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Low Earth Orbital Atomic Oxygen Interactions With Spacecraft Materials

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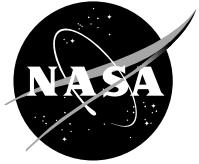
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Abstract

Atomic oxygen, formed in Earth's thermosphere, interacts readily with many materials on spacecraft flying in low Earth orbit (LEO). All hydrocarbon based polymers and graphite are easily oxidized upon the impact of ~4.5 eV atomic oxygen as the spacecraft ram into the residual atmosphere. The resulting interactions can change the morphology and reduce the thickness of these materials. Directed atomic oxygen erosion will result in the development of textured surfaces on all materials with volatile oxidation products. Examples from space flight samples are provided. As a result of the erosive properties of atomic oxygen on polymers and composites, protective coatings have been developed and are used to increase the functional life of polymer films and composites that are exposed to the LEO environment. The atomic oxygen erosion yields for actual and predicted LEO exposure of numerous materials are presented. Results of in-space exposure of vacuum deposited aluminum protective coatings on polyimide Kapton indicate high rates of degradation are associated with aluminum coatings on both surfaces of the Kapton. Computational modeling predictions indicate that less trapping of the atomic oxygen occurs, with less resulting damage, if only the space-exposed surface is coated with vapor deposited aluminum rather than having both surfaces coated.

Introduction

Although knowledge of atomic oxygen existed in the early days of space exploration, an awareness of the damaging effects on spacecraft materials was not well known until the Space Shuttle began flying missions at much lower altitudes in low Earth orbit (LEO) [1].

Early in-space observation that the residual atmosphere was interacting with spacecraft surfaces came in part as a result of comparison of day and night pictures of the space shuttle, as shown in Figure 1, where the glow from de-excitation atoms and molecules leaving shuttle surfaces oriented in the ram (forward facing) direction are shown [2 and 3]. A second indication of LEO atomic oxygen interactions came from observations of increases in the diffuse reflectance of polymers such as polyimide Kapton H due to surface texturing. Such observations lead to further tests which documented the rate of atomic oxygen erosion of commonly used spacecraft polymers, and resulting modifications to LEO spacecraft design in efforts to enable spacecraft to be durable to the LEO atomic oxygen environment.

This paper provides an overview of the LEO atomic oxygen environment, its interaction with spacecraft materials, approaches for protection from atomic oxygen, and on-orbit and computational results of protection methods.

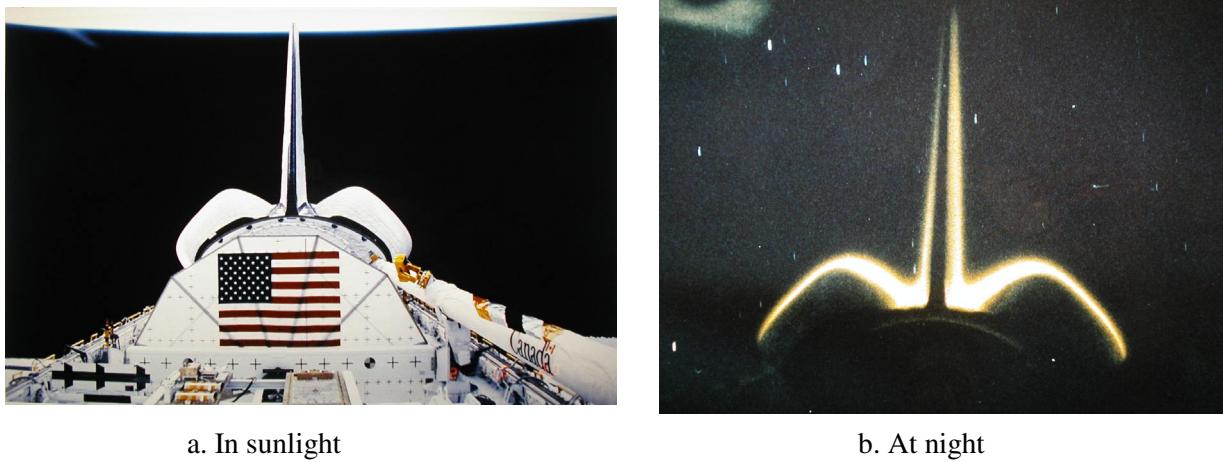


Figure 1. Space shuttle with the bay oriented in the direction of travel (ram direction).

The LEO Atomic Oxygen Environment

Atomic oxygen, in LEO, is formed by photodissociation of the residual diatomic oxygen that is exposed to the sun's ultraviolet radiation of wavelengths of less than 243 nm, in an environment where the atmospheric density is too low for competitive recombination processes to form ozone, diatomic oxygen or oxides of nitrogen. As a result, atomic oxygen is typically the most abundant species between the altitudes of 180 and 650 km [1], as shown in Figure 2.

