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14. ABSTRACT

Polyimides (PIs) such as Kapton® are used extensively in spacecraft thermal blankets, solar arrays, and space inflatable structures. Atomic oxygen (AO) in low Earth orbit (LEO) causes severe degradation of Kapton®. SiO_2 coatings impart remarkable oxidation resistance and have been widely used to protect Kapton®, yet imperfections in the SiO_2 application process and micrometeoroid/debris impact in orbit damage the SiO_2 coating leading to Kapton® erosion.

A polyimide that is self-passivating by the formation of a silica layer upon exposure to AO has been achieved by the copolymerization of a polyhedral oligomeric silsesquioxane (POSS) diamine with the Kapton® monomers, pyromellitic dianhydride and 4,4´-oxydianiline, resulting in POSS-Kapton®-polyimide. The self-passivating properties have been shown by monitoring a 1 micron deep scratch in POSS-PIs after exposure to AO. Kapton H®, SiO_2-coated Kapton HN®, and 8.75 weight % Si_8O_{11} cage "main-chain" POSS-polyimide (8.75 wt % Si_8O_{11} MC-POSS-PI) were exposed to equivalent AO fluences before and after being scratched. During the first AO exposure and outside of the scratch, these samples eroded 5.0 microns, 0 microns, and less than 200 nm respectively. During the second AO exposure, the samples eroded an additional 5.0 microns within the scratch and outside of the scratch, 7.0 microns within the scratch and 0 microns outside of the scratch, and 200 nm within the scratch and 0 microns outside of the scratch respectively.

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Polyhedral Oligomeric Silsesquioxane (POSS) Polyimides as Space-Survivable Materials

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ABSTRACT

Polyimides (PIs) such as Kapton[®] are used extensively in spacecraft thermal blankets, solar arrays, and space inflatable structures. Atomic oxygen (AO) in low Earth orbit (LEO) causes severe degradation of Kapton[®]. SiO_2 coatings impart remarkable oxidation resistance and have been widely used to protect Kapton[®], yet imperfections in the SiO_2 application process and micrometeoroid/debris impact in orbit damage the SiO_2 coating leading to Kapton[®] erosion.

A polyimide that is self-passivating by the formation of a silica layer upon exposure to AO has been achieved by the copolymerization of a polyhedral oligomeric silsesquioxane (POSS) diamine with the Kapton[®] monomers, pyromellitic dianhydride and 4,4´-oxydianiline, resulting in POSS-Kapton[®]-polyimide. The self-passivating properties have been shown by monitoring a 1 micron deep scratch in POSS-PIs after exposure to AO. Kapton H[®], SiO_2-coated Kapton HN[®], and 8.75 weight % Si_8O_{11} cage "main-chain" POSS-polyimide (8.75 wt % Si_8O_{11} MC-POSS-PI) were exposed to equivalent AO fluences before and after being scratched. During the first AO exposure and outside of the scratch, these samples eroded 5.0 microns, 0 microns, and less than 200 nm respectively. During the second AO exposure, the samples eroded an additional 5.0 microns within the scratch and outside of the scratch, 7.0 microns within the scratch and 0 microns outside of the scratch, and 200 nm within the scratch and 0 microns outside of the scratch respectively.

Surface analysis of MC-POSS-PI films exposed to a hyperthermal O-atom beam shows evidence for the formation of a SiO_2 passivation layer upon AO exposure. This is exemplified by erosion yields of 3.5 and 7 wt % Si_8O_{11} MC-POSS-PI samples which were 3.7 and 0.98 percent, respectively, of the erosion yield for Kapton H[®] at a fluence of 8.5 x 10^{20} O atoms cm^{-2}. Comparison of MC-POSS-PIs and "side-chain" POSS-PI (SC-POSS-PI) shows that these polymers have similar resistance to atomic oxygen and physical properties similar to Kapton H[®]. Erosion yields and imaging of POSS-PIs flown

on MISSE1, in a sample tray exposed to all elements (AO, UV light) of the space environment, demonstrated the greatly extended lifetime of POSS-PIs over polyimide.

