystallization of POSS macromers within the polymer matrix has been realized and allows one to build 1-

3 dimensional scaffolds. This 'building-block' capability is a key benefit of POSS nanostructured chemicals and, along with the chemical versatility of over 120 available macromers, is what has attracted numerous researchers to study the incorporation of POSS into polymer matrices. This review article will focus primarily on the history of POSS, studies specifically aimed at structure-property relationships, research for improved space-survivable materials, and future areas for exploration and commercialization.

A Quick History of Polyhedral Oligomeric Silsesquioxane(s) (POSS) and POSS-polymers

An excellent review by Pittman in 2001 covers a majority of the technical publications pertaining to POSS-polymers, which incidentally only dates back to 1991 [4]. Articles on the synthesis, structure and properties of silsesquioxane resins have been around since well before the 1940s, however two landmark publications pertaining to well-defined POSS structures were the 1946 Scott paper on completely condensed POSS cages, and the incompletely condensed POSS 'triol' characterization by Brown and Vogt in 1965 [5,6]. It was not until twenty years later that Feher initiated a research program focused on exploiting

the unique geometry and functionality of these silicon-oxygen frameworks. Feher's initial programs were aimed at the modeling of silica surfaces and development of homogenous catalysts [7,8], but his group also played a significant role later on in the development of POSS-polymers.

In 1991, Lichtenhan and the Air Force Research Laboratory received funding from the Air Force Office of Scientific Research (AFOSR) for his proposed development of POSS macromers containing a polymerizable functional group and the subsequent synthesis of a POSS copolymer [9,*10]. The University-Government collaboration between Lichtenhan and Feher rapidly expanded to include more academic collaborators including Laine [11], Mather [12] and others who were all intrigued by the physical and mechanical property improvements imparted by incorporation of these nanostructured materials into polymer systems. In the late nineties not only was government and academic interest growing, but also that of the industrial sector which desired lowers costs and larger quantities of the material.

The fall of 1998 marked the start-up of Hybrid Plastics in Fountain Valley, CA, which transitioned the government scale-up facilities to the commercial sector through a cooperative research and development agreement.

In addition, the award of a three-year multi-million dollar NIST Advanced Technology Program grant in 1998 to Hybrid Plastics was critical in both reducing the prices of the POSS feedstocks and macromers (\$5,000--\$10,000 down to \$50--\$2000 per pound) and increasing production (<20 lb/yr to >2000 lb/yr) to satisfy the more than 100 companies now investigating how the incorporation of POSS improves material properties for their applications. In the summer of 2003, Hybrid Plastics launched critical agreements with Southern Mississippi State University and the City of Hattiesburg for their development of a 26,000 sq ft production facility and a 1,500 sq ft R&D center.

The nearly exponential increase in the number of academic researchers, academic publications (Fig. 1), government programs, and industrial research efforts on POSS nanostructured chemicals has made it one of the top nanomaterials in the nanoscience/nanotechnology field. Indeed, the versatility of the POSS molecule, the more than one hundred demonstrated compatible polymer systems and the innumerable applications makes it difficult to understand and discern the current and future direction. However, it is clear to the author that at least one concerted effort with a single-minded goal of predicting and controlling structure-property relationships is needed, and is being

pursued by a number of research groups working with POSS nanostructured chemicals.

Fig. 1

Structure-Property Relationships of POSS-Polymers

As previously mentioned, the number of research groups working on POSS-polymers has increased sharply over the last few years. To include all their work into a coherent story not only goes beyond the intent of this review, but also would require such an effort as to demand an entire published volume. Rather, this section of the review will focus on six research groups whose common theme is an attempt to understand the structure-property relationships of a variety of thermoplastics containing POSS. Table 1 lists these research groups along with their more recent research focus with respect to POSS-polymers.

Table 1

Modeling and simulation has played an increasing role in describing or explaining nanoscience phenomena. In materials science this can be rationalized based on the disparity between spectroscopy at the nano level and

property testing at the macro level. Very few instruments are capable of performing both functions in real time, making it difficult to draw correlations between molecular level structure and bulk physical properties. Although the MIT Defense University Initiative on Nanotechnology for polymer nanocomposites only started studying POSS-polymers a year ago, the excellent work that will be published in 2004 is worth mentioning now.

