Synthesis and Atomic Oxygen Erosion Testing of Space-Survivability POSS (Polyhedral Oligomeric Silsequioxane) Polymides

Rene I. Gonzalez, Sandra J. Tomczak, Timothy K. Minton, Amy Brunsvold, Gar B. Hoflund

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SYNTHESIS AND ATOMIC OXYGEN EROSION TESTING OF SPACE-SURVIVABLE POSS (POLYHEDRAL OLIGOMERIC SILSESQUIOXANE) POLYIMIDES

Rene I. Gonzalez(1), Sandra J. Tomczak(1), Timothy K. Minton(2), Amy L. Brunsvoi(2), Gar B. Holfund(3)

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ABSTRACT

This paper presents several characterization studies of the surfaces of newly synthesized POSS-containing polyimides before and after exposure to atomic oxygen (AO). AO exposure testing was conducted independently at the University of Florida and Montana State University revealing comparable data. The exposed surfaces were characterized using X-ray photoelectron spectroscopy, and atomic oxygen erosion rates were calculated using stylus surface profilometry. The data indicate that AO induced erosion of polyimides containing POSS is drastically reduced as a result of a passivating silica layer is formed on the surface of the polymer.

1. INTRODUCTION

Polyimides such as Kapton, are used extensively on spacecraft primarily as flexible substrates for lightweight, high-power solar arrays because of their inherent strength, temperature stability, excellent insulation properties, UV stability and IR transparency. They are also used in conjunction with Teflon FEP as the outer layer of multi-layer thermal control insulation because of their superior optical properties, including low solar absorptance and high thermal reflectance. In these multilayer insulations a metalized layer is typically applied to the backside in order to reflect incident sunlight. In addition, polyimides are the predominant materials used to build space inflatable structures.

However, over the last twenty years, it has been well established through space-based experiments and ground simulations that polymeric materials and films, undergo severe degradation as a result of the aggressive environment encountered in low Earth orbits (LEO). In this high vacuum environment, materials are subjected to the full spectrum of solar radiation and must endure constant thermal cycling and bombardment by low and high-energy charged particles as well as high incident fluxes of AO. These harsh conditions combined with the need for lighter weight and lower cost man-made orbiting bodies necessitates the design of multi-functional, space-survivable materials.

Hybrid inorganic/organic polymers have the potential to meet the requirements of space-survivable materials by bridging the gap between ceramics and plastics, resulting in the prevention of AO and radiation damage that has hampered the widespread application of organic polymers in space. The Polymer Working Group at the Air Force Research Laboratory at Edwards AFB has incorporated inorganic POSS (Polyhedral Oligomeric Silsesquioxane) frameworks into traditional polymer systems resulting in hybrid POSS-polymers with dramatic property enhancements [1-3]. POSS frameworks (Fig. 1) are comprised of a three dimensional inorganic cage structure with a 2:3 Si:O ratio, surrounded by tailorable organic groups [4-6].

![Fig. 1. Anatomy of a POSS nanostructure](image)

They are functionalized monomers that can be copolymerized, grafted and blended into traditional polymer systems [7]. The anatomy of a POSS molecule shown in Fig. 1 is defined by the following features: (1) Single molecules with dimensions ranging in size from 0.7 nm to 3 nm with an average of 1.5 nm rendering them approximately two orders of magnitude smaller than conventional inorganic fillers (quartz tale ~ 100 μm, fused Si ~100 nm, colloidal SiO2 ~ 10 nm). (2) A thermally and chemically robust inorganic framework with well defined three-dimensional polyhedral geometries. (3) One or more functional groups which enable grafting and copolymerization. (4) Nonreactive R groups (cyclopropyl, cyclohexyl, phenyl, isobutyl, methyl) which aid in the compatibilization with the polymer matrix [3,7]. Addition of these POSS nanostructured frameworks into polymers results in increased use and

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decomposition temperatures, improved mechanical properties, and oxidation resistance.

Our previous research has shown that chemical manipulation of the unreactive organic groups surrounding the POSS cage [3,7] enables dispersion of POSS nanostructures throughout the polymer matrix at high POSS loadings via blending and copolymerization techniques [1,2,7]. We have also shown that polymers containing POSS rapidly form a ceramic-like, passivating and self-healing silica layer when exposed to high incident fluxes of AO [8-10]. We believe that this self-healing nature is a direct result of POSS compatibility and dispersion throughout the polymer matrix. If the glassy silica layer erodes or suffers a microdefect, it would quickly reform due to the uniform POSS dispersion.

