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Temperature dependence study of FEP Teflon and Kapton H erosion in a simulated LEO
atomic-oxygen environment
by Deanna Marie Buczala

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Chemistry
Montana State University
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Abstract:
Polymer degradation occurs as a result of exposure to atomic oxygen in low Earth orbit (LEO). The damaging effects of the space environment on materials have prompted the simulation of LEO to study polymer erosion. The laboratory setting provides a method of evaluating material erosion by atomic oxygen attack in an affordable and time-efficient manner: This study investigates the temperature dependence of the erosion of Kapton H and FEP Teflon when exposed to hyperthermal 5 eV atomic oxygen beam. This study extends earlier investigations of the temperature dependence of Kapton H erosion and helps unveil the reaction mechanisms that lead to erosion of Kapton H and FEP Teflon in LEO. The investigations reported in thesis relied on the use of Kapton H to calibrate the atomic oxygen exposures, so an additional study was performed to verify the linear dependence of Kapton H erosion. Surface characterizations of the eroded samples in this study were performed by surface profilometry and atomic force microscopy.

The Kapton H erosion yield grew exponentially with temperature in the range 298 K to 573 K. The temperature dependence of Kapton H erosion could be explained by temperature-dependent and -independent mechanisms. The temperature-independent mechanism dominates at lower temperatures and involves the direct reaction of O atoms with the polymer surface, with an activation energy that is easily overcome by the O-atom collision energy with the surface. The temperature-dependent mechanism becomes important at higher temperatures. Apparently, at high surface temperatures, material is removed through reactions that occur in thermal equilibrium with the surface and have an effective activation energy of 0.31 eV.

From 298 K to 423 K the erosion yield of FEP Teflon grew exponentially. The nonlinear Arrhenius behavior suggested a two-term mechanism analogous to that used to describe the temperature dependent erosion of Kapton H. At temperatures lower than 373 K the temperature-independent mechanism dominates the material erosion and at higher temperatures, a mechanism becomes important that occurs in thermal equilibrium with the surface and has an activation energy of 0.24 eV.

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APPROVAL

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Deanna Marie Buczala

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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This thesis is dedicated in the memory of my dad.

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ABSTRACT

Polymer degradation occurs as a result of exposure to atomic oxygen in low Earth orbit (LEO). The damaging effects of the space environment on materials have prompted the simulation of LEO to study polymer erosion. The laboratory setting provides a method of evaluating material erosion by atomic oxygen attack in an affordable and time-efficient manner.

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CHAPTER 1

INTRODUCTION

The International Space Station (ISS) is a monumental scientific and engineering achievement; however, it is plagued with the problem of material deterioration as it maintains orbit above the Earth. This part of the Earth's atmosphere, from 200-700 km, is commonly referred to as low Earth orbit (LEO).[1] Since the early 1980's, it has been determined through both space- and laboratory-based experiments that materials degrade after long term exposure to the LEO environment.

