

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 25-07-2011		2. REPORT TYPE Conference Paper		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Atomic Oxygen Effects on POSS Polyimides				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Sara A. Marquez, Amy L. Brunsvold, Russell Cooper, Linhan Shen, Brooks Marshall, Timothy K. Minton, Sandra J. Tomczak, Vandana Vij, Michael E. Wright, Andrew J. Guenther, Brian J. Pettyes, Lipeng Sun, George C. Schatz				5d. PROJECT NUMBER	
				5f. WORK UNIT NUMBER 484709CJ	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZSB 4 Draco Drive Edwards AFB CA 93524-7160				8. PERFORMING ORGANIZATION REPORT NUMBER AFRL-RZ-ED-TP-2011-324	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Air Force Research Laboratory (AFMC) AFRL/RZS 5 Pollux Drive Edwards AFB CA 93524-7048				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S NUMBER(S) AFRL-RZ-ED-TP-2011-324	
12. DISTRIBUTION / AVAILABILITY STATEMENT Distribution A: Approved for public release; distribution unlimited (PA#11552).					
13. SUPPLEMENTARY NOTES For presentation at the 242 nd ACS Fall National Meeting, Denver, CO, 28 Aug-3 Sep 2011.					
14. ABSTRACT Kapton polyimide is ubiquitous in space applications due to its temperature stability, insulation properties, IR transparency, low solar absorptance, resistance to UV damage, and excellent thermal properties. ¹ Despite the desirable properties of Kapton, this polyimide and all organic polymeric materials are severely degraded in low Earth orbit (LEO) as a result of reactions involving atomic oxygen (AO), ^{2,3} which can be more than 90% of the neutral component of the residual atmosphere at altitudes of 300-700 km. Polymers are typically protected by the application of a coating, often silica-based, which is resistant to degradation in the presence of AO. ^{4,5} However, imperfections in the coating created during its deposition, or by physical damage that occurs during flight, lead to erosion of the substrate. For this reason, alternative and self-regenerative methods of protection are sought for organic polymeric materials used in space.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT 3	18. NUMBER OF PAGES 3	19a. NAME OF RESPONSIBLE PERSON Sandra J. Tomczak, PhD
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (include area code) N/A

ATOMIC OXYGEN EFFECTS ON POSS POLYIMIDES

Sara A. Marquez,¹ Amy L. Brunsvold,¹ Russell Cooper,¹ Linhan Shen,¹ Brooks Marshall,¹ Timothy K. Minton,¹ Sandra J. Tomczak,² Vandana Vij,³ Michael E. Wright,⁴ Andrew J. Guenther,⁵ Brian J. Pettyes,⁴ Lipeng Sun,⁶ George C. Schatz⁶

¹Department of Chemistry and Biochemistry, Montana State University
103 Chem/Biochem Bldg., Bozeman, MT USA, tminton@montana.edu

²AFRL/RZSB, Motor Branch, Air Force Research Laboratory, 4 Draco Drive,
Bldg., 8351, Edwards AFB, CA 93524 USA

³ERC Incorporated, Materials Applications Branch, Air Force Research
Laboratory, 10 E. Saturn Blvd., Bldg. 8451, Edwards AFB, CA 93524 USA

⁴Research and Engineering Sciences Department, Chemistry Division
NAVAIR-US NAVY, China Lake, CA 93555 USA

⁵AFRL/RZSM, Materials Applications Branch, Air Force Research
Laboratory, 10 E. Saturn Blvd., Bldg. 8451, Edwards AFB, CA 93524 USA

⁶Department of Chemistry, Northwestern University, Evanston, IL 60208
USA

Introduction

Kapton polyimide is ubiquitous in space applications due to its temperature stability, insulation properties, IR transparency, low solar absorptance, resistance to UV damage, and excellent thermal properties.¹ Despite the desirable properties of Kapton, this polyimide and all organic polymeric materials are severely degraded in low Earth orbit (LEO) as a result of reactions involving atomic oxygen (AO),^{2,3} which can be more than 90% of the neutral component of the residual atmosphere at altitudes of 300-700 km. Polymers are typically protected by the application of a coating, often silica-based, which is resistant to degradation in the presence of AO.^{4,5} However, imperfections in the coating created during its deposition, or by physical damage that occurs during flight, lead to erosion of the substrate. For this reason, alternative and self-regenerative methods of protection are sought for organic polymeric materials used in space.⁶