This paper presents a characterization study of the surfaces of newly synthesized POSS-containing polyimides before and after exposure to AO. Atomic oxygen exposure testing was conducted independently at the University of Florida and Montana State University revealing comparable data. The exposed surfaces were characterized using X-ray photoelectron spectroscopy, and atomic oxygen erosion rates were calculated using stylus surface profilometry. Changes in the surface topography were measured using atomic force microscopy.

2. RESULTS AND DISCUSSION

2.1 Synthesis of POSS Polyimide Copolymers

A POSS framework 1 with two amido pendant groups was provided by Prof. Frank Fefer and prepared as described in [11]. Using this monomer, various POSS-polyimide random copolymers were synthesized as shown in Fig. 2 with POSS loadings corresponding to 0, 5, 10 and 20 wt%.

2.2 Thermo-mechanical Properties of POSS-Polyimides

The linear viscoelastic properties of polyimides with differing amounts of POSS incorporation were determined using a dynamical mechanical analyzer in tensile mode over a wide range of temperatures. Fig. 3 presents a comparison of storage modulus, $E'(T)$, as a function of temperature for polyimides with 0 wt%, 5 wt%, and 10 wt% POSS segments, respectively. All polymers exhibited a mechanical relaxation transition at temperature near 400 °C indicating the onset of large scale thermally induced motions. It is well known that this type of polyimide, Kapton, does not flow at elevated temperature. This was confirmed by the change in the magnitude of $E'(T)$ at the transition temperature, i.e., from around 1 GPa to 100 MPa. Normal (flexible) polymers would have dropped down to about 1 MPa. As shown in Fig. 3, at temperatures below this relaxation, the magnitude of $E'(T)$ was not significantly affected by the addition of POSS segments in the polymer chain. However, at temperatures above this relaxation, the magnitude of $E'(T)$ increases as the amount of POSS segments in the polymer chain increases.

![Fig. 2. Synthesis of POSS-Polyimides](image_url)

The corresponding value of the plateau moduli depends on the amount of POSS incorporation in the polymer. The appearance of these plateaus at temperatures above the mechanical relaxation transition indicate a very strong POSS-POSS interaction where the modulus of polymer was not affected by the change in temperature. These observations suggest that POSS-POSS interactions reduce the motion of the polymer chains and add mechanical strength to these polymer systems above the glass transition in a manner that could be analogous to entanglements.
the POSS containing polyimides begins at decreasing temperatures with increasing POSS content.

2.3 Profilometry and Atomic Oxygen Etching Experiments

Samples of POSS-Polyimide films underwent a series of AO etching experiments where they were exposed to an hyperthermal O-atom beam produced by a 7 Joule-pulsed CO₂ laser source. This AO source has been well characterized and described previously [12]. The resultant beam consists predominantly of fast neutrals, with a very small ionic fraction (<10⁵). Average kinetic energies of the fast species in the beam can range from 2 to 15 eV.

Fig. 7. Profilometry measurements obtained after a total AO fluence of 8.47 x 10²⁹ atoms/cm², equivalent to an approximate 10 day simulated LEO dosage. As depicted in Fig. 6, a protective screen was placed in-between the sample and beam path in order to
selectively erode only certain portions of the samples. The difference in etch depth between the eroded and protected part of the samples was then measured using stylus surface profilometry. Surface profilometry is a technique in which a diamond stylus, in contact with a sample, can measure minute physical surface variations as a function of position. It is commonly used to measure film thickness in thin film deposition and processing. By measuring the difference in height between the etched and unetched portions of the polymer sample, it is possible to calculate an AO reaction efficiency ($R_e$) or erosion rate for the material for a given flux. Profilometry measurements for the Kapton H standard and a 10 wt% POSS-Kapton polyimide sample are shown in Fig. 7 after a total fluence of $8.47 \times 10^{20}$ atoms/cm$^2$. This corresponds to 100,000 pulses of the laser atom source and correlates to an approximate 10 day simulated LEO dosage.