INTRODUCTION

Kapton® polyimide is used extensively on spacecraft in flexible substrates for lightweight, high-power solar arrays because of its inherent strength, temperature stability, excellent insulation properties, UV stability and IR transparency. It is also used in conjunction with Teflon FEP in multilayer insulation blankets for thermal control insulation because of its superior optical properties, including low solar absorptance. In these multilayer insulation blankets, aluminium (or gold) is typically applied to Kapton® due to its low emissivity.[1]

For over twenty years, it has been well established through space flight experiments and ground-based simulations of atomic oxygen in LEO that polymeric materials undergo severe degradation as a result of the aggressive environment encountered in LEO.[2-7] In this high vacuum environment, materials are subjected to the full spectrum of solar radiation and must endure thermal cycling, which can range from -50 ˚C to 150 ˚C, and bombardment by low and high-energy charged particles as well as high incident fluxes of AO.[8] These harsh conditions, combined with the need for lighter weight and lower cost man-made orbiting bodies, necessitate the design of space-survivable materials.

Atomic oxygen in LEO impacts materials with a collision energy of 4.5-6 eV. [9-11] This O-atom translational energy is enough to overcome many reaction barriers and facilitates the degradation of Kapton®. The silicon-oxygen bond has a bond energy of 8 eV, and remains in tact 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 during flight, lead to uncoated Kapton® which erodes readily in the presence of AO. Cracked or damaged silica (or aluminium) coatings on Kapton® can lead to the trapping of reactive AO. Monte Carlo simulations have shown that this reactive AO can ricochet in trapped spaces before reacting causing an undercutting effect which can burrow out cavities in the Kapton® polymer matrix thereby causing increased material erosion.[2]

The nanodispersion of Si and O throughout polyimide leads to the formation of a protective silica layer on the polyimide surface when the material reacts with AO. Polyhedral oligomeric silsesquioxane (POSS) is a silicon-oxygen cage-like molecule surrounded by tailorable organic (R) groups. These R groups can be polymerizable, or can compatiblize POSS with the polymer matrix. When POSS is copolymerized to form POSS-PI, it imparts remarkable AO resistance, with negligible altering of the storage modulus and minor effects on the glass transition temperature and coefficient of thermal expansion.[12]

Evidence for the formation of a protective silica layer on the surface of POSS-PIs upon exposure to AO was found in X-ray photoelectron spectroscopy studies of POSS-PIs flown on MISSE1, and separate studies of POSS-PIs exposed to AO in a ground-based facility. In order to observe the self-passivation effects of POSS in POSS-PIs, AO-exposed Kapton H®, SiO_2 coated Kapton HN®, and 8.75 weight % Si_8O_{11} cage "main-

chain" POSS-polyimide (8.75 wt % Si_8O_{11} MC-POSS-PI) were exposed to AO, scratched, and exposed to an equivalent amount of AO again. 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 if the silica layer formed upon exposure of POSS-PIs to AO is damaged, the formation of a new silica layer during AO exposure will occur. Physical property characterization of POSS-PIs was carried out by dynamic thermal mechanical testing (DMTA) and measurements of the coefficient of thermal expansion (CTE). The above studies, along with AO erosion of POSS-polyimide at various temperatures, will be presented in this paper.