The most abundant species in LEO is atomic oxygen. Atomic oxygen is formed when molecular oxygen is photodissociated by vacuum ultraviolet radiation.[2-6] The mean free path at LEO altitudes is large enough that recombination to form O_2 or O_3 is negligible.[7-9] In the steady state, molecular oxygen is generally less than one-tenth of the atomic oxygen density.[10] Figure 1 illustrates the number density of various neutral species at LEO altitudes. The O-atom number density at a typical shuttle altitude of 300 km is ~10^9 cm^{-3}. The number density of atomic oxygen is low, but when combined with the relative velocity between orbiting spacecraft and the ambient atmosphere (~7.4 km s^{-1}), the oxygen atoms bombard the ram surface of a spacecraft at a rate of ~10^{15} O atoms cm^{-2} s^{-1}. This corresponds to O atoms with a mean translational energy of 4.5 eV striking the leading edge of a satellite.[1,5] The kinetic temperature of roughly 1000 K for the ambient atmosphere results in
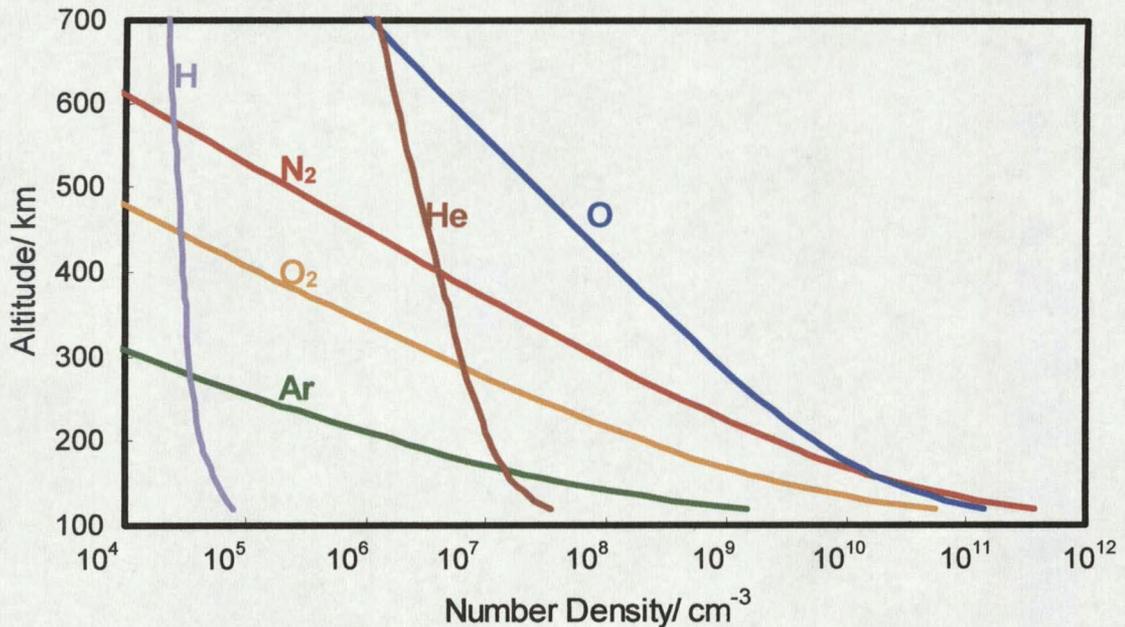
Figure 1. Number density of atomic and molecular species at low Earth Orbital altitudes.

an energy spread (full width half maximum) of ~2.5 eV in the collisions.[11]

Material exposures *in situ* have the benefit of faithfully representing the LEO environment. Unfortunately, there are many disadvantages to space exposures due to the difficultly of maintaining control over all parameters. A major problem with in-flight exposure is the severe contamination that can result from mishandling of samples, material out-gassing,[12] and long periods between pre- and post-flight analysis. In addition, there may be other damaging space effects, including solar ultraviolet radiation, solar flare x-rays, electron and proton radiation, and temperature effects.[13]

Due to the limited availability and high cost of space exposures, the laboratory setting provides a method of evaluating material erosion by atomic oxygen attack in an

affordable and time-efficient manner.[3] An ideal laboratory exposure would provide a controlled, faithful reproduction of the LEO environment; it would have a flux greater than 10^{15} atoms cm^{-2} s^{-1}, a mean collision energy of approximately 5 eV O(^3P) atoms, and no impurities present (*e.g.*, VUV light, excited species, and ions).[14] The laser-detonation source in this laboratory generates a high purity, ground state atomic/molecular oxygen beam with an O-atom translation energy of ~5 eV and a flux of >10^{15} atoms cm^{-2} s^{-1} (40 cm from the source).[12] The use of a hyperthermal atom beam source is beneficial to the study of polymer surfaces.[4] Although, the laboratory is unable to simulate LEO completely, by gaining an understanding of the erosion mechanism of polymers in the controlled laboratory environment , it should then be possible to predict the durability of a material in a variety of environments.