These measurements reveal that the average etch depth for the Kapton HN standard was 24.5 microns which corresponds to a calculated $R_e$ of $3.00 \times 10^{24}$ cm$^3$/atom. This value agrees with previously reported erosion rates based on space flown and ground tested Kapton samples [13]. However, under the same conditions, the 10 wt% POSS-Kapton polyimide etched on average only 2.2 microns corresponding to an $R_e$ of $2.56 \times 10^{22}$ cm$^3$/atom. It is interesting to note that this full order of magnitude improvement in atomic oxygen reaction efficiency is brought about by only a 10 wt% (approximately 1 mole%) addition of POSS copolymerized in the polymer matrix.

The experiment was repeated for a smaller AO fluence of $2.62 \times 10^{20}$ atoms/cm$^2$ exposing a commercially available Kapton H standard, a Kapton control sample with no POSS and a 10 and 20 wt% POSS-Kapton sample. Fig. 8 shows a multiplot of the profilometry measurements of these samples. The data for these plots reveal a decreasing average etch depth and corresponding atomic oxygen reaction efficiency as the POSS content in the polymer increases. Again, a full order magnitude improvement in the atomic oxygen reaction efficiency is obtained from addition of 10 wt% POSS, while addition of 20 wt% POSS improves the reaction efficiency by 22.5 times.

The superior performance of polyimides containing POSS is further highlighted by atomic force microscopy images before and after exposure to AO as shown in Fig. 10 and Fig. 11. These images reveal that the surface roughness increases dramatically for the Kapton control sample after AO exposure from 1.09 to 102 nm. In contrast, the surface roughness of the Kapton polyimides with POSS only slightly increases from 1.03 to 17.7 nm and from 1.55 to 6.75 nm for the 10 wt% and 20 wt% POSS respectively.

The protection provided to polyimides that contain POSS is actually much greater when looking at much longer exposure times. As can be seen in Fig. 9, erosion of the 10 and 20wt % POSS Kaptons to 400,000 AO beam pulses is drastically less than that of the Kapton control sample. This suggests that there is an equilibrium point where the surface is nearly completely protected from further AO attack resulting in negligible erosion. This is a result of the passivating and self-healing silica layer that is formed as a result of the nanodisperesed POSS moieties reacting with AO. This surface layer was characterized using X-ray photoelectron spectroscopy (XPS) as described below prevents further degradation of the underlying polymer.

![Graph](image)

**Figure 8.** Profilometry measurements obtained after a total AO fluence of $2.62 \times 10^{20}$ atoms/cm$^2$, equivalent to an approximate simulated 3 day LEO dosage.

![Graph](image)

**Figure 10.** Erosion of Kapton and POSS Kapton versus AO beam pulses.
2.4 In-situ XPS Analysis After Exposure to an ESD Atomic Oxygen Source

A 10 wt% POSS-Polyimide film has been characterized in situ by using XPS before and after incremental exposures to the flux produced by an electron stimulated desorption (ESD) atomic oxygen source. This source, developed by Hofland and Weaver [14], is ultrahigh vacuum (UHV) compatible, operates with the sample at room temperature and produces a high purity, hyperthermal AO flux with an O atom: O' ratio of ~10⁻⁶.

XPS spectra were first obtained from the as-entered, solvent-cleaned sample. The sample was then transferred into an adjoining UHV chamber that houses the atomic oxygen source via a magnetically coupled rotary/linear manipulator. There the surface was exposed to a hyperthermal AO flux and re-examined without air exposure after total exposure times of 2, 24, and 40 h. The approximate normal distance between the sample faces and source in this study was 15 cm, at which distance the flux was about 2.0 x 10¹⁵ atoms/cm²-s for the instrument settings used. The sample was maintained at room temperature during the AO exposures with a slight temperature increase to 50°C due to exposure to the X-ray source during XPS data collection. The substrate temperature was determined using a chromel-alumel thermocouple. After the 40 h AO exposure, the sample was exposed...
to air (room temperature, ~22°C, relative humidity ~60%) and again examined using XPS.

