Degradation of Spacecraft Materials in Low Earth Orbit

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On October 4, 1957 the Soviet Union launched the first satellite, Sputnik, into Earth's orbit. In the years since, the number of satellites and spacecraft for space exploration has greatly increased. Concurrent with space exploration has been a realization that the "weather" in outer space is very different than Earth's atmosphere. The environment of outer space can cause a great deal of material degradation to exposed parts of spacecraft. If scientists have the ability to predict material degradation of spacecraft surfaces, it may lead to better material design and reusable, longer lasting, lower cost spacecraft in the future.

Earth has several orbits where many types of spacecraft circle. A satellite in orbit travels in a repeating path around Earth under the influence of gravity. Low Earth orbit (LEO) is the closest orbit to Earth and is defined as 200-2,000 km above Earth's surface. Most human space exploration and many satellites are located in LEO. This includes satellites for weather, communication, spacecraft for scientific and military observation as well as manned spacecraft like the International Space Station.[1]

One material commonly used on the surface of spacecraft in LEO is called Kapton®. Kapton® (Fig. 1) is a 50-150 kDA polyimide formed by the condensation of dianhydride and diamine monomer. It is used on spacecraft because it is has some resistance to ultraviolet (UV) radiation and is stable in temperature ranges from -269 to 400°C. Because of the thermal stability it has, Kapton® is used as a substrate for solar arrays, thermal insulation and spacecraft inflatable structures.[2] However, Kapton® is known to degrade quickly in LEO. This was demonstrated by an experiment done one the Long Duration Exposure Facility. In this experiment, over 10,000 materials were put on a spacecraft in orbit and exposed to LEO. Images of Kapton® before and after exposure are shown in Fig. 1a-b. Before orbit, the Kapton® was bright orange, and after six years in orbit, it was degraded, exposing the aluminum layer underneath to contamination. [3-4]

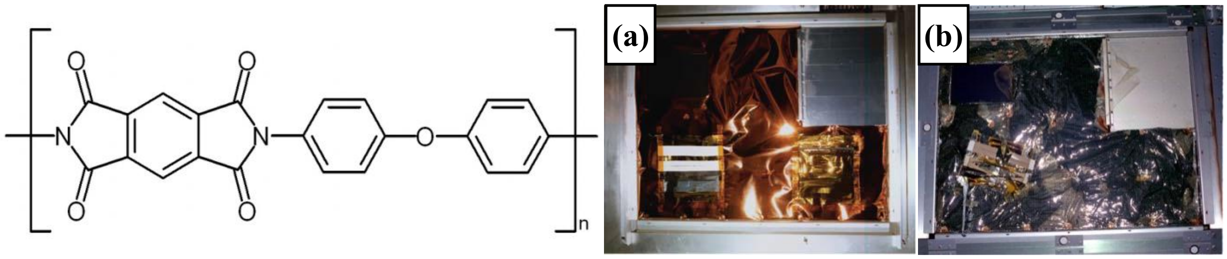


Figure 1. Molecular structure of Kapton®. Kapton® before (a) and after (b) exposure to LEO.[2-4]

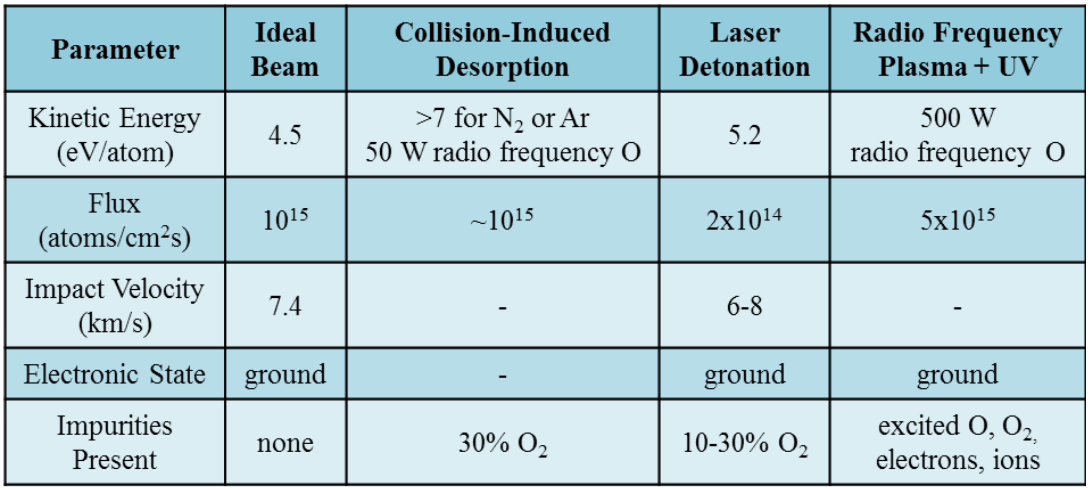
Degradation of spacecraft materials in LEO is attributed to the harsh environment that materials are exposed to. There are five main mechanisms that contribute to degradation: high energy vacuum UV radiation in wavelengths from 100 to 200 nm, temperature extremes from -175 to 160°C, collisional impacts from space debris and micrometeoroids, ionizing radiation, and the presence of atomic oxygen. Together, these cause degradation of exterior surfaces of spacecraft resulting in damage to structures necessary for flight and function.[1,5]

