Self-Passivation of POSS-Kapton-Polyimides in the Presence of Atomic Oxygen (Preprint)

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Evidence for the formation of a protective silica layer on the surface of POSS-Kapton®-PIs upon exposure to AO was found in X-Ray Photoelectron Spectroscopy (XPS) studies of POSS-Kapton®-PIs flown on the Materials International Space Station Experiment (MISSE1), and in separate studies of POSS-Kapton®-PIs exposed to AO in a ground-based facility. To directly compare the effect of AO on Kapton H®, SiO2 coated Kapton HN®, and 8.75 weight % Si8O11 cage “main-chain” POSS-Kapton®-polyimide (8.75 wt % Si8O11 MC-POSS-PI), these materials were exposed to AO, scratched, and exposed to a second equivalent AO fluence. The erosion of the three materials, inside and outside of the scratched area, was monitored by stylus surface profilometry. The results of this study indicate that the POSS Kapton® PI reproducibly eroded about 200 nm before forming a silica layer. A thin film of 7 wt % Si8O11 survived a 3.9 year flight on the MISSE1, on the International Space Station which resides at 500 km in LEO. The effects of temperature, physical property characterizations, and the MISSE1 flight will be discussed.

14. ABSTRACT

15. SUBJECT TERMS
Self-Passivation of POSS-Kapton-Polyimides in The Presence of Atomic Oxygen (Preprint)

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INTRODUCTION

Kapton® polyimide (PI) is used extensively on spacecraft as a flexible substrate for solar arrays because of its strength, temperature stability, insulation properties, UV stability, IR transparency, low solar absorptance and superior optical properties. It is also a component of spacecraft multilayer insulation blankets that thermally insulate to keep blankets that thermally insulate to keep.

It has been well established that polymeric materials undergo severe degradation in low Earth orbit (LEO), mainly due to the high concentration of atomic oxygen and its reactivity with organic materials.[2-10] Materials in LEO are also exposed to solar radiation, thermal cycling which can range from -50 °C to 150 °C, and bombardment by low and high-energy charged particles.[11]

AO in LEO impacts materials with a collision energy of 4.5-6 eV.[12-14] This O-atom translational energy can overcome many reaction barriers and facilitates the degradation of Kapton®. The silicon-oxygen bond energy is 8 eV, and this bond is intact after AO exposure. For this reason, Kapton® is typically coated with silica to impart resistance to AO. Imperfections in the silica layer created during the deposition process, or from impacts encountered during flight, lead to exposed Kapton®. It has been shown by de Groh et al at that when protective aluminium coatings over Kapton are damaged in LEO, AO erodes the polymer matrix in a manner that creates burrowed out cavities. Computer simulations have shown that these cavities are created due to AO that ricochets in eroded spaces before reacting, causing a burrowing effect.[2]

The presence of Si and O in the polyimide polymer matrix leads to the formation of a protective silica layer on the polyimide surface when the POSS-Kapton® mix material reacts with AO. Polyhedral oligomeric silsesquioxane (POSS) is a Si and O cage-like structure surrounded by tailorable organic groups, which can be polymerizable. POSS diamines have been polymerized into the Kapton polyimide (PI) backbone creating nanodispersed Si and O in the polymer matrix. Our data indicates that upon AO exposure of POSS-PI films, the surface organic matrix erodes, while the atomic oxygen reacts with the nanodispersed POSS to form a silica passivation layer, therefore imparting remarkable AO resistance with minor effects in the storage modulus, glass transition temperature, and coefficient of thermal expansion.[15]

Evidence for the formation of a protective silica layer on the surface of POSS-Kapton®-PIs upon exposure to AO was found in X-Ray Photoelectron Spectroscopy (XPS) studies of POSS-Kapton®-PIs flown on the Materials International Space Station Experiment (MISSE1), and in separate studies of POSS-Kapton®-PIs exposed to AO in a ground-based facility. To directly compare the effect of AO on Kapton HN®, SiO₂ coated Kapton HN®, and 8.75 weight % SiO₂, cage “main-chain” POSS-Kapton®- polyimide (8.75 wt % SiO₂, MC-POSS-PI), these materials were exposed to AO, scratched, and exposed to a second equivalent AO fluence. The erosion of the three materials, inside and outside of the scratched area, was monitored by stylus surface profilometry. The results of this study indicate the POSS Kapton® PI reproducibly eroded about 200 nm before forming a silica layer. A thin film of 7 wt % SiO₂ survived a 3.9 year flight on the MISSE1, on the International Space Station which resides at 500 km in LEO. The effects of temperature, physical property characterizations, and the MISSE1 flight will be discussed.