EXPERIMENTAL

Synthesis of POSS-Polyimide Copolymers

Polyimides with the same chemical formula as Kapton[®] were synthesized by using condensation polymerization of 4,4′-oxydianiline (ODA) and pyromellitic dianhydride (PMDA) in an N,N′-dimethylacetamide (DMAc) solvent[12, 13]. A POSS dianiline monomer (Figure 1) with two aniline pendant groups was synthesized using a procedure described by Prof. Frank Feher in 2003 [14]. Using this monomer, POSS-polyimide random copolymers were synthesized as shown in Figure 1 with POSS monomer loadings corresponding to 0, 5, 10, 20, and 25 wt%, which correspond to Si_8O_{11} cage loadings of 0, 1.75, 3.5, 7.0, and 8.75 wt %. ODA was recrystallized from toluene:DMF in a 10:1 vol:vol solution, and PMDA was recrystallized from dioxane. ODA, PMDA, and POSS were stored under nitrogen in amber glass jars. For all the polymerizations the mole ratio of diamine (ODA + POSS) to dianhydride (PMDA) was 1:1. In a glove box nitrogen atmosphere, POSS dianiline and ODA were combined in a 50 ml round bottom flask equipped with a stir bar. PMDA was weighed into a separate 25 ml flask followed by addition of 2 ml DMAc to forming a slurry. The PMDA/DMAc slurry was added drop-wise via a Hamilton[®] gas-tight syringe to the stirring ODA/POSS solution. DMAc was added to PMDA for continued addition and this was repeated until all PMDA was added, with the final aliquots in solution form. A viscous POSS/PMDA/ODA poly(amic acid) solution resulted and was diluted to a total of 20 ml with DMAc and stirred was overnight under nitrogen.

"Side-chain"-POSS (SC-POSS) monomer was synthesized by Wright, et al. [15] from which 3.5, 7.0 wt % Si_8O_{12} cage SC-POSS-PIs were synthesized in the same manner as described above. All poly(amic acids) were cast onto level, ethanol washed and oven dried, glass plates and cured under nitrogen at 80 ºC for four hours, 120 ºC for 1 hour, 200 ºC for 1 hour, and 300 ºC for 1 hour. The resultant POSS-PIs were readily removed from the glass by lifting a corner with a razor blade under de-ionized water.

AO Exposure of POSS-Polyimides

Polyimide sample exposures were performed with a pulsed beam, operating at a repetition rate of 2 Hz and containing hyperthermal atoms that were generated with the use of a laser-detonation source [16-19]. The hyperthermal beam contains neutral atomic

and molecular oxygen, with an ionic component of 0.01%. The mole fraction of atomic oxygen in the beam was approximately 70 %. Prior to exposure, samples were covered with a stainless steel mesh disk in order to mask areas and achieve AO exposed and $1.7 \pm 0.1 \times 10^{15}$ O atoms cm^{-2}, and the mean translational O-atom energy was 4.9-5.0 eV.
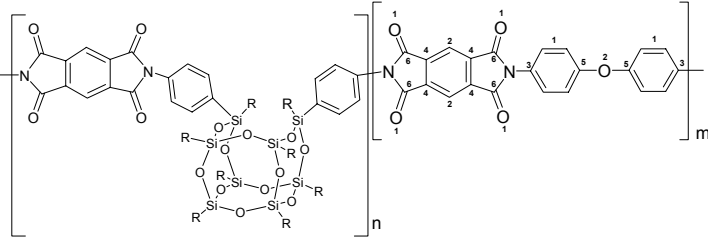

Figure 1. The structure of MC-POSS-Polyimide. R = cyclopentyl.

Surface Characterization of POSS-Polyimides

Samples were exposed to a hyperthermal O-atom beam as described previously. All samples in this work were handled in ambient air after exposure prior to etch depth, surface topography, and surface chemistry measurements.[20] To evaluate the effects of AO on samples, as seen in Figure 2, etch depths were determined by surface profilometry. These measurements were obtained with the use of a Dektak^3 (Veeco Metrology Group, Santa Barbara, CA) surface profilometer. Scan lengths ranged from two to four microns, and scan speeds were slow to medium. The etched-mesh screens used to cover the samples had a wire thickness of 100 μm, with approximately square open areas that were 500 μm wide. Average step heights for the masked samples were obtained from 30 different step height measurements on each sample