Capaldi, Boyce and Rutledge have performed lattice dynamics simulations of various crystal forms of POSS, as well as molecular dynamics simulations of POSS particles dispersed in an organic matrix at temperatures from 300 to 500 K [13]. Their simulations reveal the detailed packing structure of the organic phase as a function of distance from the center of the POSS T8 particle, for different pendant groups attached to the silicon vertices of the POSS particle. Through their simulations, they explore the dynamics of the POSS particle as it interacts with the matrix material. They observe interesting aggregation properties at lower temperatures (300 K) in their simulations, in accord with experimental observations. They also study the deformation of the POSS-polymer composite, and conclude that a fully dispersed POSS

nanocomposite is surprisingly soft, compared to expectations based on conventional composite models.

The effort perfectly complements Kopesky, Cohen and McKinley's soon-to-be-published work in *Macromolecules* which compares and contrast blends and copolymers of poly(methyl methacrylates) containing POSS. With the blended POSS an initial plasticization effect was observed, while at higher loadings aggregates/crystallites were formed which increased the viscosity. The copolymer showed increased viscosities at all loadings, indicating that aggregates/crystallites may be formed early on [14].

Bowers and Anderson have combined modeling with mass spectrometry aimed at understanding how POSS molecules affect the polymer structure. Amber molecular modeling and X-ray crystal structure data is used to accurately predict the gas phase structures of a molecule, such as POSS [15]. The information can then be used to determine cross-sectional areas. Experimentally, they combine MALDI-TOF spectroscopy with ion chromatography which yields different retention times of structural isomers. Their first publication on studying POSS macromers was targeted at unraveling the gas phase conformations of Sty_8T_8 and $(\text{PhEt})_8\text{T}_8$ as seen in Figure 2 [16].

Fig. 2

In their more recent publication they studied both completely and incompletely condensed POSS macromers in addition to varying the size of the POSS cage [17]. The agreement between calculated cross-sectional areas, retention times and the number of isomers for POSS macromers has been shown to accurately match experimental data within a 2% error. In addition, the Bowers' group has already shown that they can successfully model oligomer chains of a variety of polymer systems [18]. The next step, which is already underway, is to model short-chain oligomers of POSS-polymers to determine the interaction of the POSS moiety with the polymer backbone and compare these results to previously reported non-POSS containing polymers.

Mather and Haddad have been researching the structure-property relationships of POSS-polymers since the late 1990's [19,20]. Their POSS-norbornyl polymers (Fig. 3) are the best studied system to date and continue to be used to discern POSS interactions at the molecular level. The systematic approach included the development of blocky and random POSS-norbornyl copolymers with varying weight percent and types of POSS. Through the use of DMTA,

rheology and TEM they were able to determine that slight changes in domain size can result in dramatic changes in the glass transition state (Fig. 4).

Fig. 3

Fig. 4

Through recent variations in the organic groups on the POSS cage, Mather and Haddad reported at the 2002 POSS Nanostructured Chemicals Conference [21] that the critical cylinder diameter of POSS crystallites/aggregates is on the order of 10-20 nm. This was strongly supported by a 2000 publication that discussed the effect of different domain sizes, with the cyclopentylPOSS (Cp) cylinders having a diameter of 6nm and cyclohexylPOSS (Cy) having a diameter of 12nm [22]. Also, the Cp cylinders were about 36 nm long while the Cy cylinders were 62 nm long. The net result is that seven times as much POSS is tied up in each cylinder in the Cy case when compared to the Cp case. These results also provided the evidence that the R groups on the POSS cage affect the cylinder size and result in significant changes of bulk mechanical properties (Fig. 5).

Fig. 5

Haddad has expanded on this work to study POSS-styrene polymers with varying R groups on the POSS cage. His DMTA spectra also show an increase in $\tan \delta$ with $R = \text{Cy} > \text{Cp}$ and a plasticization effect when $R = i\text{-Bu}$ [23]. Mather directed his understanding of using POSS as building blocks to work in the area of POSS telechelics with the POSS being the end group of the PEG homopolymer. He was able to control the molecular architecture by varying the POSS addition, resulting in dramatic decreases in crystallinity of the PEO segments [24]. Rheological data is expected to be published in 2004.