EXPERIMENTAL

Synthesis of POSS-Polyimide Copolymers

Polyimides with the same chemical formula as Kapton® were synthesized by condensation polymerization of 4,4’-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) in an N,N’-dimethylacetamide (DMAC) solvent.[15, 16] A POSS dianiline monomer (Figure 1) with two 1-(4-aminophenyl)-pendant groups and eight cyclopentyl pendant groups was synthesized using a procedure described by Fehrer et al. in 2003.[17] Using this monomer, POSS-polyimide copolymers, shown in Figure 1, were synthesized with POSS loadings corresponding to 0, 5, 10, 20, and 25wt%, which correspond to SiO₂ cage loadings of 0, 1.75, 3.5, 7.0, and 8.75 wt %.[18] ‘Side-chain’-POSS (SC-POSS) monomer was synthesized by Wright, et al.[19] from which 3.5, 7.0 wt % SiO₂ cage SC-POSS-PIs were synthesized in the same manner as described above. All poly(amic acids) were cured to POSS-PIs as previously reported.[18]

Exposure of POSS-Polyimides to Low Earth Orbit

MC-POSS-Kapton®-PIs containing 0, 1.75, and 3.5 wt % SiO₂, were cast and cured onto 1 inch wide circular aluminium substrates. The samples were flown in Passive Experiment Container 1 (PEC1), in Tray 1, developed by NASA Langley Research Center (LaRC), and were assigned numbers 38, 39, 40. Prior to flight, the samples were held into place in the tray by a top plate with open circles to expose the samples. The top plate also protects the outer area from exposure to the space environment.

The flight was launched on August 10, 2001 and was retrieved after 3.9 years in LEO as described at http://misse1.larc.nasa.gov/. The samples were exposed to all aspects of the LEO environment including AO and UV light. The step height difference between the masked (unexposed) outer ring and the neighbouring exposed sample area was measured in twelve places by profilometry. The surface atomic composition of the samples was determined by XPS.

AO Exposure of POSS-Polyimides

Ground-based POSS-PI sample exposures to AO were performed with a pulsed AO beam, operating at a repetition rate of 2 Hz and containing hyperthermal O-atoms that were generated by combining oxygen with 7 Joules per pulse CO₂ laser-detonation source.[20-26] The hyperthermal beam contains neutral O-atoms and molecular oxygen, with an ionic component of 0.01%. The mole fraction of AO in the beam was above 70% and, for some exposures, above 90%. Kinetic energies of the fast O-atoms in the beam can range from 2 to 15 eV, with the average being about 5.2 eV. Prior to exposure, samples were covered with a stainless steel mesh disk in order to mask areas and achieve AO exposed and unexposed areas. The O-atom fluence was on the order of 10¹⁰ O-atoms cm⁻² for all experiments. All samples in this work were handled in ambient air after exposure and prior to etch depth determination by profilometry, surface topography, and surface chemistry measurements.[24]

Figure 1. The structure of MC-POSS-Polyimide. R = cyclopentyl.

Surface Characterization of Scratched POSS-Polyimides
Three samples each of Kapton H\(^8\), 8.75% SiO\(_1\), MC-POSS PI, and silica-coated Kapton HN\(^8\) (provided by Astral Technology Unlimited, Inc. Lot No. 00625-007, with a 130 nm SiO\(_2\) coating) were exposed to 100k pulses of the beam, along with a Kapton H\(^8\) standard. After the first exposure, the etch depths of the screened samples were measured. A set of unscreened samples underwent surface measurements. The third set of samples was scratched. For each sample, one approximately 40 µm wide and 1 µm deep scratch was made with a diamond-tipped scribe, and two approximately 20 µm wide and 1 µm deep scratches were made with a razor blade. All scratches were measured by profilometry (with a 5µm radius probe tip). Screens were placed over the scratched samples and these samples were exposed to additional 100k shots of the hyperthermal AO beam. Profilometry was used to measure step height differences between exposed and unexposed areas and to profile each scratch in AO exposed and unexposed areas.