As one goes up in altitude, the average molecular weight decreases and the temperature gradually increases as shown in Figures 3 and 4, respectively [1].

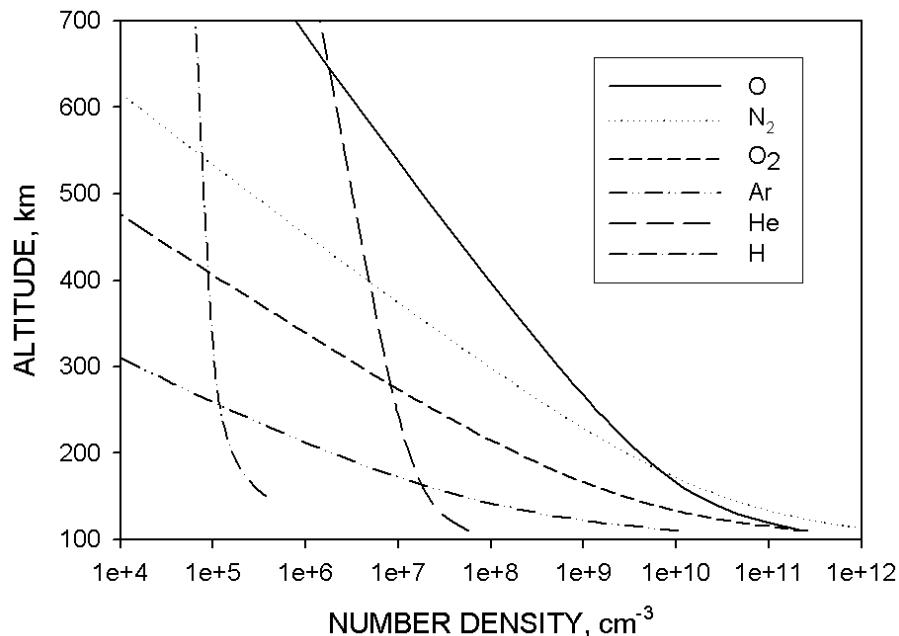


Figure 2. Density of atmospheric constituents as a function of altitude [1].

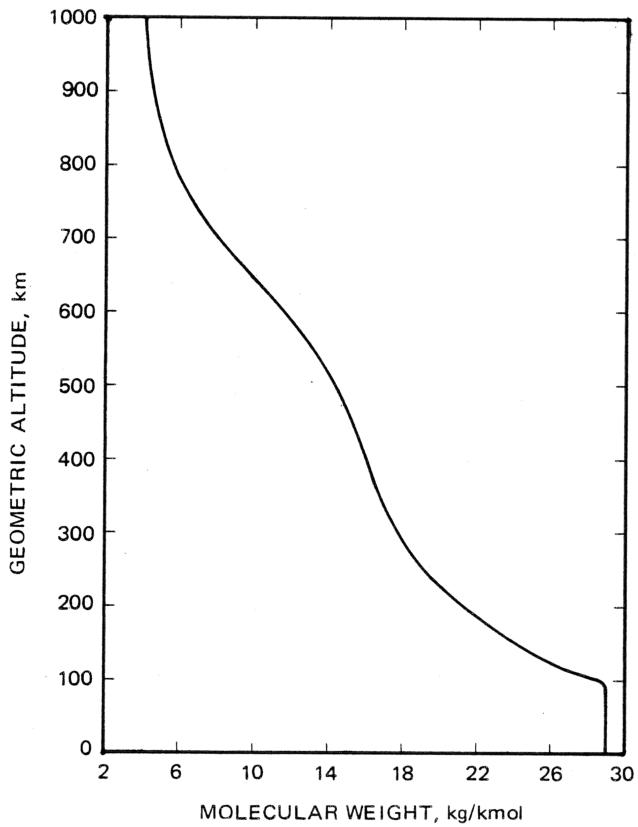


Figure 3. Average molecular weight as a function of altitude [1].