Multiple samples of Kapton H$^®$, 8.75 % Si$_8$O$_{11}$ MC-POSS PI, and silica-coated Kapton HN$^®$ (provided by Astral Technology Unlimited, Inc. Lot No. 00625-007, with a 130 nm SiO$_2$ coating) were exposed to hyperthermal AO. The beam was produced by a laser detonation source operating at 2 Hz, and previously described.[20] The sample mount was 40 cm from the source. Three samples of each type were exposed to 100k pulses of the beam, along with a Kapton H$^®$ standard. One sample of each material was covered by a screen, as described above, to provide exposed and protected areas for etch depth measurements. After the first exposure, the samples were removed from the chamber. The etch depths of the screened samples were measured. A set of unscreened samples underwent surface morphology measurements. The third set of samples was scratched. For each samples, one approximately 40 μm wide and 1μm deep scratch was made with a diamond-tipped scribe, and two approximately 20 μm wide and 1μm deep scratches were made with a razor blade. All scratches were measured by profilometry (with a 5μm radius probe tip) in several places. Screens were placed over the scratched samples and these samples were exposed to additional 100k shots of the hyperthermal AO beam. After removal of the samples from the chamber, 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 spectra were obtained with the use of non-monochromatized Mg Kα radiation (1253.6 eV) and a hemispherical CLAM 2 (VG Microtech) analyzer. Sample charging shifted the XPS lines to higher binding energies by 0.5 to 3 eV. In the present study, this shift was corrected by assuming that the binding energy of the lowest C(1s) component is 285.0 eV for the unexposed polyimide (0 wt% POSS) sample. (Note that the binding energy scale was calibrated with the use of an Ag($3d_{5/2}$) line at 368.25 eV from another sample that underwent the same AO exposure as a reference.)

Scanning electron microscopy (SEM) was performed using an ISI CL6 operating at 15 keV equipped with a Kevex X-ray detector. Elemental mapping was performed using energy dissipation X-ray analysis with IXRF Systems analysis software.

Physical Properties Characterization of POSS-Polyimides.

The cured films were cut into 3 x 20 mm rectangular samples for dynamic mechanical thermal analysis utilizing a DMTA V from TA Instruments. All polyimide samples were analyzed using a 5 ºC/min temperature ramp from room temperature to 500 ºC and a tensile geometry. Stress/strain tests were performed on all samples to identify the largest force in which the material exhibited an elastic deformation, thus limiting the pretension force used to test the samples. Strain sweeps were performed to ensure that the testing strain was within the linear viscoelastic region.

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 & 0.10 N, and the sample was heated at 5 °C/min. The CTE was calculated as $\alpha = (\Delta L \times K)/(L \times \Delta T)$ where L = length, K = a cell constant, T = temperature °C. Test variability was +/- 2.306 ppm/ °C based on five Kapton H[®] tests.

RESULTS AND DISCUSSION

MC-POSS-PI (POSS "R" group is cyclopentyl) films were etched by exposure to a hyperthermal O-atom beam. As described previously [21], the beam was produced by combining oxygen with a 7 Joules per pulse CO_2 laser source. The resultant O-atom beam consists predominantly of fast neutrals, with a very small ionic fraction ($<10^4$). 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. A stainless steel screen was placed over the sample in order to selectively erode only certain portions of the samples. The difference in etch depth between the eroded and protected areas of the samples, measured using stylus surface profilometry, made it possible to calculate an AO reaction efficiency (R_e) or erosion rate of the material for a given flux.[2]

Profilometry measurements for the Kapton H[®] standard and a 3.5 wt% POSS-Kapton[®]-PI sample were taken after a total fluence of 8.47 x 10^{20} atoms/cm^2. (1 x 10^{20} O-atoms/cm^2 is roughly equivalent to a spacecraft operating at 500 – 600 km orbit during nominal solar activity conditions for periods of at least one year. [22]) This fluence is based on the etch depth of the Kapton H[®] reference sample (25.4 microns, 1 mil) which

has an accepted erosion yield or reaction efficiency, R_e, of 3.00 x 10^{-24} cm^3/atom.[17]. Under the same conditions, the 3.5 wt% MC-POSS-PI (2 mol % POSS; 1 POSS monomer per every 50 monomers for a random copolymerization) etched an order of magnitude less with an average of 2.2 microns (0.086 mil) corresponding to a R_e of 2.56 x 10^{-25} cm^3/atom.