Fig. 12 Molecular structure of POSS-Kapton with numerically labeled atomic sites

The POSS-Kapton molecular structure with labeled atomic sites is shown in Fig. 12. XPS survey spectra obtained from a solvent-wiped 10 wt% POSS-polyimide surface before and after the 2, 24 and 40 h AO exposures and final air exposure are shown in Fig. 13. The peak assignments shown in Figure 12 pertain to all five spectra. The predominant peaks apparent in these spectra include the C 1s, N 1s, O 1s, Si 2p, Si 2s, O 2s and O Auger peaks. Significant changes in relative peak heights are observed for the C, O, and Si features following the O-atom exposures. XPS is a surface sensitive technique ideally suited for studying AO erosion of spacecraft materials. The outermost surface region which is affected to the greatest extent due to reaction with AO also makes the largest contribution to the XPS signal. The weighted average compositional values of the near-surface region determined using the homogeneous assumption are shown in Table 1 as a function of AO fluence. They provide a trend which is indicative of the chemical alterations occurring during AO exposure. This trend is supported by the chemical state alterations determined by XPS, which are discussed below.

Table 1. Near-surface composition determined from XPS data obtained from the as-entered, AO and air-exposed 10 wt% POSS-Polyimide sample

<table>
<thead>
<tr>
<th>Surface sample treatment</th>
<th>AO fluence O/cm²</th>
<th>O Composition, at.%</th>
<th>Si Composition, at.%</th>
<th>C Composition, at.%</th>
<th>N Composition, at.%</th>
<th>O:Si ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>As entered</td>
<td></td>
<td>15.9</td>
<td>4.6</td>
<td>74.5</td>
<td>4.9</td>
<td>3.4</td>
</tr>
<tr>
<td>2 h AO</td>
<td>1.44×10¹⁷</td>
<td>14.3</td>
<td>4.9</td>
<td>72.6</td>
<td>8.2</td>
<td>2.9</td>
</tr>
<tr>
<td>24 h AO</td>
<td>1.77×10¹⁸</td>
<td>11.1</td>
<td>4.4</td>
<td>79.6</td>
<td>4.9</td>
<td>2.5</td>
</tr>
<tr>
<td>40 h AO</td>
<td>4.53×10¹⁸</td>
<td>9.1</td>
<td>3.7</td>
<td>81.5</td>
<td>5.6</td>
<td>2.4</td>
</tr>
<tr>
<td>Air exposed</td>
<td>4.53×10¹⁸</td>
<td>13.9</td>
<td>3.5</td>
<td>76.8</td>
<td>5.8</td>
<td>3.9</td>
</tr>
</tbody>
</table>

As can be seen in Fig. 13, the O 1s peak decreases significantly upon exposure to the AO beam. As a result, the O/Si atomic ratio of 3.4 for the as-entered sample, decreases gradually to 2.4 after the 40 h AO exposure. This reduction of the O/Si ratio is due to AO induced surface compositional changes resulting in the removal of carbonyl groups from the polymer chain and formation of a surface silica layer as shall be explained in the high resolution spectra that follow. After exposure to air, the O/Si atomic ratio increases to 3.9 corresponding to adsorption of species present in air. An overall increase is observed in the C concentration on the surface during increased exposure. Since the surface compositions presented in Table 1 are relative, it is expected that as the O concentration decreases the C and Si would increase.

High-resolution XPS C 1s, O 1s, N 1s, and Si 2p spectra obtained from the as-entered, solvent-wiped surface before and after the 2, 24 and 40 h O-atom exposures are shown in (a)-(d) of Fig. 14 through Fig. 17. Spectra (e) of these figures were obtained after the exposure to air following the 40 h AO exposure. Variations in peak shapes and positions are observed between the nonexposed, AO-exposed, and air-exposed surfaces, indicating that the chemical species distribution is altered by exposure to the AO flux and then to air. In addition, no surface charging of the sample was evident during the experiment as this would have altered the spectra resulting in a significant binding energy (BE) shift. Differential charging would have resulted in peak broadening or peak multiplicity, however, this was not observed in this study.

Fig. 13. XPS survey spectra obtained from a 10 wt% POSS-polyimide film as entered (a), after 2 h (b), 24 h (c), and 40 h exposure to the hyperthermal AO flux (d), and air exposure after the 40 h exposure (e)

The C 1s peak for the as entered sample in Fig. 14 is broad and centered at 284.7 eV indicating the predominant form of carbon present is aromatic. A high binding energy shoulder is present at 283.6 eV corresponding to the carbonyl carbon (6) in Fig. 12. However, as is also observed Kapton, this shoulder
diminishes upon exposure to AO. This is due to erosion of the carbonyl groups from the polymer backbone. This also results in a chemical state change of nitrogen on the surface as observed in the N 1s spectra in Fig 16.

