Properties and Improved Space Survivability of POSS Polyimides

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# Properties and Improved Space Survivability of POSS Polyimides

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Outline

- Lower Earth Orbit Environment
- Assessment of state-of-the-art Space Polyimides.
- POSS: Polyhedral Oligomeric Silsesquioxane
- POSS Kapton Polyimides
- Ground Based Tests: Atomic Oxygen (AO) Erosion Studies
- Self Forming / Self Healing Silica Passivation Layer
- Modeling and Simulation of AO attack on POSS
- Flight Tests: MISSE 4, 5, 6
- Thermal and Mechanical Properties
- Summary and Conclusions
- Acknowledgments

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Atomic Oxygen (AO) Erosion of Kapton in LEO is a serious threat to spacecraft durability.

As a space vehicle orbits the Earth at orbital speed (7.8 km/sec at low altitudes) it undergoes energetic collisions with atoms and molecules in the orbital environment.

AO is the dominant species in the outer ionosphere from 200-700 km, becoming as much as 90 % of the atmosphere at 500 km, a typical altitude for the International Space Station and future space platforms.
Atomic Oxygen and Synergistic Effects on Materials

- Glow Light
- Inelastic Scattering
- Synergism between VUV & O
- Synergism between Ions & O
- Volatile Reaction Products (Possible Contaminants)
- Oxygen Atoms
- O₂ (Recombination)
- Oxidation
- Loss of Dimensional Stability
- Energy & Momentum Accommodation (Heating)
- Erosion
- Cracking and Embrittlement

Courtesy of Dr. Timothy Minton, Montana SU
Atomic oxygen is the dominant neutral component (~$10^9$ cm$^{-3}$ at 300 km)


Courtesy of Dr. Timothy Minton, Montana SU
Technical Problem
Atomic Oxygen in Lower Earth Orbit

LEO Environment
(Altitudes of 200 to 1500 km)
- Atomic Oxygen (AO): \(\sim 10^6\) - \(10^8\) atoms/cm\(^3\), up to 90% of the atmosphere at 500km (typical altitude for international space station).
- Actual AO flux on spacecraft \(\sim 10^{12} - 10^{14}\) atoms/cm\(^2\)•s
- AO Collision energy \(\sim 5\text{eV}\) (7.8 km/sec) (C-C bond energy \(\sim 4\text{eV}\), C-N \(\sim 3\text{eV}\), Si-O \(\sim 8.3\text{eV}\))
- Low-energy and high energy charged particles.
- Thermal cycling \(-50\) to \(150^\circ\text{C}\)
- Solar VUV and UV radiation \(\sim 100 - 400\) nm
- Bond scission and radical formation can lead to embrittlement.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Dissociation Energy (EV)</th>
<th>(\lambda) (nm)</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-\text{C}_6\text{H}_4\text{C(=O)\text{-}})</td>
<td>3.9</td>
<td>320</td>
<td>Kapton(^\circ)</td>
</tr>
<tr>
<td>C-N</td>
<td>3.2</td>
<td>390</td>
<td>Kapton(^\circ)</td>
</tr>
<tr>
<td>Si-O</td>
<td>8.3</td>
<td>150</td>
<td>Nanocomposite</td>
</tr>
</tbody>
</table>

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State-of-the-Art Space Polyimides

- Kapton H Protected by a sputtered on Silica layer (SiO$_2$).
- Inherent problems in protective Silica layer:
  - Defects from surface anomalies occurring during deposition process.
  - Cracks and microdefects due to micrometeoroid and debris bombardment in LEO. Underpinning Effect.
- Results:
  - Exposure of underlying Kapton layer.

- Lifetime of Kapton H protected by sputtered on silica layer:
  - Example:
  - Hubble Space Telescope:
  - Altitude = 610 km.
  - AO fluence exposure: 7.59 x 10$^{20}$ atoms/cm$^2$ for 3.6 years.
  - Revisited every 2-3 years for maintenance including replacement of solar arrays and patching of multilayer insulation blankets.

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LDEF Satellite:
Long Duration Exposure Facility.