The AO reaction efficiency of Kapton H$^®$ was used to calculate the Kapton$^®$ equivalent fluence and erosion yields of each exposure. For various exposures, the step heights (or etch depths) of POSS-PI films are plotted as a function of the step height of the Kapton H$^®$ film in Figure 2 (top). The derivative plot in Figure 2 (bottom) gives the rate of change of the step height of POSS-PI films as a function of exposure. The derivative functions indicated that the 3.5 and 7.0 wt % Si_8O_{11} POSS polyimide films reached erosions rates of 3.7 and 0.98%, respectively, of the erosion rate for Kapton H$^®$ after 395,000 beam pulses (8.47 x 10^{20} atoms cm^{-2}).[23, 24] 8.75 wt% Si_8O_{11} POSS-PI samples had an erosion rate that was 0.3 percent of the erosion rate for Kapton H$^®$, and 1/3 of 7.0 wt % POSS-PI at a fluence of 8.5×10^{20} atoms cm^{-2}. These results support the formation of a passivating silica layer that is formed as a result of the nano-dispersed POSS moieties reacting with AO.
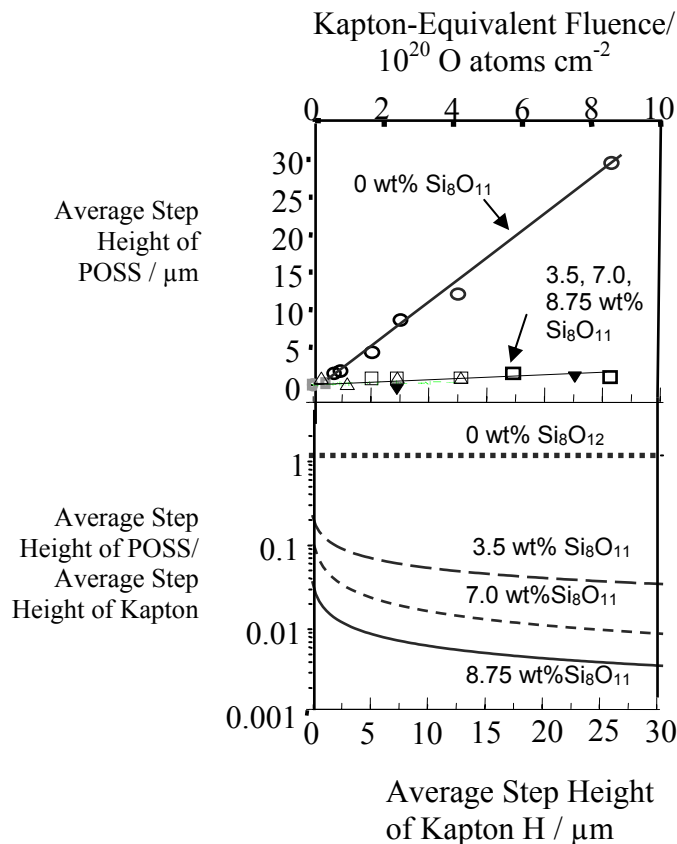

Figure 2. (top) Etch depth measurements for 0, 10, and 20 wt% POSS polyimide as a function of O-atom fluence, represented by etch depth of the Kapton H witness samples and (bottom) etch rates of POSS samples (derivatives of curves, top figure).

A "self-passivation test" was carried out to better assess the protective silica layer formation witnessed by XPS of POSS-PIs. Kapton H®, SiO_2 coated Kapton HN®, and 8.75 wt % Si_8O_{11} MC-POSS-PI were exposed to equivalent AO fluences. The etch depth of the Kapton H® after the initial exposure was 7.0 ± 0.2 μm, indicating an O-atom fluence of 2.3 x 10^{20} O atoms cm^{-2}. This sample appeared significantly roughened after exposure. The etch depth of 0.26 ± 0.15 μm of the 8.75 wt % Si_8O_{11} MC-POSS-PI film was difficult to measure since the overall etch depth was not much greater the slight roughness caused by the exposure. For the SiO_2 coated Kapton HN® the etch depth was below the practical measurement limit of the profilometer and the sample surface appeared unaffected.