Coughlin and Farris have provided a visual model of a POSS-copolymer based on the morphology of POSS-polybutadiene and polyethylene copolymers. The hybrid inorganic/organic polymers were made by either ring-opening metathesis copolymerization or single site catalysis, both allowing for good control of POSS incorporation [25-27]. Physical and mechanical data were taken of the materials and a visual model was proposed (Fig. 6). This model matches their TEM data, displaying the 'raft-like' or lamellae structure of POSS within the polymer matrix [28]. Two dimensional networks are the highest possible architecture that a POSS copolymer can adopt due to the

constraints of the polymer chain, while three dimensional structures can be expected for most POSS-polymer blends. Thermal gravimetric analysis of the POSS-polyethylene (12 wt% POSS) showed a 70 °C improvement in the onset of decomposition.

Fig. 6

Coughlin is studying hemi-telechelics of POSS-polystyrenes and is investigating whether the POSS moieties within the polymer matrix are lamellae or cylinder in nature [29]. His initial work shows no improvements in mechanicals since the POSS crystallize and do not mix into the polystyrene phase.

A majority of Lee's structure-property studies have been in the areas of blends [30] and thermosets [31]. However, Lee and Haddad's recent work on POSS-SBS polymers, which has been submitted for publication in Macromolecules, follows his hypothesis which states that three plateau-like regions exist in the thermoplastic which are glassy, POSS-POSS and polymer entanglement. With true nanocomposites one should realize and be able to utilize this hypothesis to have improved properties below T_g and in the terminal zone while also improving processability in the rubbery

plateau regime due to the reduced polymer-polymer interaction [32]. For their POSS-SBS copolymers (Fig. 7) they have shown that the POSS does enhance the T_g of the butadiene segment as expected, but also improves the storage modulus at temperatures where the styrene begins to soften (Fig. 8).

Fig. 7

Fig. 8

Space-Survivable, Self-Healing POSS-Polymers

The application of polymeric materials on orbiting bodies in low Earth orbit (LEO) is prevalent in spite of their inability to withstand the severe environment. Atomic Oxygen (AO) and vacuum ultraviolet radiation rapidly degrade even the best organic-based polymers such as Kapton and Teflon. Creative solutions include the use of coatings & multi-layered materials. However, in both cases the production process of these materials and impingement by microdebris in space cause cracks and microdefects in protective layers/coatings. Underpinning by the atomic oxygen still causes significant erosion resulting in a dramatic reduction in predicted lifetime of such materials

in space [33]. Hybrid inorganic/organic materials offer a unique advantage over traditional materials, both in their ability to protect the bulk material from VUV degradation and withstand AO collisions of approximately 5 eV in energy.

POSS materials fit into this category and can offer true nanodispersion of the inorganic component. This leads to the formation of nanocomposites that impart multifunctional benefits into traditional polymeric materials for space applications. Unlike the bonds of organic molecules which undergo scission at about 4 eV, the Si-O bond requires 8 eV for disruption, which is greater than the energy provided by AO colliding into orbiting space vehicles. Furthermore, the Si to O ratio of 1.5 and low oxidation energy for oxidation to SiO₂ are perhaps the most important benefits of the POSS chemical structure. The earliest work in 1996 by Gilman, Schlitzer and Lichtenhan [34], along with continuing work in 1999-2001 by Hoflund and Gonzalez [35,*36,37], established that both silicon-based and organic-based polymers containing POSS rapidly lost their surface-exposed organic groups and formed a SiO₂ network upon exposure to AO. This thin silica layer passivated the surface from further AO erosion.

More recent work by Minton, Tomczak and Gonzalez has focused on the development and space-survivable testing of POSS-modified high performance polymers such as polyimides. Two POSS-polyimide copolymers have been reported separately by Wright & Feher and Gonzalez & Hoflund [38, 39]. Both polymer systems incorporate the difficult-to-synthesize POSS dianiline first prepared by Feher (Fig. 9, 10).