XPS data was obtained with the use of non-monochromatized Mg K\(_{\alpha}\) radiation (1253.6 eV) and a hemispherical CLAM 2 (VG Microtech) analyzer. Scanning electron microscopy (SEM) was performed using an ISI CLE operating at 15 keV equipped with a Kevex X-ray detector, at 100k magnification.

**Physical Properties Characterization of POSS-Polyimides.**

Polyimide samples were analyzed by a DMTA VA from TA Instruments using a 5 °C/min temperature ramp from room temperature to 500 °C and a tensile geometry.[18] Measurements of the coefficient of thermal expansion (CTE) were taken on a thermo mechanical analyzer (TMA 2940) from TA Instruments with a film fiber attachment, in a nitrogen atmosphere. The cured films were cut into 15mm by 3mm samples, the force applied was 0.05N & 0.1 N, and the sample was heated at 5 °C/min. The CTE was calculated as

\[
\Delta L / L = constant, T = temperature \degree C
\]

Test variability was +/-2.306 ppm/°C based on five Kapton H\(^8\) tests.

**The Effect of Temperature on Erosion of POSS-Polyimides by a Hyperthermal O-Atom Beam.**

The erosion of 0 wt %, 3.5 wt % and 7.0 wt % SiO\(_1\), POSS-polyimides exposed to a hyperthermal O-atom beam has been studied at 25 °C, 100 °C, 150 °C, 220 °C, and 300 °C. Two samples of each type of material were exposed simultaneously. One of each sample type was covered with a screen during exposure. Each exposure was 50,000 pulses of the hyperthermal O-atom beam, and included a “screened” Kapton H\(^8\) reference sample. The O-atom fluence was on the order of 1 x 10\(^{11}\) atoms/cm\(^2\) for each exposure. An O/O\(_2\) ratio in the beam was 0.650 ± 0.035. For the 25 °C temperature, the films (which were not cast on substrates) were placed in the sample holder. For the higher temperature exposures, the films were cast on germanium discs that were in contact with a controlled silica-coated Kapton H\(^8\) reference sample. The O-atom fluence was on the order of 1 x 10\(^{11}\) atoms/cm\(^2\). These results support the formation of a passivating silica layer that is a result of the reaction of AO with nano-dispersed POSS. A "self-passivation test" was carried out to better assess the protective silica layer formation witnessed by XPS of POSS-Pis. Kapton H\(^8\), SiO\(_2\) coated Kapton H\(^8\), and 8.75 wt % SiO\(_1\), MC-POSS PI were exposed to equivalent AO fluences. The etch depth of the Kapton H\(^8\) after the initial exposure was 7.0 ± 0.2 µm, indicating an O-atom fluence of 2.3 x 10\(^{12}\) O atoms cm\(^{-2}\). The etch depth of 0.26 ± 0.15 µm of the 8.75 wt % SiO\(_1\), MC-POSS-PI film was difficult to measure since the overall etch depth was not much greater than the slight roughness caused by the exposure. For the SiO\(_2\) coated Kapton H\(^8\), the etch depth was below the practical measurement limit of the profilometer and the sample surface appeared unaffected. After the initial AO-exposure, Kapton H\(^8\), SiO\(_2\)-coated Kapton H\(^8\), and 8.75 wt % SiO\(_1\), MC-POSS PI were scratched and underwent a second exposure to 2.3 x 10\(^{12}\) O atoms cm\(^{-2}\). SEM images of the results are shown in Figure 2. For the SEM image of Kapton H\(^8\), the exposed region is in the left side of the image and has a more roughened surface with a deepened scratched area. The etch depth of the Kapton H\(^8\) sample outside of the scratch was about 5.5 µm. The unexposed scratch was 20 µm wide and 1 µm deep, and increased in depth to 1.4 µm after the second exposure. The top of the SiO\(_2\)-coated Kapton H\(^8\) image was exposed to AO and only had erosion in the scratched area with unaffected neighboring silica-coated Kapton H\(^8\), demonstrating the effects of damage to silica coatings on Kapton H\(^8\). Here the unexposed scratch was 20 µm wide and 1 µm deep and the exposed scratch was 8 µm deep relative to the neighboring exposed surface, amounting to 7 µm of erosion in the scratch. 8.75 wt % SiO\(_1\), MC-POSS-PI was exposed to AO in the darkened upper right area in Figure 2c. A difference in step height between exposed and unexposed scratched areas of the 8.75 wt % SiO\(_1\), MC-POSS-PI was < 200nm and is not visible by microscopy. In Figure 2c, the scratch was 35 µm wide and 1.4 µm deep unexposed and about 1.8 µm deep after AO exposure. This result indicates that 8.75 wt % SiO\(_1\), MC-POSS-PI experienced about 400 nm of erosion inside the scratch during AO exposure. In comparison, Kapton H\(^8\) eroded about 5 µm inside and outside the scratch, plus Kapton H\(^8\) eroded an additional 0.200 µm in the scratch during exposure. These results are summarized in Table 1.