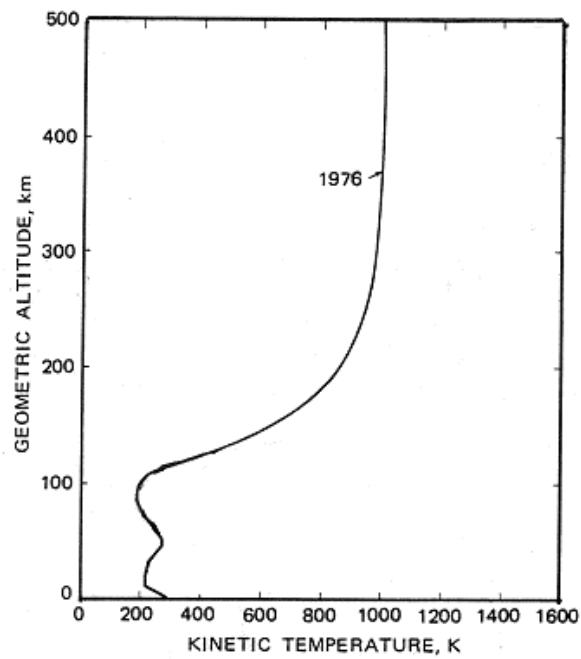


Figure 4. Kinetic temperature of LEO atomic oxygen as a function of altitude [1].

The Earth's thermosphere co-rotates with the Earth giving atomic oxygen a velocity in the direction of the Earth's rotation. However, the orbital velocity of spacecraft is much greater and through most parts of an orbit is at an inclined angle to the equatorial plane. This orbital velocity vector, the Earth's co-rotation vector, and the random thermal velocity of the hot Maxwellian atomic oxygen gas causes a distribution of the arrival flux with angle of attack as well as a statistical variation in the energy atomic oxygen as it impacts spacecraft surfaces, as shown in Figures 5 and 6, respectively. Although Figure 6 is for circular orbits, highly inclined orbits would result in much greater impact energies.

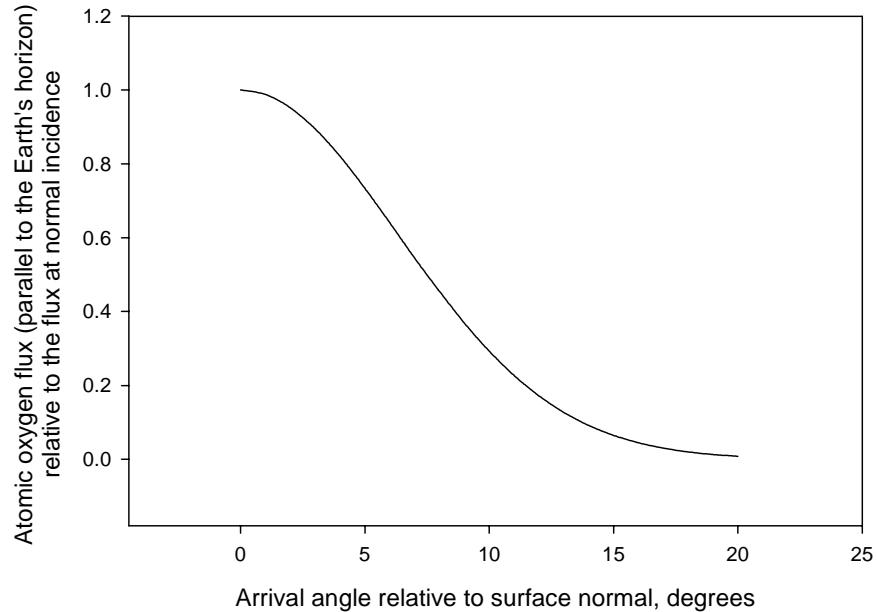


Figure 5. LEO atomic oxygen arrival flux versus arrival angle from ram direction for surfaces perpendicular to the ram direction.

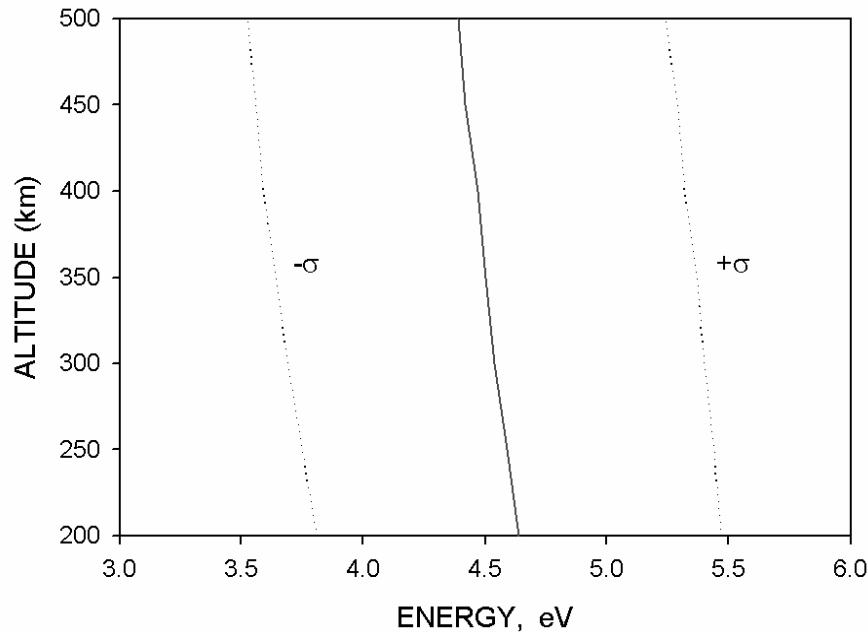


Figure 6. LEO Atomic oxygen energy versus orbital altitude for 28.5° inclined circular orbits.