Fig. 9

Fig. 10

The POSS dianiline is copolymerized into the polymer backbone in the condensation polymerization and transparent films of POSS-polyimide films can be made containing as high as 25 wt% POSS macromer. Hoflund and Gonzalez first exposed these materials to AO impingement and showed that the rate of silica formation was linearly dependent on the wt% of POSS in the polymer matrix.

Further work by Minton and Gonzalez included AO exposure of samples with protected and unprotected areas followed by depth profilometry erosion studies. As shown in Figure 11, ten wt % POSS Polyimide exhibits an order of

magnitude decrease in erosion step height after exposure to AO relative to space certified Kapton H [40].

Fig. 11

Minton and Tomczak expanded on this work, which will soon be published in the Journal of High Performance Polymers. They used depth profilometry and AFM imaging to determine O-atom etching on the surface, and compared their data directly to space-certified Kapton-H. Figure 12 shows the results of step height measurements for 0, 10, and 20 wt% POSS polyimide films that were exposed to various numbers of hyperthermal O-atom beam pulses. Step heights (or etch depths) of POSS samples are plotted in Figure 12a as a function of the step height of the Kapton H reference sample for each exposure. The erosion yield of the 0 wt% POSS sample appeared to increase linearly with fluence. After an initial rapid increase with fluence, the erosion yield for the POSS-containing samples appeared to increase very slowly after a fluence that etched 12.3 μm of Kapton H (4.10×10^{20} O atoms cm^{-2}). For Figure 12b, the step heights of each of the POSS polyimide films were divided by the corresponding step height of the Kapton H reference sample, and plotted against the Kapton H step height. Figure 12b thus gives the rate of change of the step height

(proportional to erosion rate) of the POSS samples as a function of exposure duration. This 2nd order derivative plot (Fig. 12b) indicated that the 10 and 20 wt% POSS polyimides reached erosion rates of 3.7 and 0.98 percent respectively compared to those of Kapton H. This, along with supporting x-ray photoelectron spectroscopy data, not only confirms the formation of a passivating layer, but also shows how the etching rate approaches zero for the 20 wt% POSS-Kapton.

Fig. 12

Additional space-survivability testing is ongoing as part of the Materials on the International Space Station Experiment and also GEO testing by the Aerospace Corporation, which will include exposure to charged particle dosages (protons, electrons) with and without VUV. These results are expected to be published in 2005.

Conclusions & Future Direction

The study of POSS-polymers over the last 13 years has yielded conclusive proof that incorporation of the POSS into a polymer matrix can result in significant improvements in a variety of physical and mechanical

properties due to the reinforcement at the molecular level and the inorganic framework's ceramic-like properties. Recent work has shown that the physical cross-links formed by the POSS can significantly retard thermal motion, while at the same time the individual POSS cages can act as flow-aids at elevated temperatures. In addition, the silicon oxide core can react with atomic oxygen in simulated low Earth orbit environments and rapidly form a protective SiO₂ layer, which can self-heal just as quickly due to the uniform dispersion of POSS throughout the organic matrix. Such multi-functional behavior allows for implementation in a variety of applications.

An understanding and control over the molecular-level architecture is critical and already underway. Models based on spectroscopic studies that show the optimum size (~10-20nm) and structure (2-D sheets for copolymers) of POSS moieties have been developed by Mather, Coughlin, Haddad and others for particular polymers systems who are now studying if there is applicability across different classes of polymer systems. The overall dimensions of the POSS aggregates/crystallites have been shown to dictate polymer properties, but much more research is required in order to shape and apply generic models for both the research and industrial community.

As can be seen upon reading this review, a significant portion of the research and development efforts for POSS-polymers are focused on the synthesis and characterization of the polymer systems. In the near future, a redirection will be needed to study how to process the POSS-modified polymers to create, add or break-up POSS networks; thus, tailoring desired property enhancements. Also, the study of cooperative relationships of various nanocomposites is needed since it has become apparent that each interacts differently with the polymer matrix and thus imparts different property enhancements.

