A Study of the Self-Passivation of Space-Survivable POSS Kapton Polyimides

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A Study of the Self-Passivation of Space-Survivable POSS Kapton Polyimides Poster Session

Sandra Tomczak; Vendana Vij; Darrell Marchant; Timothy Haddad; Joseph Mabry

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unclassified

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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 based on hybrid organic/ inorganic nanocomposite incorporation
3. Has superior optical properties, low solar absorptance, high thermal reflectance
4. Has excellent mechanical thermal properties.
LEO Environment (Altitudes of 200 to 1500 km)
- Atomic Oxygen (AO): \( \sim 10^6 - 10^8 \ \text{atoms/cm}^3 \), up to 90% of the atmosphere at 500 km (typical altitude for international space station).
- Typical orbital speed of spacecraft is 7.8 km/sec
- Actual AO flux on spacecraft \( \sim 10^{12} - 10^{14} \ \text{atoms/cm}^2\cdot\text{s} \)
- AO Collision energy \( \sim 5\text{eV} \) (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°C
- Solar VUV and UV radiation (~ 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>(-C_6H_4-C(=O)-)</td>
<td>3.9</td>
<td>320</td>
<td>Kapton®</td>
</tr>
<tr>
<td>C-N</td>
<td>3.2</td>
<td>390</td>
<td>Kapton®</td>
</tr>
<tr>
<td>Si-O</td>
<td>8.3</td>
<td>150</td>
<td>Nanocomposite</td>
</tr>
</tbody>
</table>
MLI were flown 5.8 yrs in LEO on the Long Duration Exposure Facility.

Total AO Exposure: $9 \times 10^{21}$ atoms/cm$^2$

95% of Al-Kapton underwent underpinning.

Fluence atoms/cm$^3$:
Eroded material divided by
Kapton erosion yield of $3 \times 10^{21}$ cm$^3$/atom.
POSS-Kapton Polyimides

- Transparent films at 25 wt % POSS.

- POSS Polyimides do not lose rigidity above the glass transition temperature.
- Tg of POSS polyimides is 5 - 10 % lower than polyimides (414°C).
- Room temperature modulus unaffected by POSS.
- High temperature modulus (above 430°C) is increased with POSS content.
O-Atom Etching Experiment

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

Hyperthermal AO Beam ($CO_2$ laser, $\theta = 4.93-8.42$ eV)

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

Kapton H Standard
Average etch depth: 25.4 $\mu$m; 1.0 mils

Kapton 10 wt% (2 mole %) POSS
Average etch depth: 2.2 $\mu$m; 0.087 mils

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AFM Images of POSS Polyimides With increasing AO Flux.
(10 × 10 µm; z scale = 500 nm)

0 wt % POSS Polyimide

rms roughness → 2.48 nm  70 nm  120 nm  126 nm

10 wt % POSS Polyimide

rms roughness → 2.47 nm  22.4 nm  34.3 nm  78.9 nm

20 wt % POSS Polyimide

rms roughness → 2.86 nm  17.2 nm  23.7 nm  39.1 nm

AO fluence (O atoms/cm²)

0.0 cm²  3.8×10¹⁹  1.6×10²⁰  4.1×10²⁰

Note:
1 × 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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Surface Atomic Concentrations (%) determined from XPS (X-ray Photoelectron Spectroscopy) Survey Scans before and after exposure to Atomic Oxygen.

<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>

Calculated at%: 0 wt% POSS PI: C = 75.9, O = 17.2, Si = 0, N = 6.9
10 wt% POSS PI: C = 75, O = 17.2, Si = 1, N = 6.4.
20 wt% POSS PI: C = 75, O = 17.2, Si = 1.8, N = 6.0
1st AO Erosion experiment:
The erosion rate of the 10 and 20 wt% POSS Polyimide samples were 3.7 and 0.98 percent, respectively, of the erosion rate for Kapton H at the highest fluence used in this experiment (8.5x10²⁰ atoms cm⁻²).

2nd AO Erosion Experiment:
The new 25 wt% POSS polyimide samples had an erosion rate that was 0.3 percent of the erosion rate for Kapton H at a fluence of 8.5x10²⁰ atoms cm⁻².