The N 1s spectrum for the as-entered sample is centered at 400.6 eV, corresponding to nitrogen bound as an imide functional group. However, as with regular Kapton, as the N-C=O bonds are broken upon removal of the carbonyl groups to form CO and CO₂, a lower binding energy shoulder begins to emerge in the N 1s spectra.

The chemical state changes in carbon and nitrogen associated with erosion also coincide with chemical state changes in the O 1s and Si 2p spectra in Fig. 16 and Fig. 17, which as with other POSS-polymer, reveal the formation of a silica layer on the outer surface. Upon inspection, it is evident from these spectra that a transition occurs for oxygen and silicon from a lower binding energy corresponding to the silsesquioxane to a higher binding energy and oxidation state associated with the formation of SiO₂ on the surface. These surface changes are presumably responsible for the reduced erosion rates and improved AO reaction efficiencies discussed presented herein.

**Fig. 14.** XPS C 1s spectra obtained from a 10 wt% POSS-polyimide film as entered (a), after 2 h (b), 24 h (c), and 40 h exposure to the hyperthermal AO flux (d), and air exposure after the 40 h exposure (e)

**Fig. 15.** XPS N 1s spectra obtained from a 10 wt% POSS-polyimide film as entered (a), after 2 h (b), 24 h (c), and 40 h exposure to the hyperthermal AO flux (d), and air exposure after the 40 h exposure (e)

**Fig. 16.** XPS O 1s spectra obtained from a 10 wt% POSS-polyimide as entered (a), after 2 h (b), 24 h (c), and 40 h exposure to the hyperthermal AO flux (d), and air exposure after the 40 h exposure (e)
3. CONCLUDING REMARKS

The incorporation of POSS nanostructures into polyimides should significantly extend the usable lifetime of these materials in LEO applications. They exhibit a significantly improved oxidation resistance due to a rapidly formed ceramic-like, passivating and self-healing silica layer when exposed to high incident fluxes of atomic oxygen. The formed layer prevents further degradation of underlying virgin polymer. This technology could be easily adapted to other polymeric systems, such as structural polymers like polyethylene and polypropylene, revolutionizing the field of space-survivable materials.

4. REFERENCES


Synthesis and Atomic Oxygen Erosion Testing of Space-Survivable POSS (Polyhedral Oligomeric Silsesquioxane) Polyimides

9th International Conference on Materials in a Space Environment
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Polymeric Materials

• Cost is the variable plaguing all space missions. ($5,000 to $10,000/1b to put payload in orbit)

• Materials are one of the main drivers of cost for space missions.

• Polymers offer many advantages (lightweight, easy to process, versatility)

• However, polymers are subject to severe degradation in Low Earth Orbit space environment
LEO Environment  
(Altitudes of 200 to 1500 km)

• Atomic Oxygen
  – \( \sim 10^8 \) atoms/cm\(^3\)
  – Formed from photo-dissociation of \( \text{O}_2 \) in atmosphere.
  – Actual flux on spacecraft traveling at 8 to 12 km/s \( \sim 10^{15} \) atoms/cm\(^2\)\(\cdot\)s
  – Collision energy \( \sim 5\text{eV} \)  (C-C \( \sim 4\text{eV}, \) C-N \( \sim 3\text{eV} \))

• Low-energy and high energy charged particles.

• Thermal cycling  -50 to 150\(^\circ\)C

• Solar UV and VUV radiation
  – VUV wavelengths in LEO extend below 290nm.
  – Bond scission and radical formation can lead to embrittlement.
**Goal: Develop Multi-Functional, Space-Survivable Materials**

<table>
<thead>
<tr>
<th>Atomic Oxygen Reaction Efficiency cm$^3$/atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>Kapton</td>
</tr>
<tr>
<td>Polyethylene</td>
</tr>
<tr>
<td>FEP Teflon</td>
</tr>
<tr>
<td>FEP Teflon (Solar Max)</td>
</tr>
<tr>
<td>Siloxane-imide block copolymers(25% /75%)</td>
</tr>
<tr>
<td>Epoxy</td>
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**Satellites & Space Systems**

**Objectives**

- Increase Space Survivability (AO, particle & VUV radiation, thermal cycling) of Polymeric Materials