Total AO Exposure: $9 \times 10^{21}$ atoms/cm$^2$
Depths of >0.0127cm (> 5mils) of Kapton sheets were eroded away after 5.8 yrs in LEO on the ram AO surface of the LDEF

Scanning Electron Micrograph Of Kapton MLI Surface.

Underpinning Effect

Goal

Our goal is to create an efficient drop-in replacement for Kapton that:

1. Has increased space survivability due to resistance to atomic oxygen, thermal cycling, solar UV and VUV radiation, protons and electrons.
2. Is Self-Passivating and Self-Healing based on hybrid organic/inorganic nanocomposite incorporation.
3. Has superior optical properties, low solar absorptance, high thermal reflectance.
4. Has excellent mechanical thermal properties.
Goal: Develop High Performance Polymers that REDEFINE material properties

- Hybrid plastics bridge the differences between ceramics and polymers

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Why Use POSS?

- Multifunctionality - including no negative effects on processing (or can even get improvements)

- Properties previously not attainable (extended temp range, flame retardancy)

- Turnkey Utility

- Control of molecular architecture
Anatomy of a POSS Nanostructure

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

Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

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.

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

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POSS Incorporation into Polymers

Cross-linker

Pendant Polymer

Bead Copolymer

POSS Blending

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New Polymer Feedstock Technology

POSS-based macromers are available through either Gelest or Aldrich.

POSS technology is commercialized by Hybrid Plastics in Fountain Valley CA.
POSS: Where We Were (1996)

- Cost: $5,000-$10,000/lb
- Volume: ~20 lbs/yr
- Production time: min 11 days, max 6 months
- Versatility: ~6 POSS feedstocks, ~30 POSS macromers
- No successful POSS blends
- Made only by U.S. Government

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## Why POSS and Why Nano?

<table>
<thead>
<tr>
<th>Field</th>
<th>Property</th>
<th>Critical Length</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electronics</strong></td>
<td>Tunneling</td>
<td>1-100 nm</td>
</tr>
<tr>
<td><strong>Optical</strong></td>
<td>Quantum Well</td>
<td>1-100 nm</td>
</tr>
<tr>
<td></td>
<td>Wave Decay</td>
<td>10-1000 nm</td>
</tr>
<tr>
<td><strong>Polymers</strong></td>
<td>Primary Structure</td>
<td>0.1-10 nm</td>
</tr>
<tr>
<td></td>
<td>Secondary Structure</td>
<td>10-1000 nm</td>
</tr>
<tr>
<td><strong>Mechanics</strong></td>
<td>Dislocation Interaction</td>
<td>1-1000 nm</td>
</tr>
<tr>
<td></td>
<td>Crack Tip Radius</td>
<td>1-100 nm</td>
</tr>
<tr>
<td></td>
<td>Entanglement Rad.</td>
<td>10-50 nm</td>
</tr>
<tr>
<td><strong>Therm-Mech.</strong></td>
<td>Chain Motion</td>
<td>0.5-50 nm</td>
</tr>
<tr>
<td><strong>Nucleation</strong></td>
<td>Defect</td>
<td>0.1-10 nm</td>
</tr>
<tr>
<td></td>
<td>Critical Nucleus Size</td>
<td>1-10 nm</td>
</tr>
<tr>
<td></td>
<td>Surface Corrugation</td>
<td>1-10 nm</td>
</tr>
<tr>
<td><strong>Catalysis</strong></td>
<td>Surface Topology</td>
<td>1-10 nm</td>
</tr>
<tr>
<td><strong>Biology</strong></td>
<td>Cell Walls</td>
<td>1-100 nm</td>
</tr>
<tr>
<td><strong>Membranes</strong></td>
<td>Porosity Control</td>
<td>0.1-5 nm</td>
</tr>
</tbody>
</table>

- 1 mm: Sewing Needle, Razor Blade Thickness
- 100 µm: Human Hair
- 10 µm: Most Cells & Fibers
- 1 µm: Bacteria, Fillers & Polymer Morphology
- 100 nm: Viruses & Nanofillers
- 10 nm: POSS® Building Blocks, Macromolecules
- 1.0 nm: Atoms / Small Molecules
- 0.1 nm: Nucleation

---

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Nanostructured™ POSS Chemicals
Physical Form of Products

Hybrid™ Plastics

>120 POSS Monomers, Polymers and Feedstocks Available

Crystalline Solids
Wide melting range 24°C to 400°C+

Waxes
Wide viscosity range 40cSt. to 400cSt

Liquids & Oils

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What Property Enhancements Can You Get From Using POSS?