Post-flight analysis of materials from early space flights identified the damaging effects of LEO on polymer surfaces.[14] Many polymer films have desired mechanical and optical properties (solar absorptance and thermal emittance); in addition, they are easily fabricated and installed.[13] The interest in these materials is due to their many applications on spacecraft: structural materials, space robots, manipulator arms, solar arrays, thermal blankets, and second-surface mirrors.[12,15] Unfortunately, these materials experience degradation in optical and mechanical properties when exposed to LEO for extended periods of time, *i.e.*, weight loss, change in physical properties, loss of surface gloss, premature aging, and a reduction of thermal properties.[1,8,9,13]

After several Space Shuttle operations, multiple studies found that the erosion of

polymeric material was caused by $O(^3P)$, enhanced by the presence of VUV radiation.[6,11,16,17]

For example, the Long Duration Exposure Facility (LDEF, 5.8 years in space) and the

Hubble Space Telescope (HST, 3.6 years in space) have provided evidence of space degra-

dation.[18] Fluoroethylene propylene (FEP) Teflon and Kapton H polymers recovered from

the leading edge of LDEF demonstrated significant erosion, with rough, sharp peaks that

pointed in the direction of the atomic oxygen flow. When shuttle mission STS-41(LDEF)

returned to Earth in January 1990, the Kapton H surfaces on a multilayer insulation blanket

were oxidized and experienced weight loss due to surface erosion.[18] The effect of incident

angle on erosion was observed but not measured. FEP located on the trailing edge of LDEF

received mostly VUV and little atomic oxygen bombardment. The morphology observed

was a hard brittle layer not detected on the leading edge materials.[19] The FEP multilayer

insulation recovered from HST showed evidence of severe embrittlement along solar fac-

ing surfaces.[17] The embrittled layer was not observed on polymers exposed primarily to

atomic oxygen.[19] The damaging effects of the space environment on materials has prompted

the simulation of LEO to study polymer erosion.

Kapton H (pyromellitic dianhydride-oxydianiline (PMDA-ODA) polyimide) is one

of the most studied polymers. The structure of Kapton is shown in figure 2. This polyimide

polymer has been extensively studied because of its flexible and lightweight structure, tem-

perature stability, excellent insulation properties, UV stability, and IR transparency.[10] It is a

structural material used for solar array blankets due to its mechanical strength and electrical

properties. Kapton H is the standard polymer reference used by the space effects commu-
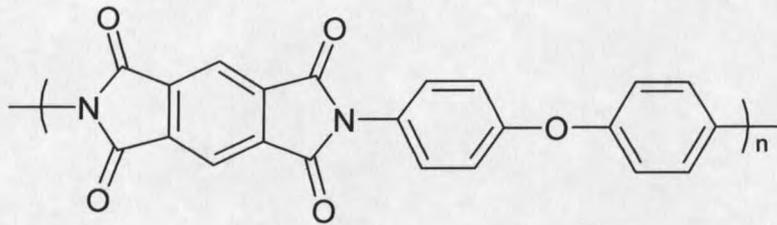
Figure 2. Strucutue of Kapton H (pyromellitic dianhydride-oxydianiline (PMDA-ODA) polyimide).

nity to determine the atomic oxygen fluence of an exposure test. The accepted O-atom-induced erosion yield of Kapton H is 3.00×10^{-24} cm^3 atom^{-1}.