We have produced relatively durable polymers through the incorporation of polyhedral oligomeric silsesquioxane (POSS) into Kapton through copolymerization of POSS amine monomers.⁷⁻¹⁰ POSS is a unique family of nanoscale inorganic/organic hybrid cage-like structures that contain a silicon/oxygen framework (RSiO_{1.5}), surrounded by alkyl or aryl groups that can be utilized as polymer compatibilizers or as polymerizable functional groups.¹⁰ We have found with a POSS-containing, Kapton-like polyimide that appropriate POSS amines can be incorporated into the poly(amic acid) polymerization without changes to polymerization conditions, or changes to the subsequent cure cycles. We have conducted a variety of studies of POSS polyimides by exposing their surfaces to beams of hyperthermal oxygen atoms and measuring mass loss *in situ* or surface recession, morphology, and chemistry *ex situ*. We have also carried out similar studies of POSS polyimides that were exposed to an atomic-oxygen environment on the International Space Station.

Experimental Details

Preparation 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. A POSS dianiline monomer with two 1-(4-aminophenyl)-pendant groups and eight cyclopentyl pendant groups was synthesized. Using this monomer, "main-chain" (MC) 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 Si₈O₁₁ cage loadings of 0, 1.75, 3.5, 7.0, and 8.75 wt %. "Side-chain" (SC) POSS monomer was also synthesized, from which many wt% Si₈O₁₂ cage SC-POSS polyimides were synthesized (Figure 2).

Low Earth orbit exposure of POSS polyimides. MC-POSS polyimide films were coated on aluminum substrates and flown in LEO on the outside of the International Space Station as part of MISSE-1. The samples were exposed to the ram, with the AO fluence being $\sim 8 \times 10^{21}$ atoms cm⁻². Free standing films of MC-POSS polyimide were sewn to a

Kapton blanket and exposed to a sweeping ram in LEO on MISSE-5, with an estimated AO fluence of 1.8×10^{20} atoms cm⁻². Free-standing films of MC- and SC-POSS polyimide films were exposed to the LEO environment on MISSE-6 in the ram direction, with a total AO fluence of 2×10^{21} atoms cm⁻². The step-height difference between the unexposed sample area and the neighboring exposed sample area was measured by profilometry. In some cases, the atomic composition of sample surfaces was determined by x-ray photoelectron spectroscopy (XPS). Additional samples of SC-POSS polyimides were prepared by spin-coating quartz crystal microbalance (QCM) discs with films of different POSS loading. These QCM samples were placed on MISSE-6.

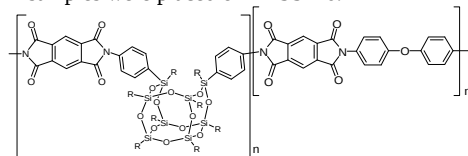


Figure 1. MC-POSS Kapton structure demonstrating the PMDA-MC-POSS repeat unit and the PMDA-ODA repeat unit. R = cyclopentyl.

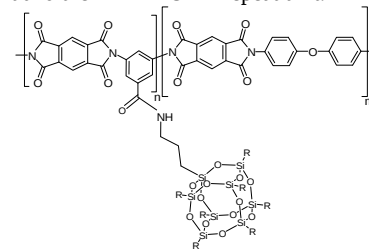


Figure 2. SC-POSS Kapton structure demonstrating the PMDA-SC-POSS repeat unit and the PMDA-ODA repeat unit. R = iso-butyl.

Exposure of POSS polyimides to atomic oxygen. Ground-based AO exposures were performed with a pulsed AO beam, operating at a repetition rate of 2 Hz and containing O atoms that were generated by the laser-detonation of O₂ gas in a conical nozzle with the use of a 7-joule-per-pulse CO₂ laser.^{2,8} Kinetic energies of the fast O atoms in the beam averaged 5.2 eV. For some studies, samples were covered with a stainless steel mesh, prior to exposure, in order to mask areas and achieve both AO exposed and unexposed areas for step-height measurements. For other studies, samples of POSS polyimide and control (no-POSS) polyimide films were spin-cast onto QCM discs. Some scattering experiments were also carried out, where the hyperthermal AO beam was directed at a surface, and the reaction products that scattered from the surface were detected with a rotatable mass spectrometer detector.² Some samples were analyzed by AFM or SEM after exposure.