SEM images of Kapton H®, SiO_2-coated Kapton HN®, and 8.75 wt % Si_8O_{11} MC-POSS-PI that were AO-exposed, scratched, and underwent a second exposure to 2.3 x 10^{20} O atoms cm^{-2} are shown in Figure 3. Examples of profilometer traces of the scratches in AO-exposed and unexposed areas are shown in Figure 4. For the SEM image of Kapton H®, 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® sample outside of the scratch was about 5.5 μm. The scratch was 20 μm wide and 1μm deep unexposed and 1.4 μm deep relative to the neighboring eroded surface after the second exposure. The top of the SiO_2-coated Kapton HN® image was exposed to AO and only had erosion in the scratched area with unaffected neighboring silica-coated Kapton HN®, demonstrating the effects of damage to silica coatings on Kapton®. Here the unexposed scratch was 20 μm wide and 1μm 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 % Si_8O_{11} MC-POSS-PI was exposed to AO in the darkened upper right area in Figure 4c. A difference in step height between exposed and unexposed unscratched areas of the 8.75 wt % Si_8O_{11} MC-POSS-PI was < 200nm and is not visible by microscopy. In Figure 4c, 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 % Si_8O_{11} MC-POSS-PI experienced 400 nm of erosion inside the scratch during AO exposure. In comparison, Kapton H® eroded about 5 μm inside and outside the scratch, plus Kapton H® eroded an additional 0.400 μm in the scratch during exposure. In all instances, the scratched regions apparently eroded slightly more than the unscratched exposed areas. This may be explained by the undercutting effect described above where the O-atoms are focused deeper into the polymer matrix by scattering from the sidewalls of the scratches. These results are summarized in Table 1.
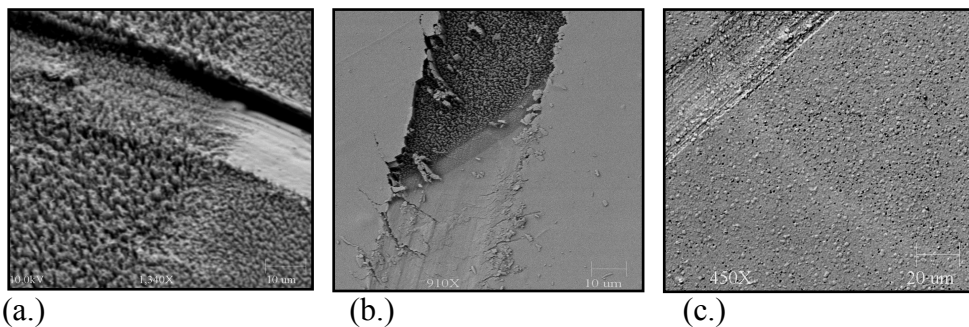

(a.)   (b.)   (c.)

Figure 3. SEM images of results from a self-passivation experiment. (a.) Kapton H®, (b.) SiO_2 coated Kapton HN® (Provided by Astral Industries Inc.), and (c.) 8.75 wt %

Si_8O_{11} cage MC-POSS-PI. Samples were exposed to 2.3 x 10^{20} atoms/cm^2, scratched, covered by a wire screen and exposed again to 2.3 x 10^{20} 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 1. Self-Passivation Experiment Summary