- Increased $T_g$
- Increased $T_{dec}$
- Oxidation resistance
- Reduced flammability
- Extended use temperature range
- Altered mechanicals
- Reduced heat evolution
- Lower thermal conductivity
- Lower density
How to use POSS
(Blends or Drop-In Nanofillers)

50 Wt % POSS Blends in 2 Million MW PS

R = cyclopentyl

Cp₈T₈

Domain Formation

POSS Nanodispersion/Transparent

Coughlin Building Block Model (POSS Blends & Copolymers)

Bottom-up Approach (Self-Assembly)

Top-down Approach

Bryan Coughlin-UMass

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1. As a solid, POSS crystallizes
Nanoengineering with POSS

Bryan Coughlin-UMass

PBD-POSS4 (43wt%POSS)

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## Prof. Andre Lee i-PP/POSS Blends

<table>
<thead>
<tr>
<th></th>
<th>Dow data</th>
<th>Neat i-PP (processed)</th>
<th>i-PP blended 2 wt% Methyl₈ₚ₈</th>
<th>i-PP blended 5 wt% Methyl₈ₚ₈</th>
<th>i-PP blended 10 wt% Methyl₈ₚ₈</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tensile Strength @ Yield; ASTM D638</strong></td>
<td>5000 psi (34.5 MPa)</td>
<td>4800 psi (33.0 MPa)</td>
<td>5000 psi (34.5 MPa)</td>
<td>5100 psi (35.1 MPa)</td>
<td>5200 psi (35.8 MPa)</td>
</tr>
<tr>
<td><strong>Flexural Modulus (0.05 in/min); ASTM D790A</strong></td>
<td>240,000 psi (1.655 GPa)</td>
<td>235,000 psi (1.620 GPa)</td>
<td>251,000 psi (1.730 GPa)</td>
<td>255,000 psi (1.757 GPa)</td>
<td>262,000 psi (1.80 GPa)</td>
</tr>
<tr>
<td><strong>HDT @ 66 psi, as injected; ASTM D648</strong></td>
<td>210 °F (99 °C)</td>
<td>210 °F (99 °C)</td>
<td>221 °F (105 °C)</td>
<td>239 °F (115 °C)</td>
<td>255 °F (124 °C)</td>
</tr>
<tr>
<td><strong>Impact Izod @25C ASTM D256A</strong></td>
<td>0.5 ft-lb/in</td>
<td>0.55 ft-lb/in</td>
<td>0.55 ft-lb/in</td>
<td>0.62 ft-lb/in</td>
<td>0.75 ft-lb/in</td>
</tr>
</tbody>
</table>

- The above data (other than Dow’s data) is an average of at least 10 samples for each test with acceptable S.D. of 5% or better.

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POSS: Where Are We Now (2004)
1996 data in red

- Cost: $20-$5000/lb ($5000-$1000/lb)
- Volume: Multi-ton (~20lb/yr)
- Production time: min 1 hour (11 days),
  max 14 days (6 months)
- Versatility: >120 POSS (36 POSS)
  monomers, feedstocks, polymers
- Many successful POSS blends
- Commercialized by Hybrid Plastics
  www.hybridplastics.com

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Polyhedral Oligomeric Silsesquioxanes (POSS)

RSiX₃ acid or base hydrolysis

Blendables

Resin

Incompletely condensed cages

Brown & Vogt: JACS, 1965, 4313

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POSS-Kapton Polyimides

- transparent films
- no aggregates formed

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First POSS-Aniline Synthesis

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

Yet Critical for Development of POSS Polyimides!!!