Results and Discussion

A series of SC-POSS polyimides was exposed to AO with a total fluence of 2.7×10^{20} O atoms cm⁻². Results, in Table 1, indicate dramatic decreases in surface erosion with increasing content of SC-POSS. SC-POSS polyimide and MC-POSS polyimide had comparable AO erosion yields (not shown in Table 1). The existing data indicate that the AO-induced erosion yields of MC-POSS polyimide and SC-POSS polyimide are comparable. Thus, the level of erosion resistance afforded by POSS appears to depend on the wt% of the monomer and not how it is bound to the polymer chain.

Table 1. Laboratory AO erosion data of SC-POSS polyimides.

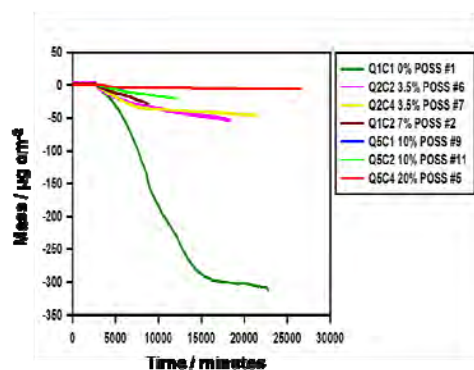
Weight % Si ₈ O ₁₂ in SC-POSS Polyimide	Kapton - Equivalent Fluence / 10 ²⁰ O atoms cm ⁻²	Erosion Depth (μm)	% Erosion of Kapton H Witness Sample
1.75	2.71	1.99 ± 0.01	24.5
3.5	2.66	1.29 ± 0.05	16.15
7.0	2.68	0.390 ± 0.04	4.9
8.8	2.68	0.132 ± 0.02	1.64
10.5	2.71	0.249 ± 0.03	3.06
12.3	2.71	0.113 ± 0.03	1.39
14.0	2.71	Undetectable	~ 0

Table 2. MISSE-1 flight MC-POSS polyimide erosion data.

Sample	^a Average Step Height in microns	Standard Deviation in microns	Erosion in 3.9 years
0 wt % Si ₈ O ₁₁ MC-POSS Polyimide	32.6	0.9	^b 240
1.75 wt % Si ₈ O ₁₁ MC-POSS Polyimide	5.8	1.3	5.8
3.5 wt % Si ₈ O ₁₁ MC-POSS Polyimide	2.1	0.3	2.1

MC-POSS polyimide films were flown on MISSE-1. The 0 wt% POSS polyimide was completely eroded in less than four months. It was determined that the thickness of the 0 wt% POSS polyimide was $32.6 \pm 0.9 \mu\text{m}$. The erosion data are shown in Table 2. XPS measurements showed that the atomic percentages of the top 10 nm of both POSS polyimide films were 34% Si, 59% O, and 7% C. The XPS data are thus consistent with the formation of a passivating silica (SiO₂) layer on the POSS polyimides.

Several SC-POSS polyimide films were exposed on MISSE-6, and their mass losses were measured *in situ* with QCMs (see Figure 3). Although all QCMs failed long before the end of the mission, it is clear from the data that were collected that POSS-containing polyimides suffered significantly less mass loss than a 0 wt% POSS polyimide control. The mass loss rate appears to be higher initially on the POSS polyimide samples and then decrease with exposure duration. In contrast, the no-POSS control polyimide loses mass at a roughly constant rate, regardless of the exposure duration, until the sample has



been almost completely eroded away.

Figure 3. Mass loss, measured by quartz crystal microbalances, of various SC-POSS polyimide films as a function of exposure duration on the MISSE-6 space flight experiment.

Measurements of mass loss with QCM samples in the laboratory yielded much more precise data than what was collected with the MISSE-6 experiment. Figure 4 shows mass loss as a function of exposure duration for two MC-POSS polyimides, one SC-POSS polyimide, and a no-POSS polyimide control. These results demonstrate clearly that the mass loss rate of POSS-containing polyimides decreases with exposure duration and that higher POSS content leads to a lower mass loss rate. The observation of a decreasing mass loss rate for the POSS polyimides and a constant mass loss rate for the polyimide control is further evidence for the formation of a passivating layer as the POSS polyimides are exposed to AO. The mass loss rates of the POSS polyimides did not go to zero in the experiments, suggesting the possibility that the passivating layer at the POSS loadings studied never becomes completely impervious to AO; thus, the mass loss rate may be ultimately finite, albeit very low.