Lastly, the concept of utilizing nanofillers as compatibilizers between immiscible polymer blends and as interfacial modifiers in composite systems is an exciting area that is starting to be explored. The tailorability and versatility of the POSS macromers make them ideally suited, as demonstrated by Mather and Hsiao [41].

Acknowledgements

This work was supported in part by the AFOSR, Air Force Research Laboratory, and NSF. We would also like to thank all of our colleagues and collaborators including S. Anderson, M. Bowers, M. Boyce, R. Cohen, B. Coughlin, A. Esker, G. Hoflund, B. Hsiao, J. Koo, E. Kopesky, R. Laine,

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Figure Legends

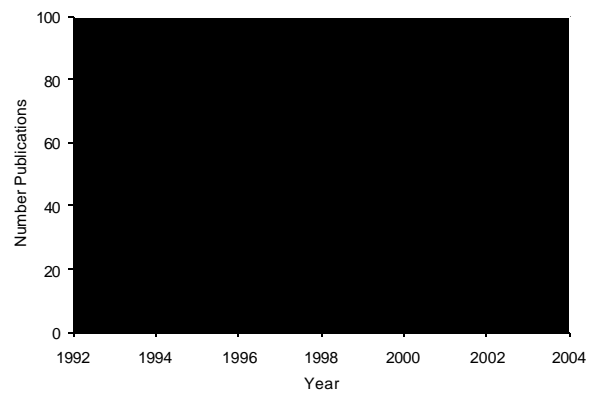


Fig. 1. Plot of the number of POSS publications versus the year in which they were published.

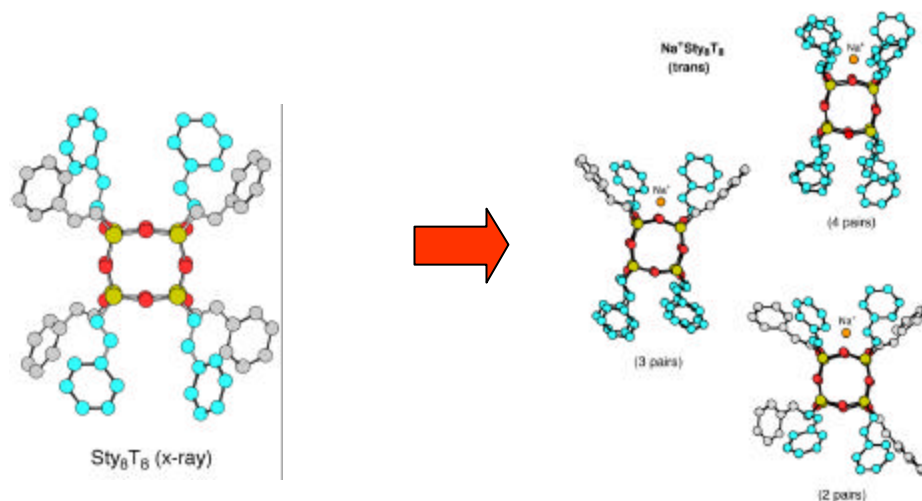


Fig. 2. Bowers at UCSB took the X-ray structure of Styryl₈T₈ POSS, modeled it with AMBER to yield three types of gas-phase structures, all of which were observed by MALDI-TOF ion chromatography.

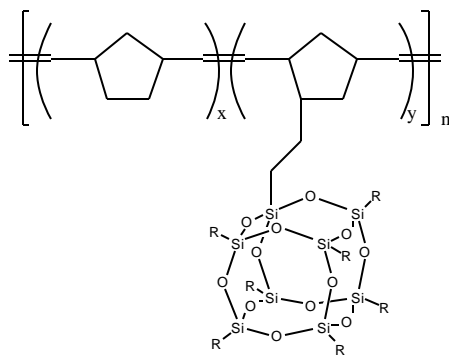


Fig. 3. Simple schematic of POSS-polynorbornenyl polymer where the R= i-Bu,Cy,Cp,Ph group on the POSS cage.