Organic Materials Interaction With Atomic Oxygen

LEO atomic oxygen is a highly reactive form of oxygen which also has sufficient energy to break chemical bonds. As a result, it is thought to have a probability of approximately 14 % for reacting upon initial impact with materials such as carbon [4] or polyimide Kapton H [5]. The amount of erosion of polymers is equal to the product of the erosion yield of the polymer and the atomic oxygen fluence. Where the erosion yield is the number of cubic centimeters of the polymer that is eroded per incident oxygen atom (cm^3/atom) and the atomic oxygen fluence is the number of atoms impacting per square centimeter (atoms/cm^2). The atomic oxygen erosion yields for numerous materials are listed in Table 1.

Table 1. Atomic oxygen erosion yields for various materials.

Material	Abbrev.	Trade Names	Predicted Erosion Yield in LEO by Different Correlations [7] ($\times 10^{-24} \text{ cm}^3/\text{atom}$)		Measured Erosion Yield in LEO ($\times 10^{-24} \text{ cm}^3/\text{atom}$) and references
			γ' mod-Correlation	Oxidation Index Correlation	
Acrylonitrile butadiene styrene	ABS	Cyclocac; Lustran	2.3	3.1	
Carbon					0.9–1.7 [5]
Carbon (highly oriented pyrolytic graphite)	HOPG	Graphite	1.0	1.3	1.04–1.2 [6]; 1.2–1.7 [7]; 1.2 [5]
Carbon (pyrolytic polycrystalline)	PG	Graphite			0.61–1.2 [6]; 1.2 [5]
Carbon (single crystal natural Class IIA diamond)		Diamond			0.0000 ± 0.000023 [6]; 0.021 [5]
Cellulose acetate	CA	Cellidor; Tenite Acetate	6.8	3.2 (5.2)	
Cellulose nitrate	CN	Celluloid; Xylonite	13.1		
Crystalline polyvinylfluoride w/white pigment	PVF	White Tedlar	3.4	3.0	0.29 [6]; 3.2 [7]
Diallyl diglycol and triallyl cyanurate	ADC	CR-39	6.1	4.6	6.1 [7]
Epoxide or epoxy	EP	Epoxy resin	2.9	2.3	2.7 [7] Epoxy Resin 5208; 1.7 [5]
Ethylene vinyl acetate copolymer	EVAC	Elvax	3.9	3.5	
Ethylene vinyl alcohol copolymer	EVAL (EVOH)	Eval	3.5	3.0	
Ethylene/propylene/diene	EPTR (EPDM)	Nordel; Keltan	2.9	3.0	

Table 1. Atomic oxygen erosion yields for various materials (continued).

Material	Abbrev.	Trade Names	Predicted Erosion Yield in LEO by Different Correlations [7] ($\times 10^{-24} \text{ cm}^3/\text{atom}$)		Measured Erosion Yield in LEO ($\times 10^{-24} \text{ cm}^3/\text{atom}$) and references
			γ' mod-Correlation	Oxidation Index Correlation	
Fluorinated ethylene propylene	FEP	Teflon FEP	0.0	n/a	$0.337 \pm 0.005^*$ [6]; 0.35 [6]; 0.03–0.05 [7]; 0.037 [6]; 0.0–<0.05 [5]
Halar ethylene-chlorotrifluoroethylene	ECTFE	Halar	2.0	n/a	2.0–2.1 [6]; 1.9 [7]
Melamine formaldehyde resin	MF	Melmex; Melopas	3.4		
Phenol formaldehyde resin	PF	Bakelite; Plenco; Durex	2.3	2.5	
Poly-(p-phenylene terephthalamide)	PPD-T (PPTA)	Kevlar 29	2.5	2.9	1.5 ± 0.5 Kevlar 29 [6]; 2.1–4.1 Kevlar 29 [7]; 4.0 ± 0.5 Kevlar 49 [6]; 2.1–4.1 Kevlar 49 [7]
Polyacrylonitrile	PAN	Acilan; Barex; Orlon	2.5	4.5	
Polyamide 6 or nylon 6	PA 6	Caprolan; Akulon K; Ultramid	3.7	3.6	2.8 ± 0.2 [6]; 4.2 [7]
Polyamide 66 or nylon 66	PA 66	Maranyl; Zytel; Durethane	3.7	3.6	2.8 ± 0.2 [6]
Polybenzimidazole	PBI	Celazole	1.9	1.8	1.5 [7]; 1.5 [5]
Polycarbonate	PC	Lexan; Makrolon	2.9	3.2	2.9 [7]; 6.0 [5]
Polychlorotrifluoroethylene	PCTFE	Kel-F; Aclar	1.0	n/a	$1.97 \pm 0.12^*$ [6]; 0.9 [7]
Polyetheretherketone	PEEK	Victrex PEEK; Hostatec	2.3	2.1	3.7 ± 1.0 [6]; 2.3 [6]; 3.2–4.5 [7]
Polyethylene	PE	Alathon; Lupolen; Hostalen	3.0	4.2	3.97 ± 0.23 [6]; 3.2–4.5 [7]; 3.3 [5]; 3.7 [5]
Polyethylene oxide	PEO	Alkox; Polyox	7.1	5.8	