In LEO, atomic oxygen is thought to be the predominant cause for material degradation. Atomic oxygen is generated by photodissociation of molecular oxygen by intense UV light. Because LEO is a vacuum, the chance of recombination of atomic oxygen is lowered. It is the predominant gas in LEO and at typical spacecraft altitudes, there are 10^9 atoms/cm^3(~2 pM).[6-7] Atomic oxygen has a high kinetic energy of 4.5 eV/atom (~430 kJ/mol) and when it impacts a surface in LEO the average flux is 10^{15} atoms/cm^2s and the impact velocity is 7.4 km/s. In LEO, atomic oxygen exists in the ground electronic state with two unpaired electrons.

The energetic collisions of atomic oxygen with surfaces cause oxidation and erosion. Materials in their highest oxidation state are not oxidized and are less affected by atomic oxygen. Collisions of atomic oxygen with hydrocarbon-based polymers (like Kapton®) can break C-C and C-H bonds and cause oxidation. This results in ejection of gases such as CO_2 and CO and the loss of mass results in considerable material erosion.[7-8]

Laboratory modeling is a potential way to predict how materials will behave in the LEO environment. Real space exposure is time consuming and expensive; and laboratory models may be a faster, more cost-effective alternative. An ideal laboratory model of atomic oxygen degradation would produce a beam that mimics the LEO environment. This includes the parameters stated before (Table I). Thus far, no ideal beam has been realized, but there has been a fair amount of research in degradation of polymers such as Kapton® with laboratory models.[9]

Table I. Beam parameters of ideal atomic oxygen beam and laboratory generated beams.



Parameter	Ideal Beam	Collision-Induced Desorption	Laser Detonation	Radio Frequency Plasma + UV
Kinetic Energy (eV/atom)	4.5	>7 for N_2 or Ar 50 W radio frequency O	5.2	500 W radio frequency O
Flux (atoms/cm^2s)	10^{15}	~10^{15}	$2x10^{14}$	$5x10^{15}$
Impact Velocity (km/s)	7.4	-	6-8	-
Electronic State	ground	-	ground	ground
Impurities Present	none	30% O_2	10-30% O_2	excited O, O_2, electrons, ions

One method used to understand the mechanism of atomic oxygen degradation is called collision-induced desorption and was described by Minton et *al.*[10] In their system, a plasma containing atomic oxygen was generated by introducing a radio frequency into molecular oxygen. The beam parameters are shown in Table I. In addition, there was a hyperthermal beam source of inert Ar or N_2. The high energy collision of inert gas with the oxidized surface caused ejection of CO_2 and CO. In their experiments they measured time-of-flight distributions of products ejected from laboratory synthesized polyimide films that had been spin-coated onto silicon. Their results demonstrated that increasing incident kinetic energy of the hyperthermal Ar or N_2 from 7 eV/atom to 16 eV/atom increased ejection of CO_2 from the polyimide surface. The data demonstrated that a collisional process assists in CO_2 ejection from an oxidized polymer surface; however, because the incident kinetic energy was so high it did not accurately reproduce the LEO environment and may not be a good method for future degradation studies.[10]

Another method used for laboratory modeling of atomic oxygen degradation is called laser detonation. In this system a pulsed CO_2 laser was introduced into O_2 gas creating atomic oxygen plasma. The plasma was directed at the sample and mass loss was measured. In this setup, the atomic oxygen beam parameters were similar to the ideal beam parameters previously described (Table 1).[8,11] Experiments by Minton et *al* [2] in 2012 used this method to compare degradation of polyimide in the laboratory to polyimide exposed to LEO on the International Space Station. In the laboratory experiment, mass loss of the polyimide was constant until no more degradation occurred after 250 min. The sample on the International Space station also experienced constant mass loss, but at a slower rate, and degradation stopped at 250 hours. The reason for the rate difference was not explained but it could be due to higher incident kinetic energy or impurities present in the laboratory system. If this system is calibrated to real atomic oxygen it could be used in the future to predict how materials will behave in LEO.[2]