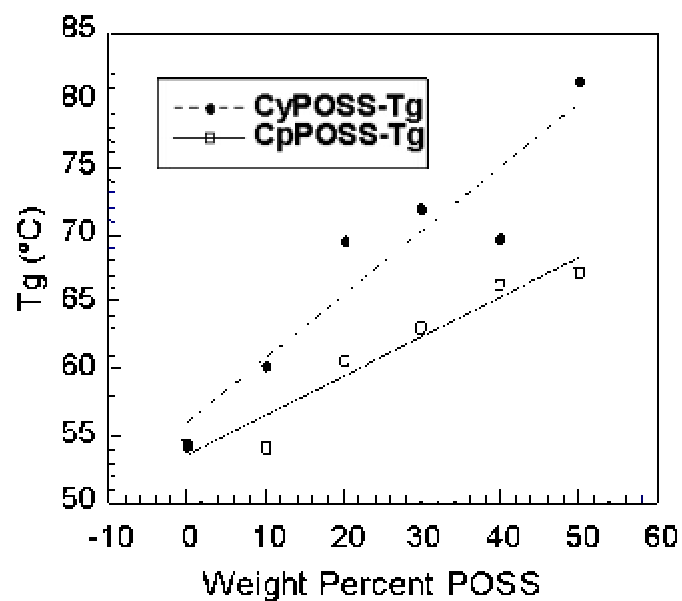


Fig. 4. Glass transition data taken from DMTA of POSS-polynorbornyl polymer where R group on POSS cage is cyclohexyl or cyclopentyl.

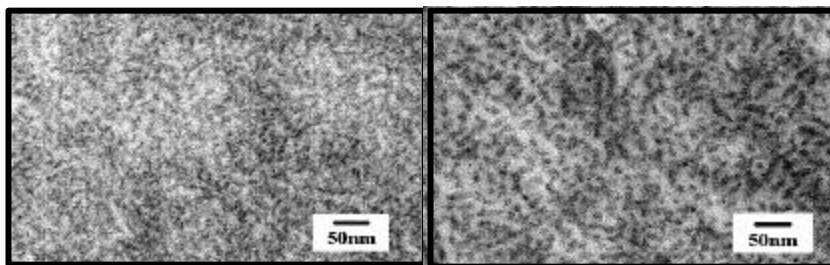


Fig. 5. TEMs of POSS-norbornyl polymer. At left the fine CpPOSS rich domains are ~6nm cylinders and at right the coarse CyPOSS rich domains are ~12nm cylinders.

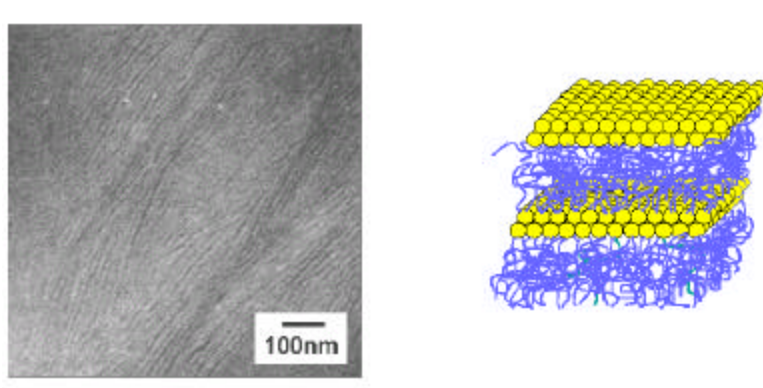


Fig. 6. Coughlin model for structure of POSS-copolymer. At left the TEM image of a POSS-polybutadiene copolymer (43 wt% POSS) shows raft-like structure, while at right is a model of the 2-D crystallization of the POSS macromers.