Table 1. Atomic oxygen erosion yields for various materials (continued).

Material	Abbrev.	Trade Names	Predicted Erosion Yield in LEO by Different Correlations [7] ($\times 10^{-24} \text{ cm}^3/\text{atom}$)		Measured Erosion Yield in LEO ($\times 10^{-24} \text{ cm}^3/\text{atom}$) and references
			γ' mod-Correlation	Oxidation Index Correlation	
Polyethylene terephthalate	PET	Mylar; Tenite	3.5	3.1	3.4–3.6 Mylar A [6]; 3.4–3.7 Mylar A [5]; 3.0 Mylar D [6]; 2.9–3.0 Mylar D [5]; 3.4–3.9 [7]; 1.5–3.9 [5]
Polyimide (PMDA)	PI	Kapton HN	2.9	2.0	3.0 [7]; 3.0 [5]
Polyimide (PMDA)	PI	Kapton H	2.9	2.0	3.0 [6]; 2.89 ± 0.6 [6]; 3.0 [7]; 3.0 [5]; 1.5–3.1 [5]
Polyimide (PMDA)	PI	Black Kapton			1.4–2.2 [5]
Polymethyl methacrylate	PMMA	Plexiglas; Lucite	5.1	4.5	6.3 ± 0.3 [6]; 3.9–4.8 [7]; 3.1 [5]
Polyoxymethylene; acetal; polyformaldehyde	POM	Delrin; Celcon; Acetal	8.0–12.0	5.0	
Polyphenylene	PPH		1.8		
Polyphenylene isophthalate	PPPA	Nomex	2.5	2.9	
Polypropylene	PP	Profax; Propathene	2.9	4.1	4.4 [6]
Polystyrene	PS	Lustrex; Polystyrol; Styron	2.1	6.0	4.17 ± 0.17 [6]; 1.8 [7]
Polysulphone (Polysulfone)	PSU	Udel; Ultrason/S	2.5	2.4–3.0	2.3 [6]; 2.1 [7]; 2.4 [5]
Polytetrafluoroethylene	PTFE	Fluon; Teflon; Halon	0.0	n/a	0.20 [6]; 0.37 ± 0.06 [6]; 0.03–0.05 [7]; 0.0–0.2 [5]
Polyvinyl acetate	PVA	Elvacet	6.2		
Polyvinyl alcohol	PVA(L)	Elvanol	7.1	4.1	
Polyvinyl fluoride	PVF	Tedlar			3.8 clear [6]; 1.3–3.2 clear [5]; 0.05–0.6 white [5]

Table 1. Atomic oxygen erosion yields for various materials (concluded).

Material	Abbrev.	Trade Names	Predicted Erosion Yield in LEO by Different Correlations [7] ($\times 10^{-24} \text{ cm}^3/\text{atom}$)		Measured Erosion Yield in LEO ($\times 10^{-24} \text{ cm}^3/\text{atom}$) and references
			γ' mod-Correlation	Oxidation Index Correlation	
Polyvinylidene chloride copolymers	PVDC	Saran	5.1	n/a	
Polyvinylidene fluoride	PVDF	Kynar	1.1	n/a	0.9–1.1 [7]; 0.6 [5]
Polyxylylene	PX	Parilene; Parylene	2.1		
Pyrone	PR	Pyrone	2.4		2.3 [7]; 2.5 [5]
Tetrafluorethylene-ethylene copolymer	ETFE	Tefzel ZM	1.1	n/a	1.2 [7]
Urea formaldehyde	UF	Beetle; Avisco	5.1	3.0	