- Self-Passivating/Self-Rigidizing/Self-Healing based on **Hybrid** organic/ inorganic nanocomposite incorporation
Goal: Develop Multi-Functional, Space-Survivable Materials

<table>
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<tr>
<th>Bond</th>
<th>Dissociation Energy (EV)</th>
<th>λ (nm)</th>
<th>Material</th>
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<tbody>
<tr>
<td>-C₆H₄-C(=O)-</td>
<td>3.9</td>
<td>320</td>
<td>Kapton®</td>
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<tr>
<td>C-N</td>
<td>3.2</td>
<td>390</td>
<td>Kapton®</td>
</tr>
<tr>
<td>CF₃-CF₃</td>
<td>4.3</td>
<td>290</td>
<td>FEP Teflon®</td>
</tr>
<tr>
<td>CF₂-F</td>
<td>5.5</td>
<td>230</td>
<td>FEP Teflon®</td>
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<tr>
<td>Si-O</td>
<td>8.3</td>
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<td>Zr-O</td>
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<tr>
<td>Al-O</td>
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Objectives

- Increase Space Resistance (AO, particle & VUV radiation, thermal cycling) of Polymeric Materials

- Self-Passivating/Self-Rigidizing/Self-Healing based on nanocomposite incorporation
Hybrid Inorganic/Organic Polymers

Goal: Develop High Performance Polymers that REDEFINE material properties

- Hybrid plastics bridge the differences between ceramics and polymers.
Polyhedral Oligomeric Silsesquioxanes (POSS) Synthesis

RSiX₃ acid or base hydrolysis

Blendables

Resin

Incompletely condensed cages

Brown, Feher, AFRL, Hybrid Plastics
Polymer Working Group - Research

Basic R&D (6.1) PROGRAMS AFOSR
- POSS Synthesis and Characterization
- POSS Polymer Processing
- POSS for Space-Survivable Materials

Applied R&D (6.2) PROGRAMS AFRL
- Solid Rocket Motor Insulation/Casing
- Liquid Rocket Engine Ducting
- High Temp Lubes/Jet Canopies/Radomes

Technology Transfer
Anatomy of a POSS Nanostructure

Nonreactive organic (R) groups for solubilization and compatibilization.

Nanoscopic in size with an Si-Si distance of 0.5 nm and a R-R distance of 1.5 nm.

May possess one or more functional groups suitable for polymerization or grafting.

Thermally and chemically robust hybrid (organic-inorganic) framework.

Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.
### Why POSS and Why Nano?

<table>
<thead>
<tr>
<th>Field</th>
<th>Property</th>
<th>Critical Length</th>
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<tbody>
<tr>
<td>Electronics</td>
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<td>Optical</td>
<td>Quantum Well</td>
<td>1-100 nm</td>
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<tr>
<td></td>
<td>Wave Decay</td>
<td>10-1000 nm</td>
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<td>Polymers</td>
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<tr>
<td></td>
<td>Secondary Structure</td>
<td>10-1000 nm</td>
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<tr>
<td>Mechanics</td>
<td>Dislocation Interaction</td>
<td>1-1000 nm</td>
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<td></td>
<td>Crack Tip Radius</td>
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<td></td>
<td>Entanglement Rad.</td>
<td>10-50 nm</td>
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<td>Therm-Mech.</td>
<td>Chain Motion</td>
<td>0.5-50 nm</td>
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<td>Nucleation</td>
<td>Defect</td>
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<td>Critical Nucleus Size</td>
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<td>Membranes</td>
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</table>
POSS Polymer Incorporation

Cross-linker  Pendant Polymer  Bead Copolymer

POSS Blending
POSS Macromers For Nanocomposites

R-Groups

Cyclohexyl  Phenyl
Cyclopentyl  Ethyl  isoButyl

Completely New Polymer Feedstock Technology

Halides  Nitriles  Silanes  Styryls
Alcohols  Amines  Silanols  a-olefins
Esters  Isocyanates  Silylchlorides  Acrylics
Bisphenols  Epoxides  Norbornenyls

POSS-based macromers are available through either Gelest or Aldrich
POSS technology is commercialized by Hybrid Plastics in Fountain Valley CA
Importance of R groups: Affect compatibility with polymer matrix