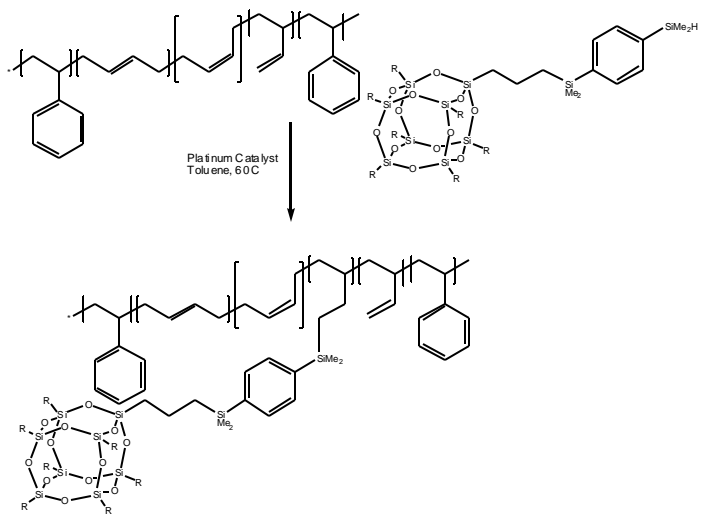


Fig 7. Simple schematic showing the grafting of POSS-hydride macromer onto SBS backbone.

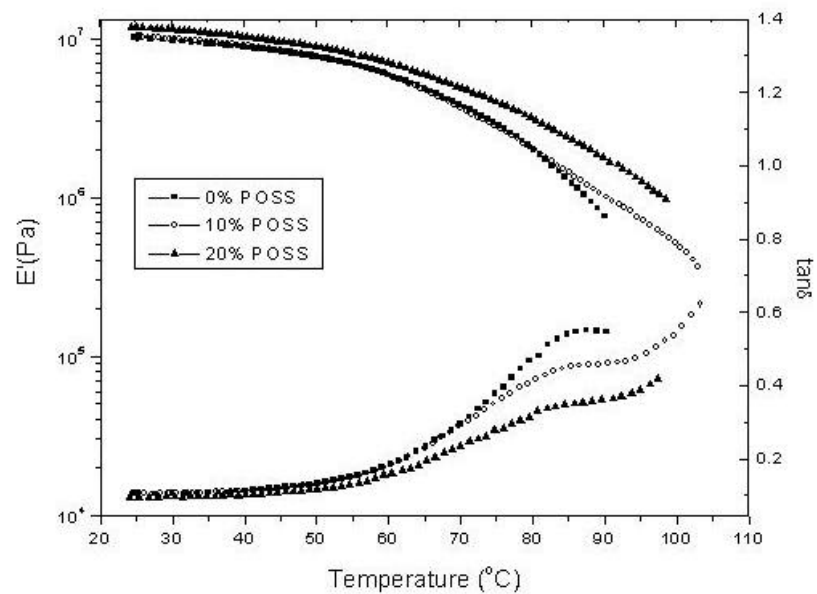


Fig. 8. Dynamic mechanical analysis of the POSS-SBS copolymer shown in Fig. 7.

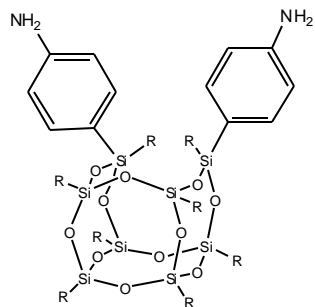


Fig. 9: Simple schematic of the POSS-diamine used in POSS-polyimide syntheses.

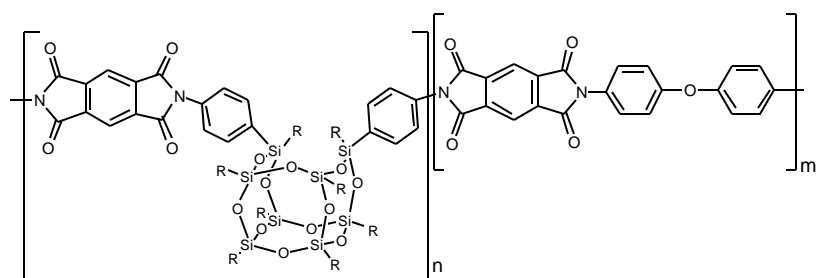


Fig. 10: Simple schematic of the structure of POSS polyimide copolymer.