* Corrected for LDEF ram fluence of $9.09 \times 10^{21} \text{ atoms/cm}^2$

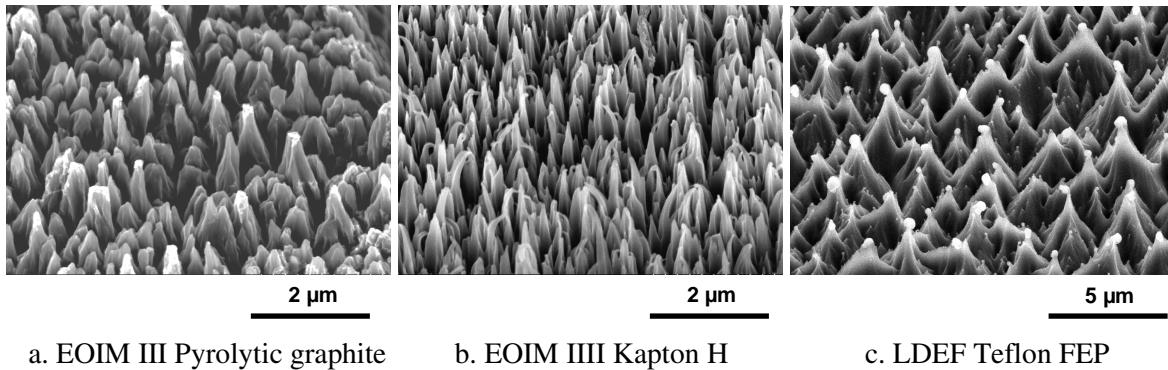


Figure 7. Scanning electron microscope images of pyrolytic graphite, polyimide Kapton and Teflon FEP exposed to directed LEO atomic oxygen on EOIM III or the LDEF.

It is interesting to note that carbon, in the form of single crystal class IIa diamond does not erode in atomic oxygen. This is thought to be due to the formation of a protective surface formed by closely spaced oxygen atoms that have replaced hydrogen atoms at the terminations of tetrahedrally-coordinated carbon on the external surface of diamond. The atomic oxygen erosion yield is not a meaningful number for materials such as most metals and silicones where the majority of the oxidation products are non-volatile.

The atomic oxygen erosion for fixed direction arrival with all materials that have volatile oxides is such that it causes the surfaces to erode to produce left-standing cones that represent a small fraction of the erosion depth. Examples of fixed direct atomic oxygen arrival textures for three materials (pyrolytic graphite, polyimide Kapton and Teflon FEP) from the Environmental Oxygen Interaction with Materials III (EOIM III) and Long Duration Exposure Facility (LDEF) space flight experiments are provided in Figure 7.

The development of surface texture occurs whether or not the material is crystalline or amorphous and is a stochastic process which develops in a similar manner as to the meandering of rivers. Computational modeling of the surfaces also predicts the development of such surface cones [8 and 9]. Such surfaces have significant biomedical applications because they greatly increase cell attachment [8].

The length of cones increase with atomic oxygen fluence as the square root of the fluence [8]. The length of the cones relative to the average erosion depth for pyrolytic graphite, polyimide Kapton H and Teflon FEP are shown in Figure 8 at protected mesa locations. Calculated values for average cone height relative to the average erosion depth is provided in Table 2 for these flight samples, exposed at various atomic oxygen fluences on LDEF and EOIM III.

As can be seen in Table 2, the ratio of cone length to erosion depth appears to be material dependent. However, based on Reference 8, one would expect that for each material the ratio of cone length to erosion depth would decrease with atomic oxygen fluence.

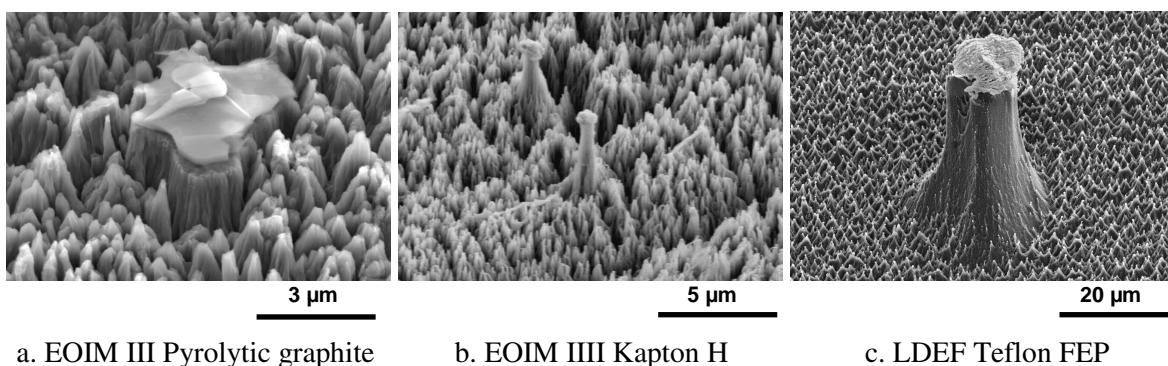


Figure 8. Scanning electron microscope images at protected mesas of pyrolytic graphite, polyimide Kapton and Teflon FEP exposed to directed LEO atomic oxygen on EOIM III or LDEF.