Conclusions

A large amount of data have been collected on the effects of hyperthermal AO on POSS polyimides with various weight percentages of POSS and with POSS cages that are bound to the polymer backbone in different ways. Only representative data have been presented here. In general, the following conclusions have been reached: During POSS polyimide exposure to atomic oxygen, organic material is degraded and a passivating silica layer is formed. This silica layer protects the underlying polymer from further degradation. Depending on the weight percentage of

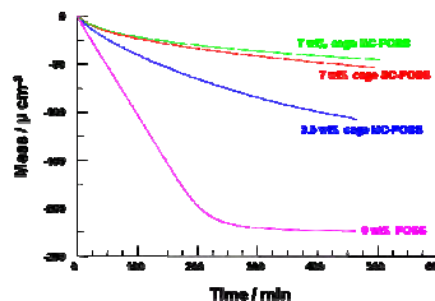


Figure 4. Mass loss of various POSS polyimides as a function of exposure to a hyperthermal AO beam in the laboratory.

the POSS cage, the erosion yield of the POSS polyimide may be as little as 0.01 that of the pure polyimide. The POSS polyimide surface has been shown to re-grow the passivating layer ("self-heal") if the initial silica layer is scratched. Studies involving O-atom beam-surface scattering reveal the main reaction products to be OH, H₂O, CO, and CO₂. The kinetics of the decrease in reactivity of the surface with exposure time have been studied by measuring mass loss in real time with a quartz crystal microbalance and by monitoring the decrease in the intensity of the individual reactive products with a mass spectrometer. It has been found that the resistance of POSS polyimide to O-atom attack depends more on the weight percentage of the POSS cage in the polymer than on the copolymerized moiety of the POSS molecule in the polyimide backbone. The results demonstrate great promise for POSS polyimides as drop-in replacements for Kapton in spacecraft applications.

Acknowledgements. This work has been supported by several grants and contracts from the Defense Advanced Research Projects Agency and the Air Force Office of Scientific Research.

References

- (1) Heltzel, S.; Semprinoschnig, C. O. A. *High Perform. Polym.* **2004**, *16*, 235-248.
- (2) Minton, T. K.; Garton, D. J., "Dynamics of Atomic-Oxygen-Induced Polymer Degradation in Low-Earth Orbit," in *Advanced Series in Physical Chemistry--11: Chemical Dynamics in Extreme Environments*, Ed. Dressler, R. A. (World Scientific, Singapore, **2001**, pp. 420-489.
- (3) Dooling, D.; Finckenor, M. M., "Material Selection Guidelines to Limit Atomic Oxygen Effects on Spacecraft Surfaces, NASA/TP – **1999** – 209260.
- (4) Rutledge, S. K.; Mihelcic, J. A., "The Effect of Atomic Oxygen on Altered and Coated Kapton Surfaces for Spacecraft Applications in Low Earth Orbit," *Proceedings of a Symposium Sponsored by TMS-ASM Joint Corrosion and Environmental Effects Committee and the 199th Annual Meeting of the Minerals, Metals, and Materials Society* (Anaheim, CA, February 17-22, **1990**).
- (5) Rutledge, S. K.; Olle, R. M., "Space Station Freedom Solar Array Blanket Coverlay Atomic Oxygen Durability Testing Results," *Proceedings from the 38th International SAMPE Symposium* (Anaheim, CA, May 10-13, **1993**).
- (6) Gonzalez, R. I.; Phillips, S. H.; Hoflund, G. B. J. *Spacecraft and Rockets* **2000**, *37*(4), 463 – 467.
- (7) Tomczak, S. J.; Marchant, D.; Svejda, S.; Minton, T. K.; Brunsvold, A. L.; Gouzman, I.; Grossman, E.; Schatz, G. C.; Troya, D.; Sun, L. P.; Gonzalez, R. I. *Materials Research Society Symposium Proceedings* **2005**, *851*, 395 – 406.
- (8) Brunsvold, A. L.; Minton, T. K.; Gouzman, I.; Grossman, E.; Gonzalez, R. I. "An Investigation of the Resistance of POSS Polyimide to Atomic-Oxygen Attack," *High Perform. Polym.* **2004**, *16*(2), 303 – 318.
- (9) Gonzalez, R. I., "Synthesis and In-Situ Atomic Oxygen Erosion Studies of Space-Survivable Hybrid Organic/Inorganic POSS Polymers," *Ph.D. Dissertation*, Chem. Eng. Department, University of Florida, **2002**, <http://purl.fcla.edu/fcla/etd/UFE1000127>
- (10) Phillips, S. H.; Haddad, T. S.; Tomczak, S. J. *Current Opinion in Solid State and Materials Science* **2004**, *8*, 21-29.