The change in surface morphology after exposure to the LEO environment results in the development of a rough "shag-carpet." It was noted that needle-like structures form on the surface when exposed to hyperthermal rather than thermal oxygen atoms. Since thermal oxygen atoms did not alter the surface topography, this suggests that translational energy and/or direction of O-atom attack may be a factor influencing polyimide erosion.[20] Tagawa *et al.*[21] studied the synergistic effects of atomic oxygen and VUV light on Kapton-like polymer surfaces. They reported that the erosion yield was similar to LEO when both atomic oxygen and VUV light were present. When atomic oxygen alone bombarded the surface, the erosion yield was significantly lower than the accepted value. The effect of VUV light alone was not studied. Volatile species were measured using a residual gas analyzer (RGA) detecting the release of CO and CO_2 products. The CO_2 product increased when both atomic oxygen and VUV were present. The increase in the gasification to CO_2 suggests the possible presence of a synergistic effect. Despite the amount of knowledge gained about the erosion of Kapton, the mechanism is still unknown.

Recently, Tagawa et al.[22] studied the temperature dependence of Kapton-like polyimide erosion when the polymer was exposed to a 5 eV atomic oxygen beam similar to the beam in our laboratory. The polyimide film was formed when a polyamic amide acid was spin coated onto a quartz crystal microbalance (QCM) and cured at high-temperatures. X-ray photoelectron spectroscopy (XPS) confirmed the structure was similar to Kapton H. The mass of the film was measured every 10 seconds from shifts in the resonance frequency of the quartz oscillator during the exposure. The exposure measurements were obtained during the initial erosion of the polymer, with a fluence range of 2.6×10^{14} to 6.5×10^{16} atoms cm^{-2}. The sample temperature range was 253 K to 353 K $\pm$ 0.1 K with a flux of 2.6×10^{14} atom $cm^{-1}s^{-1}$. A plot of the natural log of the erosion yield (ln R_e) versus inverse temperature (T^{-1}) for this limited temperature range gave a linear Arrhenius plot, with an activation energy (E_a) of 5.7×10^{-4} eV (0.055 kJ mol^{-1}).

Fluoroethylene propylene (FEP) Teflon is a commonly used polymer due to its relatively high resistance to oxygen atoms; therefore, in space it has not been protected.[18] The atomic oxygen effect on FEP erosion is small compared to other organic molecules that consist of carbon, hydrogen, and oxygen.[23] The structure of FEP is shown in figure 3. When coated with silver or aluminum backing, it has a high thermal emittance and reflection of incident solar energy, which are desirable properties for thermal insulating materials and flexible solar reflectors.[1,9,24] It is commonly used for thermal control on exterior spacecraft surfaces, the top layer in multi-layer insulation, or a second-surface mirror on radiator panels. When ground and space exposure data are compared, both indicate a small degra-
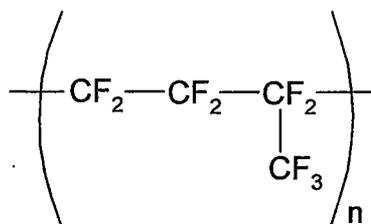
$$-\left(CF_2-CF_2-\underset{\underset{CF_3}{|}}{CF_2}\right)_n$$

Figure 3. The structure of
Fluoroethylene propylene
(FEP) Teflon.

dation of thermal properties.[18] FEP Teflon is prone to erosion, cracking, and subsequent

mechanical failure in LEO.[9,18] In space, factors that may contribute to FEP Teflon degrada-

tion are solar radiation, atomic oxygen, debris and micrometeoroid impacts, and thermal

cycling, in addition to the stress applied by its configuration.[18]

This study investigates the temperature dependence of the erosion of Kapton H and

FEP Teflon when these materials are exposed to a hyperthermal atomic oxygen beam. This

study extends earlier investigations of the temperature dependence of Kapton H erosion

and helps unveil the reaction mechanism responsible for surface erosion. The effect of

temperature on FEP Teflon erosion is studied to understand the chemistry occurring on the

polymer's surface. Surface characterization of the eroded samples in the present study was

performed by surface profilometry and atomic force microscopy.

Chapter 2 describes the experimental details of the molecular beam apparatus, the

sample geometry for each exposure, the sample preparation, and surface characterization

methods.

Chapters 3 and 4 describe the results and discussion for the Kapton H erosion and

temperature study. Chapter 3 presents the results and analysis of the experimental data of