Table 2. Ratio of cone length to erosion depth as a function of fluence for various materials exposed to directed LEO atomic oxygen.

Material	Ratio of average cone length to erosion depth	Space Mission	Atomic oxygen fluence, atoms/cm ²
Pyrolytic graphite	0.60	EOIM III	2.3×10^{20}
Kapton H	0.28	EOIM III	2.3×10^{20}
FEP Teflon	0.07	LDEF	8.43×10^{21}

Protective Coatings

The rate of erosion of polymers such as polyimide Kapton is sufficiently high that protective coatings which are durable to atomic oxygen are typically applied to prevent or reduce the rate of attack of underlying polymers. Such coatings typically consist of metal oxide or metal thin films which are atomic oxygen durable and prevent atomic oxygen from reaching the underlying polymer. A protective coating of 1300 Angstroms of sputter deposited SiO_x (where 1.9 < x < 2) have been applied to the International Space Station solar array Kapton H blankets. The

durability of such coatings is dependent upon the density and size of pin window and scratch defects in the protective coating. Vacuum deposited aluminum coatings contain much greater defect densities than sputter deposited SiO_x coatings [10] thus allowing atomic oxygen to attack the polymer through undercutting oxidation at the microscopic defect sites as shown in Figure 9.

Surface particle contaminants and microscopic scratches, rills and cracks cause incomplete surface coverage of the protective film leading to atomic oxygen attack and undercutting at such sites. As atomic oxygen erodes at exposed polymer sites, the undercut cavities eventually connect leading to structural failure of the polymer. The density of defects is large for microscopically rough surfaces such as graphite epoxy composites. However the number of defects, in some cases, can be reduced from 180,000 defects/cm² to ~1000 defects/cm² through the application of surface leveling coatings [11].

The effects of LEO atomic oxygen undercutting can lead to complete loss of the underlying polymer if the defect density is sufficient and if the atomic oxygen is trapped when protective coatings are applied to both surfaces of the polymer. An on-orbit example is shown in Figure 10 where defects in vapor deposited aluminum coatings on both surfaces of a Kapton covering on the International Space Station solar array blanket boxes allowed atomic oxygen to become trapped, completely oxidizing the underlying Kapton [10].

A Monte Carlo computational model has been developed which simulates the interactions and resulting oxidative erosion of atomic oxygen impinging upon polymers [2, 9, and 10]. This model predicts that if just the space-exposed surface of the Kapton had been coated with vapor deposited aluminum, then there would have been less trapping of the atomic oxygen which would have tended to preserve the presence of the protected polymer, as shown in Figure 11.