Make a cost efficient POSS Polyimide that is amenable to scale up and performs as well as current POSS Polyimide (POSSdi1 Polyimide).

This will involve:

- **Cost efficient synthesis** of next generation POSS diamine monomers.
- **Copolymerization** of next generation POSS diamine monomers to form POSS Polyimides.
- **Testing** of thermal and mechanical properties and range of optical clarity.
- **Molecular modeling and simulation** of oxygen atom, photon, electron, and proton attack on next generation POSS Polyimides.
- **Simulated LEO and GEO exposure** ground based testing.

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AFM Images of Unexposed Polyimides Copolymerized With Various Weight Percents of POSS

0 wt % POSS

5 wt % POSS

10 wt % POSS

15 wt % POSS

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Three dimensional AFM Images
10 wt % POSS Polyimide Films

Unexposed

Exposed

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O-Atom Etching Experiment
Total AO fluence of $8.47 \times 10^{20}$ atoms cm$^{-2}$ (100,000 pulses)

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

Kapton H Standard
Average etch depth:
25.4 mm; 1.0 mils

Kapton 10 wt% POSS
Average etch depth:
2.2 mm; 0.087 mils

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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.
AFM Images of Unexposed POSS Polyimide Films

0% POSS
rms roughness: 1.55 nm

10% POSS
rms roughness: 1.03 nm

20% POSS
rms roughness: 1.09 nm

AFM Images of Exposed POSS Polyimide Films 100,000 Pulses of Hyperthermal 5 eV AO Beam

0% POSS
rms roughness: 10.2 nm

10% POSS
rms roughness: 6.75 nm

20% POSS
rms roughness: 17.7 nm
AFM Images of POSS Polyimides With increasing AO Flux.

(10 × 10 μm; z scale = 500 nm)

rms roughness → 2.48 nm 70 nm 120 nm 126 nm

0 wt % POSS Polyimide

rms roughness → 2.47 nm 22.4 nm 34.3 nm 78.9 nm

10 wt % POSS Polyimide

rms roughness → 2.86 nm 17.2 nm 23.7 nm 39.1 nm

20 wt % POSS Polyimide

AO fluence (O atoms/cm²) → 0.0 cm² 3.8×10¹⁹ 1.6×10²⁰ 4.1×10²⁰

Note:
1 x 10²⁰ O atoms/cm² is roughly equivalent to a spacecraft operating at 500 - 600 km orbit during nominal solar activity conditions for periods of at least 1 year.

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1 x 10²⁰ O atoms/cm² is roughly equivalent to a spacecraft operating at 500 - 600 km orbit during nominal solar activity conditions for periods of at least 1 year.

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Note:
1 x 10²⁰ O atoms/cm² is roughly equivalent to a spacecraft operating at 500 - 600 km orbit during nominal solar activity conditions for periods of at least 1 year.
## X-ray Photoelectron Spectroscopy Analysis of POSS Polyimides

### Surface Atomic Concentrations (%) determined from XPS Survey Scans following Atomic Oxygen Exposure

<table>
<thead>
<tr>
<th>Sample</th>
<th>Exposure (beam pulses)</th>
<th>Kapton-equivalent atomic oxygen fluence ($10^{20}$ O atoms cm$^{-2}$)</th>
<th>C</th>
<th>O</th>
<th>Si</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 wt% POSS polyimide</td>
<td>0</td>
<td>0</td>
<td>72</td>
<td>19.5</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>~0.1</td>
<td>69</td>
<td>20</td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.63</td>
<td>69</td>
<td>24</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>4.10</td>
<td>55</td>
<td>36</td>
<td>0</td>
<td>9</td>
</tr>
<tr>
<td>10 wt% POSS polyimide</td>
<td>0</td>
<td>0</td>
<td>77</td>
<td>16</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>~0.1</td>
<td>73</td>
<td>18.5</td>
<td>5</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.63</td>
<td>48</td>
<td>30</td>
<td>19</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>4.10</td>
<td>20</td>
<td>56</td>
<td>23.5</td>
<td>0.5</td>
</tr>
<tr>
<td>20 wt% POSS polyimide</td>
<td>0</td>
<td>0</td>
<td>70</td>
<td>20</td>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>~0.1</td>
<td>66</td>
<td>24</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>1.63</td>
<td>20</td>
<td>54</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>4.10</td>
<td>12</td>
<td>60</td>
<td>26</td>
<td>1</td>
</tr>
</tbody>
</table>
Etch depths for 0, 10, and 20 wt % POSS Polyimide films as a function of O-atom fluence.