A third example of laboratory modeling of atomic oxygen was described by Gouzman et *al*.[12-13] Their laboratory setup used a radio frequency generated oxygen plasma but also had a UV source that supplied 115-200 nm UV light to the sample surface in order to include the effect of vacuum UV with atomic oxygen degradation. The beam parameters are described in Table 1. In their experiments they measured mass loss from uncoated and TiO_2 coated commercial Kapton® and laboratory synthesized polyimide. Their results demonstrated that the TiO_2 coating reduced degradation to 2% of the uncoated Kapton® and polyimide. If the TiO_2 coated samples were to be exposed to LEO, it would likely experience much less degradation. Unfortunately, they did not compare the degradation with and without UV light, so the effect of UV light is uknown.[12-13]

Understanding degradation of spacecraft materials by atomic oxygen will be critical for future spacecraft design for LEO. Together, these experiments demonstrate that atomic oxygen degradation can be seen in laboratory experiments. None of the examples were ideal; however, if there is more development in the field, predictions using laboratory modeling will become more common. Future directions in these studies may include synergistic modeling with other degradation mechanisms, computational studies, and comparison to erosion already seen in LEO.

References

1. Yang, J.C.; de Groh, K.K. Materials Issues in the Space Environment. *MRS Bulletin* **2010**, *35*, 12-16.
2. Minton, T.K.; Wright, M.E.; Tomczak, S.J.; Marquez, S.A.; Shen, L.; Brunsvold, A.L.; Cooper, R.; Zhang, J.; Vij, V.; Guenthner, A.J.; Petteys, B.J. Atomic Oxygen Effects on POSS Polyimides in Low Earth Orbit. *ACS Appl. Mater. Interface.* **2012,** *4*, 492-502.
3. Miller, S.K.R.; Banks, B. Degradation of Spacecraft Materials in the Space Environment. *MRS Bulletin* **2010**, *35*, 20-24.
4. O'Neal, R.L.; Levine, A.S.; Kiser, C.C. *Photographic Survey of the LDEF Mission;* NASA, Hampton, VA, 1996; pp 334-336.
5. Murr, L.E.; Kinard, W.H. Effects of Low Earth Orbit. *Am. Sci.* **1993**, *81*, 152-165.
6. Verker, R.; Grossman, E.; Gouzman, I. A novel method for on-orbit measurement of space materials degradation. *Rev. Sci. Instrum*. **2011**, *82*, 023901.
7. Minton, T.K.; Garton, D.J. Dynamics of Atomic-Oxygen-Induced Polymer Degradation in Low Earth Orbit, *Chemical Dynamics in Extreme Environments*; Dressler, R.A., Ed.: World Scientific: Singapore, 2001; pp 420-423.
8. Zhang, J.; Garton, D.J.; Minton, T.K. Reactive and inelastic scattering dynamics of hyperthermal oxygen atoms on a saturated hydrocarbon surface. *J. Chem. Phys*. **2002**, *117*, 6239-6251.
9. Tagawa, M.; Minton, T.K. Mechanistic Studies of Atomic Oxygen Reactions with Polymers and Combined Effects with Vacuum Ultraviolet Light. *MRS Bulletin* **2010**, *35*, 35-40.
10. Minton, T. K.; Zhang, J.; Garton, D.J.; Seale, J.W. Collision-Assisted Erosion of Hydrocarbon Polymers in Atomic-Oxygen Environments. *High Perform. Polym*. **2000**, *12*, 27-42.
11. Buczala, D.M.; Brunsvold, A.L.; Minton, T.K. Erosion of Kapton H® by Hyperthermal Atomic Oxygen. *J. Spacecr. Rockets* **2006**, *43*, 421-425.
12. Shpilman, Z.; Gouzman, I.; Lempert, G.; Grossman, G.; Hoffman, A. RF plasma system as an atomic oxygen exposure facility. *Rev. Sci. Instrum*. **2008,** *79*, 025106.
13. Gouzman, I.; Girshevitz, O.; Grossman, E.; Eliaz, N.; Sukenik, C.N. Thin Film Oxide Barrier Layers: Protection of Kapton from Space Environment by Liquid Phase Deposition of Titanium Oxide. *ACS Appl. Mater. Interface*. **2010,** *2*, 1835-1843