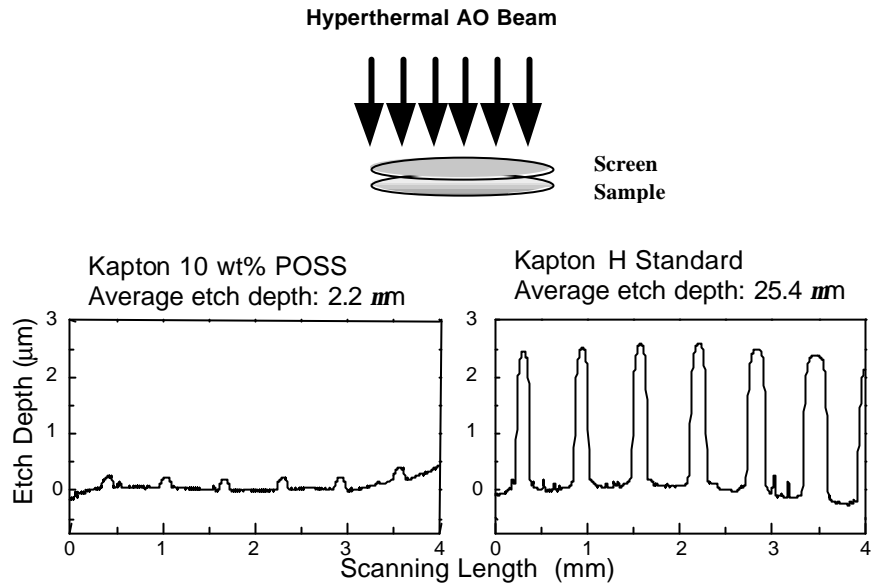


Fig. 11. Profilometry measurements obtained after a total AO fluence of 8.47×10^{20} atoms/cm², equivalent to an approximate 10 day simulated LEO dosage.

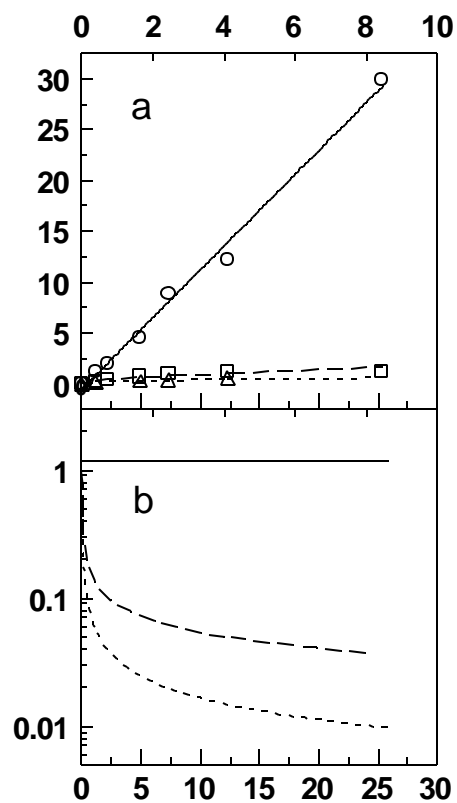


Fig. 12. POSS-polyimide erosion testing showing (a) step height measurement of 0, 10 and 20 wt% POSS polyimide after O-atom erosion and (b) the erosion rate of each POSS-polyimide sample. Legend: \circ = 0 wt% POSS, $--$ = 10 wt% POSS, $---$ = 20 wt% POSS.

TABLES

Air Force Research Lab - Edwards (T. Haddad)	Synthesis and Characterization of POSS macromers and polymers
Michigan State University (A. Lee)	Characterization of POSS thermosets, blends and copolymers
MIT (M. Boyce, R. Cohen, E. Kopesky, G. McKinley, G. Rutledge, E. Thomas)	Modeling, Synthesis and Characterization of POSS- polymers
U of California, Santa Barbara (M. Bowers and S. Anderson)	Macromers and polymer structure elucidation through modeling & mass spectrometry
U of Connecticut (P. Mather)	Synthesis and characterization of POSS copolymers
U of Massachusetts (B. Coughlin)	Synthesis and characterization of POSS copolymers and blends

Table 1. Research Lab (along with lead investigator) and primary POSS research area.