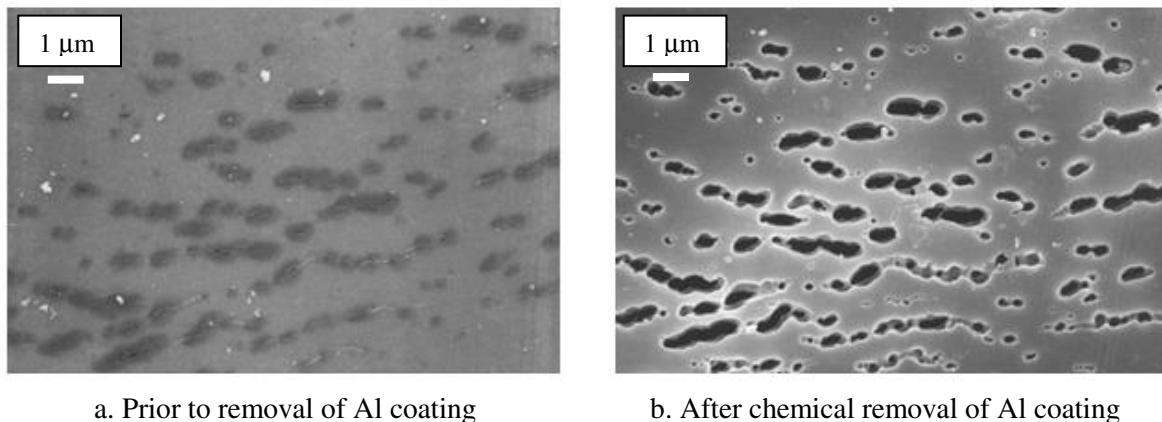
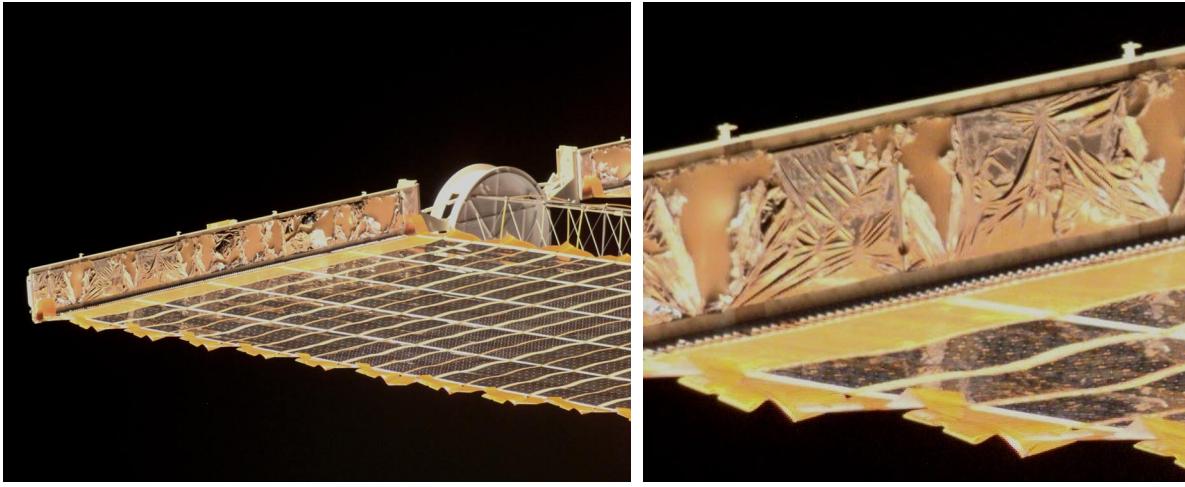


Figure 9. Atomic oxygen undercutting of scratches or cracks in aluminized Kapton retrieved from the Long Duration Exposure Facility.



a. ISS solar array blanket box.

b. Close-up of damage.

Figure 10. International Space Station solar array blanket box after one year in LEO showing only the vacuum deposited aluminum coatings are present after complete oxidation of the underlying Kapton [10].



a. Prediction for protective coatings on both sides of the underlying Kapton.



b. Prediction for a protective coating on only the space exposed side of the underlying Kapton.

Figure 11. Computational model predictions for protective coatings on either both sides of the underlying Kapton or on only the space exposed side of the underlying Kapton.

Summary

Atomic oxygen formed in low Earth orbit, has sufficient energy and flux to oxidize and erode most hydrocarbon polymers. There is a distribution in atomic oxygen arrival angle of attack caused by the orbital inclination, the Earth's co-rotation and the random thermal velocity of the hot Maxwellian atomic oxygen gas. The spatially random erosion processes causes the surfaces of all materials that have volatile oxidation products to become microscopically rough with cone structures that point in the direction of arriving atoms.

Atomic oxygen protective coatings of metal oxides and metals is a valuable means of reducing oxidative attack. However, microscopic particle contaminants, scratches, rills and cracks cause incomplete surface coverage of the protective film leading to atomic oxygen attack and undercutting at such sites. For this reason, coating only the atomic oxygen exposed side of a

hydrocarbon polymer is desirable to prevent trapped atomic oxygen from severely undercutting the polymer substrate. The use of metal oxide protective coatings and surface leveling coatings can greatly reduce the density of defects in comparison to aluminized protective coatings.

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Atomic oxygen, formed in Earth's thermosphere, interacts readily with many materials on spacecraft flying in low Earth orbit (LEO). All hydrocarbon based polymers and graphite are easily oxidized upon the impact of ~4.5 eV atomic oxygen as the spacecraft ram into the residual atmosphere. The resulting interactions can change the morphology and reduce the thickness of these materials. Directed atomic oxygen erosion will result in the development of textured surfaces on all materials with volatile oxidation products. Examples from space flight samples are provided. As a result of the erosive properties of atomic oxygen on polymers and composites, protective coatings have been developed and are used to increase the functional life of polymer films and composites that are exposed to the LEO environment. The atomic oxygen erosion yields for actual and predicted LEO exposure of numerous materials are presented. Results of in-space exposure of vacuum deposited aluminum protective coatings on polyimide Kapton indicate high rates of degradation are associated with aluminum coatings on both surfaces of the Kapton. Computational modeling predictions indicate that less trapping of the atomic oxygen occurs, with less resulting damage, if only the space-exposed surface is coated with vapor deposited aluminum rather than having both surfaces coated.			
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