50 Wt % POSS Blends in 2 Million MW PS

\[ \text{Cp}_8 \text{T}_8 \]

Domain Formation

\[ \text{Cp}_7 \text{T}_8 \text{Styryl} \]

Partial Compatibility

\[ \text{Vi}_8 \text{T}_8 \]

Immiscible POSS Crystallites

\[ \text{Phenethyl}_8 \text{T}_8 \]

Complete Compatibility-POSS Nanodispersion/Transparent

Polypropylene and Methyl₈T₈

POSS Drop Test
Me₈T₈/i-PP
Dr. R. Blanski,
AFRL
Test Duration:
15:01
Time Lapse 20X
8 Feb 2001

- Test run at 190 °C
- 1 Kg weight
- 10% POSS gave a 28 % improvement
AO undercutting of LDEF Aluminized-Kapton Multilayer Insulation

Siloxanes

- Siloxanes systems exhibit superior resistance to AO
  - High Si-O bond strength ~ 8 eV (C-C ~ 4 eV, C-N ~ 3 eV)
  - Oxyphilicity

\[
\text{HO-Si-O-Si-OH} \quad R = \text{CH}_3, \quad \text{C}
\]

- However, pure siloxane systems have disadvantages
  - Chain Scission
  - Volatile cyclic species which recondense on optical surfaces

Cyclo(Me₂SiO)₅
Cyclo(Me₂SiO)₆
Cyclo(Me₂SiO)₇
Cyclo(Me₂SiO)₃
Cyclo(Me₂SiO)₄
Oxygen Atom Source

1. Adsorption
   - maximize pressure

2. Permeation
   - membrane thickness
   - temperature

3. Desorption (ESD)
   - electron current
   - N adsorbed neutrals
POSS-Siloxane

1. \[
\text{Me} \quad \begin{array}{c}
\text{Me} \\
\text{Me}
\end{array} \\
\text{Si} \quad \begin{array}{c}
\text{Me} \\
\text{Me}
\end{array} \\
\text{Si} \quad \begin{array}{c}
\text{Me} \\
\text{Me}
\end{array} \\
\text{Si} \quad \begin{array}{c}
\text{Me} \\
\text{Me}
\end{array} \\
\text{Si} \quad \begin{array}{c}
\text{Me} \\
\text{Me}
\end{array}
\]

2. Excess

\[
\text{Me} \\
\text{Me}
\]

R = cyclohexyl

POSS-PDMS Copolymer

n = 43
XPS survey spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.
High Resolution C 1s and O 1s spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.
High Resolution Si 2p spectra obtained from a solvent-cleaned, POSS-PDMS film (a) after insertion into the vacuum system, (b), after a 2-hr (c) 24.6-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 4.75-hr air exposure following the 63-hr AO exposure.
SEM of (a) unexposed and (b) exposed POSS-siloxane copolymer surfaces. The simulated LEO exposure “healed” the micro-cracks present initially in the POSS-siloxane sample.

POSS-Polyurethane

R = cyclopentyl
POSS-TMP diol

Et3N/DBTDL
PTMG (Mn=2000)
1,4-butanediol


XPS Survey Spectra from a 60 wt% POSS-PU (a) after insertion into the vacuum system, (b) after a 2-hr (c) 24-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 3.3-hr air exposure following the 63-hr exposure.
High Resolution Si 2p spectra from a 60 wt% POSS-PU (a) after insertion into the vacuum system, (b) after a 2-hr (c) 24-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 3.3-hr air exposure following the 63-hr exposure.
Solar arrays
Space inflatable structures

Superior optical properties, low solar absorptance, high thermal reflectance
Excellent mechanical thermal properties
First POSS-Aniline Synthesis

Multiple step synthesis
Moisture and air sensitive
Not amenable to scale up

Yet Critical for Development of POSS-polyimides!!!
POSS-Kapton Polyimides

- transparent films
- no aggregates formed
POSS High Performance Polyimides

POSS-Kapton polyimide

POSS processable ether-imide

POSS-Fluorinated colorless polyimide
Beam-Surface Scattering/Atomic Oxygen Test Facility

Pulsed CO$_2$ Laser Atomic Oxygen Generator

2-15 eV AO at high fluxes of $10^{16}$ atoms cm$^{-2}$ sec$^{-1}$
Surface Topographical Analysis/Profilometry