The results of the study of the effect of temperature on AO erosion of POSS-polyimides show that polyimide and POSS-Pis experience increasing erosion with increasing temperature. For each temperature, the etch-depths of the POSS-Pis divided by the etch depth of Kapton H\(^8\) are given in Table 2. The erosion of the 0 wt % POSS-PI exhibited the strongest temperature dependence, with the etch depth increasing by a factor of about 3.6 from 25 °C to 300 °C. 8.75 wt % and 7.0 wt % SiO\(_1\), POSS-Pis showed less temperature dependence in their erosion. The etch depths of these samples increase by factors of 2.2 and 2.4, respectively, with the increase from 25 °C to 300 °C, and the uncertainty in the measurements may bring these factors closer.

![Figure 2. SEM images of results from a self-passivation experiment.](Image 239 to 285)

(a.) Kapton H\(^8\), (b.) SiO\(_2\) coated Kapton H\(^8\) (Provided by Astral Industries Inc.), and (c.) 8.75 wt % SiO\(_1\), cage MC-POSS-PI. Samples were exposed to 2.3 x 10\(^{12}\) atoms/cm\(^2\) scratched, covered by a wire screen and exposed again to 2.3 x 10\(^{12}\) atoms/cm\(^2\). The area covered by the wire screen was (a.) the right side, (b.) the bottom portion, and (c.) the left side.

<table>
<thead>
<tr>
<th>Material</th>
<th>Kapton H(^8)</th>
<th>SiO(_2)-coated Kapton H(^8)</th>
<th>8.75 wt % SiO(_1), MC-POSS-PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>After 1st exposure.</td>
<td>5.5 µm</td>
<td>~ 0 µm</td>
<td>~ 0.200 µm</td>
</tr>
</tbody>
</table>
The incorporation of POSS nanostructures into polyimides has been shown to significantly extend the lifetime of these materials in LEO. Studies on the effect of a hyperthermal O-atom beam on POSS-Pis have shown the improved oxidation resistance imparted to polyimides by the addition of POSS. XPS data of both the AO-exposed and space-flown POSS-Pi materials indicated that the improved oxidation resistance of these materials is due to a silica layer that is formed upon exposure of POSS-Pis to high incident fluxes of atomic oxygen.

A study of the response of scratched materials to AO showed that if a Kapton H® surface is scratched, the scratched material will erode at roughly the same rate as undamaged Kapton H®. A SiO₂ coating of 130 nm protected underlying polyimide from AO attack, but after the coating was compromised, the exposed polymer eroded (during AO exposure) at approximately the same rate that uncoated Kapton® eroded. The 8.75 wt % SiO₂ MC-POSS-PI experienced roughly 1 - 2 % the erosion yield of Kapton H® that was exposed to an equivalent amount of AO.