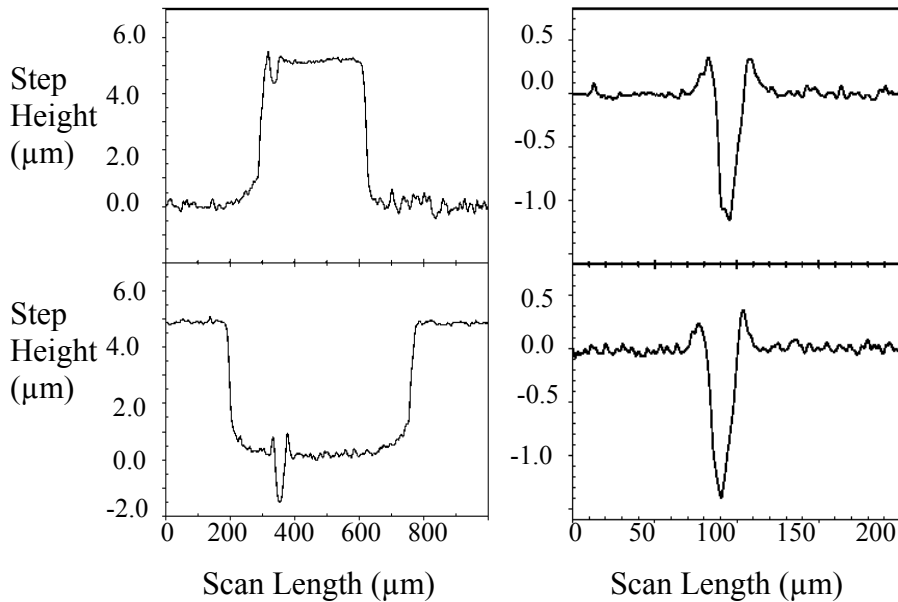| Material	Kapton H[®]	SiO$_2$-coated Kapton HN[®] with Aluminum under-coating	8.75 wt % Si_8O_{11} MC-POSS PI
Erosion depth after 1st exposure.	5.5 μm	~ 0 μm	0.200 μm
Erosion depth outside of the scratch after 2nd exposure.	5 μm	~ 0 μm	~ 0 μm
Erosion depth inside of the scratch after 2nd exposure.	5 μm	7 μm	~ 0.400 μm

Figure 4. Profilometer traces of scratches in covered (top) and uncovered (bottom) areas of the Kapton H[®] (left) and 8.75 wt % Si_8O_{11} MC-POSS-PI (right). The covered areas were exposed to 2.3x10^{20} oxygen atoms cm^{-2}, scratched, and covered with a stainless steel screen. The uncovered areas were exposed to 2.3x10^{20} oxygen atoms cm^{-2}, scratched, and again exposed to 2.3x10^{20} oxygen atoms cm^{-2}.

The physical properties of POSS-PIs were evaluated by DMTA and have been discussed previously.[12] The glass transition temperatures (Tg) were as follows: 420 ºC for 0 % POSS PI, 394 ºC for 3.5 % Si_8O_{11} MC-POSS-PI, 390 ºC for 7 % Si_8O_{11} MC-POSS-PI, 383 ºC for 8.75 % Si_8O_{11} MC-POSS-PI. The 7 % Si_8O_{11} MC-POSS-PI exhibited a tan δ peak very similar in intensity and breadth to the 0 % POSS PI peak, while the 3.5 and 8.75 wt % Si_8O_{11} MC-POSS-PI tan δ peaks were slightly greater than half the height and of similar width to the 0 and 7 wt % POSS samples. This unique behavior of the 7 wt % Si_8O_{11} MC-POSS-PI may be from similar chain packing to the 0 % POSS-PI sample.   A side-chain POSS (SC-POSS) monomer has been synthesized by Wright et al. and was readily copolymerized to form POSS polyimides with POSS as a pendant group. In an AO exposure, 7 % Si_8O_{12} SC-POSS-PI had an erosion yield that was 3.3 % of Kapton H®. In a previous AO exposure study, 7 % Si_8O_{11} MC-POSS-PI had an erosion yield that was 3.8 % of Kapton H®. These results indicate that MC- and SC-POSS-PIs have equal, or near equal, AO resistance.   DMTA measurements have shown that the Tg of 7 wt % Si_8O_{12} SC-POSS-PI is 400 ºC, and decreases to 378 ºC after exposure to 2.3×10^{20} oxygen atoms cm^{-2}. The tan δ peaks for this material were slightly more intense and broader than commercial Kapton H®, but were not yet compared to 0 % POSS-PI.