Hyperthermal AO Beam

Screen Sample

Kapton H

Kapton 10 wt% POSS
O-Atom etching experiment of POSS-Kapton polyimides
Total AO fluence of $2.62 \times 10^{20}$ atoms/cm$^2$ (~ 3 Days in LEO)

Hyperthermal AO Beam

Screen Sample

20 wt% POSS in Kapton results in over 20 time improvement in erosion resistance.
O-Atom Etching Experiment (~10 DAYS IN LEO)
Total AO fluence of $8.47 \times 10^{20}$ atoms cm$^{-2}$ (100,000 pluses)

Hyperthermal AO Beam

Screen Sample

Kapton 10 wt% POSS
Average etch depth: 2.2 $\mu$m

Kapton H Standard
Average etch depth: 25.4 $\mu$m

Significantly improved oxidation resistance due to a rapidly formed ceramic-like, passivating and self-healing silica layer preventing further degradation of underlying virgin polymer.
AFM Images of Unexposed POSS Polyimide Films

0% POSS
rms roughness: 1.09 nm

10% POSS
rms roughness: 1.03 nm

20% POSS
rms roughness: 1.55 nm
AFM Images of Exposed POSS Polyimide Films 100,000 Pulses of Hyperthermal (5 eV) AO Beam

0% POSS
rms roughness: 102 nm

10% POSS
rms roughness: 17.7 nm

20% POSS
rms roughness: 6.75 nm
Erosion of POSS Polyimides by a Beam of Hyperthermal (5eV) O Atoms

![Graph showing the erosion of POSS Polyimides by a beam of hyperthermal oxygen atoms. The graph plots average step height (μm) against average step height of Kapton (μm).](image-url)
MATERIALS INTERNATIONAL SPACE STATION EXPERIMENT

18 MONTH EXPOSURE TO LEO

POSS in Space

POSS-Polymers Fly on STS 105 Discovery and are deployed on the Int'l Space Station
16 August 2001

Footage courtesy of NASA
POSS-Polymeric Materials Group
Materials Application Branch
AFRL, Edwards AFB

Efficient cost effective POSS-Aniline Monomer and POSS-Polyimide Synthesis. Development, characterization, and testing of POSS-Polyimide composite materials with high temperature stability and space survivability.

POSS Incorporation in Triton’s High Performance Polyimide Resins: Triton RTM PMR polyimides and NASA and Triton’s co-developed Phosphine Oxide Polyimides. Scale up and Validation.

Space Survivability Testing: Includes erosion yields, surface Topographical, and in-situ analysis of POSS polymers following atomic oxygen and vacuum ultraviolet radiation exposure.

Michigan State University
Thermal, mechanical, and dielectric Properties of POSS-polyimides.

Space Survivability Testing: Includes simulated GEO exposure and mechanical property testing prior to and following exposure.
AFM Images of Unexposed Polyimides Copolymerized With Various Weight Percents of POSS
Three dimensional AFM Images
10 wt % POSS Polyimide Films

Unexposed

Exposed

Digital Instruments Nanoscope
Scan size: 10.08 μm
Scan rate: 1.00 Hz
Number of samples: 256
Image Data: Height
Cut scale: 300.0 nm
Enable X Pos: -19781.4 nm
Enable Y Pos: -42151.3 nm

Nanoscope II
Parameters:
Z: 91.6 A U
XY: 1014.0 A A
Samples: 400/scan

10% POSS AD 10CK
Data taken Thu Oct 17 16:19:44 2003
Buffer S((GPS100K,SIL)). Rotated 0°, XY axes [nm]. Z axis [nm]
In a solar/laser thermal rocket, solar or laser light is collected and focused to heat a propellant working fluid such as hydrogen. The collector mirrors are silvered balloon-like inflatable structures or thin sheets of silvered plastic supported by lightweight inflatable trusses. The light passes through a high temperature quartz window or into an open cavity on the side of the engine and focuses to a point to either directly heat the hydrogen propellant or heat a material such as graphite which then heats the hydrogen propellant. (Air force Phillips Laboratory and the NASA Marshall Spaceflight Center.)
Polyimides in Propulsion

SRS Technologies’ (Huntsville, Alabama), solar concentrators are made almost entirely of castable, clear polyimide film, a lightweight material compared to glass or metal optics.