The erosion yields* of the 10 and 20 wt % POSS Polyimide samples were 3.7 and 0.98 percent, respectively, of the erosion yield for Kapton H at the highest fluence used in this experiment (8.5x10^{20} atoms cm^{-2}).

*Erosion Yield = \frac{erosion depth \times step height (cm)}{AO fluence atoms/cm^3}

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Molecular dynamics calculations of $O(^3P)$ collisions (5 eV) with POSS ($Si_8O_{12}H_8$) cages

Possible Reaction Channels:

- H abstraction to give OH
- H elimination (O adds to the cage)
- Cage opening (O adds to the cage)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of trajectories</td>
<td>103</td>
</tr>
<tr>
<td>Impact parameter</td>
<td>7 a.u.*</td>
</tr>
<tr>
<td>Inelastic</td>
<td>63</td>
</tr>
<tr>
<td>H abstraction</td>
<td>3</td>
</tr>
<tr>
<td>H elimination</td>
<td>22</td>
</tr>
<tr>
<td>Cage opening</td>
<td>15</td>
</tr>
</tbody>
</table>

*(~Half diagonal of the Si4 faces + 3 a.u.)*

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Model System: POSS Coated Alkane Thiol Self-Assembled Monolayer (SAM) on a Gold Surface.

- **Molecular dynamics** calculations of $O^{(3P)}$ collisions (5 eV) with “functionalized” POSS.
- **Method:** Classical trajectories with a QM/MM (quantum mechanics / molecular mechanics) hybrid potential.
  - QM part: $O^{(3P)}$, POSS cage and 1st methylene unit of the bound chains.
  - MM part: All of the SAM but the 1st methylene unit of the bound chains.

- **Results:** Of limited trajectories studied, similar mechanisms of $O$ atom attack on POSS ($Si_8O_{12}H_8$) Cages were found to apply to the studies of the POSS coated SAM.

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Molecular Modeling Objectives

1. AO degradation pathways of polyimide when exposed to 5 eV oxygen.

2. Oxidation of POSS cage by 5 eV AO.

3. Penetration of 5 eV AO through POSS and silica layers to determine the SiO2 layer thickness needed to quench reaction with an underlying polymer layer.
POSS-Polymers Fly on STS 105 Discovery and are deployed on the International Space Station 16 Aug 2001, MISSE 4

AO, UV, VUV exposure.

POSS-Polymers awaiting flight on ISS, MISSE 5
AO exposure only.
SALT Sprayed Samples!

Footage courtesy of NASA

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MISSE-6 Experiment Tray Layout:
AO and UV Side

Data Loggers!
Quartz Crystal Microbalances!

Same amount of space on “UV only” tray!

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POSS Polyimides do not lose rigidity above the Tg.

Room temperature modulus (stiffness) unaffected by POSS.

High temperature (430°C) modulus exhibits a maximum with POSS PI loading at 20 wt%:

@ 430°C, the modulus of 20 % POSS Polyimide doubles relative to 0 % POSS polyimide.

Tg of POSS polyimides is 5 - 10 % lower than polyimides (414°C).
Tan δ peaks for the 20 and 25 wt% are lower intensity and broader indicating that at POSS loadings greater than 20 wt% there exists interactions between the POSS molecules strong enough to significantly affect polymer chain dynamics.
Acknowledgments

Polymer Working Group: Dr. Tim Haddad, Dr. Joe Mabry, Mr. Pat Ruth, 2Lt. Laura Moody, Mrs. Sherly Large, 2Lt. Amy Palecek.

Previous Group Members: Capt. Rene Gonzalez, Ph. D.