The sudden temperature changes experienced by materials in the LEO environment make the coefficient of thermal expansion (CTE) a highly important material property.   Mismatches in the CTEs between polymeric materials and their coatings lead to cracks, crazing, and mechanical material failure. POSS-PIs eliminate the need for AO-resistant coatings. In order for POSS-PIs to be a drop-in replacement for Kapton®, it is necessary that the new material have predictable CTEs with similar values to Kapton®. The CTE values for several samples are shown in Table 2. 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) [25, 26] and the CTE of the silica passivation layer formed on POSS-PIs in the presence of AO is expected be close in value. This mismatch between the silica passivation layer and the underlying POSS-PI is likely to cause cracks in the silica passivation layer, which will again form silica in the POSS-PI exposed areas.

Table 2. Coefficients of Thermal Expansion for POSS polyimide films.

Sample	*CTE (μm/m°C)*
Kapton H®	30.25
0% POSS-PI	33.11
7 % MC-POSS-PI	33.5
8.75 % MC-POSS-PI	35
7 % SC-POSS-PI	35.86
7 % cage SC-POSS-PI exposed AO[†] to	33.64

*Test variability based on 5 Kapton H® tests = ± 2.306 ppm/°C.
[†]2.3×10^{20} oxygen atoms cm^{-2}

MC-POSS-PI films were recently retrieved from the Materials International Space Station Experiment after being flown in LEO for 4 years on a sample holder that was

exposed to all aspects (AO, UV) of the LEO environment. These films included a 0, 1.75, and 3.5 wt % Si_8O_{11} MC-POSS-PIs. The inner area of the circular samples eroded more than the outer portion. The outer portion neighbors the edges that were covered by an aluminum mask throughout the flight, and therefore remained unexposed to the space environment. The step heights from the unexposed (masked) area and the neighboring outer portion of the sample were measured. It was found that a 32.55 ± 0.87 μm thick polyimide film completely eroded, 1.75 % MC-POSS-PI showed some survival with the inner portion completely eroded and a step height of 5.79 ± 1.31 μm from the outer portion and the masked area, and 3.5 % MC-POSS-PI film remained throughout with a step height of 2.12 ± 0.34 μm from the outer portion and the unexposed area. It was determined by XPS that the atomic percentages of the top 10 nm of the films were 34 % Si, 59 % O, and 7 % C for both the 1.75 and 3.5 wt% Si_8O_{11} MC-POSS-PI samples.

CONCLUSION

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 indicate that the improved oxidation resistance of these materials is due to a rapidly formed silica layer upon exposure of POSS-polymers 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 SiO_2 coating of 130 nm protects an underlying polymer from AO attack, but if the coating is compromised the exposed polymer will erode during AO exposure at approximately the same rate that the pristine polymer would erode. The 8.75 wt % Si_8O_{11} POSS-PI exposed to an equivalent amount of AO had roughly only 1 - 2 % the erosion yield of Kapton H®. This is presumably due to a silica layer formed on the surface of the material during AO exposure. When this layer was removed by a scratch, newly exposed material had the same low erosion yield, indicating that a silica passivating layer has formed in the scratched area.

The incorporation of the POSS slightly reduces the glass transition temperature (Tg) of Kapton® type polyimide, however, the Tg values are well above the temperatures experienced by materials in LEO. The CTE of POSS-PIs is similar to the CTE of commercial Kapton H®. A new SC-POSS monomer has been synthesized and imparts about the same AO resistance to polyimides as the MC-POSS monomer. The modulus, Tg, and CTE of SC-POSS-PIs were measured before and after exposure to atomic oxygen, and are in the range of Kapton H®.

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