This erosion rate is one third that of the previously synthesized 20 wt% POSS polyimide.
Self-passivation of POSS Polyimide
Upon Exposure to 2.3x10^{20} O atoms cm^{-2}.

Screen-protected samples were exposed to 2.3x10^{20} O atoms cm^{-2}, unprotected, scratched with a diamond scribe 1 μm deep, screen-protected, and re-exposed to 2.3x10^{20} O atoms cm^{-2}.

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## Summary of Self-Passivation Study

<table>
<thead>
<tr>
<th></th>
<th>SiO$_2$ coated Kapton HN with Al under-coating</th>
<th>Kapton H</th>
<th>25 wt % POSS polyimide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erosion depth after 1$^{st}$ exposure to 2.3x10$^{20}$ O atoms cm$^{-2}$.</td>
<td>~ 0 μm</td>
<td>5 μm</td>
<td>0.200 μm</td>
</tr>
<tr>
<td>All samples were scratched 1 μm deep.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Erosion depth outside of the scratch after 2$^{nd}$ exposure to 2.3x10$^{20}$ O atoms cm$^{-2}$.</td>
<td>~ 0 μm</td>
<td>5 μm</td>
<td>~ 0 μm</td>
</tr>
<tr>
<td>Erosion depth inside of the scratch after 2$^{nd}$ exposure to 2.3x10$^{20}$ O atoms cm$^{-2}$</td>
<td>7 μm</td>
<td>5 μm</td>
<td>0.200 μm</td>
</tr>
</tbody>
</table>

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SEM of Kapton H surface after the Second Atomic Oxygen Exposure

Exposed Area

Scratch 20 μm wide, 1 μm deep.

Area protected by wire screen

Scratch = 1 μm

Erosion Depth > 5 μm

Scan Length / μm

Step Height / μm

SEM by Marietta Fernandez, Edwards AFRL

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SEM Images of Scratch on SiOx Coated Kapton After Second AO Exposure

- **Side View**
- **AO Exposed Area**
- **Scratch**

Profilometry Trace

- **Scratch Depth 1 μm**
- **Erosion Depth 7 μm**
- **Scratch Depth 1 μm**

SEM by Marietta Fernandez Edwards AFRL

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SEM of 25 wt % POSS Polyimide Surface After the Second Atomic Oxygen Exposure

Area protected by wire screen

Exposed Area

Scratch 35 μm wide, 1 μm deep

Scratch Depth 1.25 μm

Erosion Depth ~ 200 nm

Profilometry Trace

Profile
Step Height / μm
-1.5 -1.0 -0.5 0.0 0.5 1.0
0 50 100 150 200
Scan Length / μm

SEM by Marietta Fernandez, Edwards AFRL
New POSS Monomer

China Lake Naval Air Warfare Center, Weapons Division collaborators: Dr. Michael Wright, Dr. Brian Petteys, Dr. Andy Guenthner, Dr. Gregory Yandek.

Recently synthesized: Side-chain POSS diamine monomer which is relatively inexpensive and of facile synthesis. Resultant POSS Polyimides are transparent flexible films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Kapton-Equivalent Fluence/10^{20} O atoms cm^{-2}</th>
<th>Erosion Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kapton H</td>
<td>4.10</td>
<td>12.3</td>
</tr>
<tr>
<td>20 wt % main-chain POSS polyimide</td>
<td>4.10</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Is 3.8 % of that of Kapton H.</td>
</tr>
<tr>
<td>Kapton H</td>
<td>3.53</td>
<td>10.6</td>
</tr>
<tr>
<td>7 Si8O12 wt % side-chain POSS polyimide.*</td>
<td>3.53</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Is 3.3 % of that of Kapton H.</td>
</tr>
</tbody>
</table>

AO resistance is similar between main-chain and side-chain POSS polyimides.

* equivalent SiO content to 20 wt % main-chain POSS PI

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Acknowledgments

Polymer Working Group: Dr. Rusty Blanski, Mr. Pat Ruth, Mrs. Sherly Largo, Ms. Sarah Mazzella, 2Lt. Amy Palecek, 2Lt. Laura Moody.

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Michigan State University: Dr. Andre Lee

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