Branch Chief: Dr. Shawn Phillips

Collaborators:

Aerospace Corporation; Dr. Mike Meschiznic, Dr Howard Katzman, Dr. Alan Hopkins, Dr. Gary Steckle

Hybrid Plastics
University of Montana State; Dr. Tim Minton
Northwestern University: Dr. George Schatz

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Summary and Conclusions

- Our goal is to create an efficient drop-in replacement for Kapton that is:
  - Space survivable
  - Self passivating
  - Self healing
  - Low in solar absorptance
  - Excellent in mechanical properties

- POSS Polyimides form a protective Si-O layer when exposed to Atomic Oxygen

- Modeling and Simulation Plan has shown that AO adds to the POSS molecule and does not pass through POSS.

- Thermal and Mechanical Testing indicate:
  - POSS Polyimides do not lose rigidity above the Tg.
  - Tg of POSS polyimides is 5 - 10% lower than polyimides (414°C).
  - Analysis of tan δ curves indicate that polymer chain dynamics are affected by the addition of POSS

- POSS-Polymers awaiting flight on ISS, MISSE 5 and scheduled to fly on MISSE 6.

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Abstract

Polyimides such as Kapton are used extensively in spacecraft thermal blankets, solar concentrators, and space inflatable structures. Atomic oxygen (AO) in lower earth orbit (LEO) causes severe degradation in Kapton resulting in reduced spacecraft lifetimes. One solution is that SiO₂ coatings impart remarkable oxidation resistance and have been widely used to protect Kapton. Imperfections in the SiO₂ application process and micrometeoroid / debris impact in orbit damage the SiO₂ coating leading to erosion of Kapton.

A self passivating, self healing silica layer protecting underlying Kapton upon exposure to AO may result from the nanodispersion of silicon and oxygen within the polymer matrix. Polyhedral oligomeric silsesquioxane (POSS) composed of a inorganic cage structure with a 2:3 Si:O ratio surrounded by tailor able organic groups is a possible delivery system for nanodispersed silica. A POSS diamine was copolymerized with pyromellitic dianhydride and 4,4' -oxydianiline resulting in POSS Kapton Polyimide. The glass transition temperature (Tg) of 5 to 20 weight % POSS Polyimide was determined to be 5 - 10 % lower than that of unmodified polyimides (414 ºC). Furthermore the room temperature modulus of polyimide is unaffected by POSS, and the modulus at temperatures greater than the Tg of the polyimide is doubled by the incorporation of 20 wt % POSS.

To simulate LEO conditions, POSS Polyimide films were exposed to a hyperthermal O-atom beam. Surface analysis of exposed and unexposed films conducted with X-ray photoelectron spectroscopy, atomic force microscopy, and surface profilometry support the formation of a SiO₂ self healing passivation layer upon AO exposure. This is exemplified by erosion yields of 10 and 20 weight % POSS Polyimide samples which were 3.7 and 0.98 percent, respectively, of the erosion yield for Kapton H at a fluence of 8.5 x 10²⁰ O atoms cm⁻².
POSS-Siloxane

1. \[ \text{POSS-Monomer} \]

2. Excess

\[ R = \text{cyclohexyl} \]

POSS-PDMS Copolymer

\[ n = 43 \]
POSS Siloxane

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.

Composition, at %

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<th>Si</th>
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DISTRIBUTION A. Approved for public release; distribution unlimited.
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.
POSS-Polyurethane

R = cyclopentyl
POSS-TMP diol

4.4-methylenebis(phenyl isocyanate)

\[ \text{POSS-TMP diol} + \text{4.4-methylenebis(phenyl isocyanate)} \]

\[ \stackrel{(\text{CH}_2)_4\text{O}}{\text{O}} \]

or

\[ \stackrel{\text{POSS}}{\text{O}} \]


DISTRIBUTION A. Approved for public release; distribution unlimited.
### Composition, at %

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<th>Sn</th>
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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.
POSS High Performance Polyimides

POSS processable ether-imide

POSS-Kapton polyimide

POSS-Fluorinated colorless polyimide

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