Table 3. Coefficients of Thermal Expansion for POSS-PI films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CTE (µm/m°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kapton H®</td>
<td>30.25</td>
</tr>
<tr>
<td>5% POSS-PI</td>
<td>33.11</td>
</tr>
<tr>
<td>7% SiO₂ MC-POSS-PI</td>
<td>33.5</td>
</tr>
<tr>
<td>8.75% SiO₂ MC-POSS-PI</td>
<td>35</td>
</tr>
<tr>
<td>7% SiO₂ SC-POSS-PI</td>
<td>35.86</td>
</tr>
<tr>
<td>7% SiO₂ SC-POSS-PI exposed to AO</td>
<td>33.64</td>
</tr>
</tbody>
</table>

*Test variability based on 5 Kapton H® tests = ± 2.306 ppm/°C. 2.3x10⁻² oxygen atoms cm⁻².

MC-POSS-Pl films were flown on MISSE1 at about 500 km for 3.9 years. Various images of the samples were taken throughout the flight which show that the 0 % POSS-polyimide was completely eroded in less than four months. The innermost portion of the retrieved samples were thinner indicating they experienced greater erosion than the portion closer to the unexposed (masked) area, and/or they were thinner in this center area before flight. The step heights from the unexposed area and the neighboring exposed portion of the sample were measured in 12 places around the circumference of the exposed sample area. From these measurements, it was determined that the thickness of the masked 0 % POSS-polyimide is 32.55 ± 0.87 µm. 1.75 % MC-POSS-PI showed some survival with a step height of 5.79 ± 1.31 µm between the exposed outermost portion and the masked area, although an inner portion of this sample completely eroded. 3.5 % MC-POSS-PI film remained throughout with a step height of 2.12 ± 0.34 µm from the outermost portion and the unexposed area. It was determined by XPS that the atomic percentages of the top 10 nm of both POSS-Pi films were 34 % Si, 59 % O, and 7 % C for both the 1.75 and 3.5 wt% SiO₂ MC-POSS-PI samples.

CONCLUSION

The sudden temperature changes experienced by materials in the LEO environment make the coefficient of thermal expansion (CTE) an important material property. The CTE values for several samples are shown in Table 4. The addition of POSS slightly increases the CTE, and a slight decrease is seen after exposure of the SC-POSS-PI to AO. The CTE of fused silica is about 0.55 (µm/m°C) [27, 28] and the CTE of the silica passivation layer formed on POSS-Pis in the presence of AO is expected to be close to that of silica in value. This mismatch between the silica passivation layer and the underlying POSS-PI is likely to cause cracks in the silica. The self-passivating properties of the POSS-Pis are expected to form a silica passivation layer in the areas where cracks or damage have occurred, once again protecting the underlying POSS-PI.

Table 4. MISSE1 Step Height Erosion Data in Microns.

<table>
<thead>
<tr>
<th>Data From 12 Step Height Measurements.</th>
<th>0% POSS PI</th>
<th>5% POSS PI</th>
<th>10% POSS PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total average</td>
<td>32.6</td>
<td>5.8</td>
<td>2.1</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.9</td>
<td>1.3</td>
<td>0.3</td>
</tr>
<tr>
<td>*erosion 3.9 yr</td>
<td>240</td>
<td>5.8</td>
<td>2.1</td>
</tr>
</tbody>
</table>

*0 % POSS-PI total erosion estimated using an AO fluence, estimated for the total flight time, of 8 x 10²⁰ atoms/cm².

Figure 3. Scanning Electron Micrographs of (a.) (b.) 1.75 wt % SiO₂, MC-POSS-PI flown on MISSE1 and (c.) 3.5 wt % SiO₂, MC-POSS-PI flown on MISSE1.

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determined before and after exposure to atomic oxygen, and are comparable to the values of these properties for Kapton HN. Kapton-PI and POSS-Kapton-PIs were flown in LEO for 3.9 years. The polyimide sample completely eroded before 4 months, and a thin film of the 3.5 wt % SiO$_2$ POSS-polyimide remained after the flight demonstrating the space-survivability of POSS-PIs. Higher loadings of POSS in the PI matrix are expected to give improved flight results.

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