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## O-Atom Degradation Mechanisms of Materials

Daniel R. Coulter  
Ranty H. Liang  
Shirley Y. Chung  
Keri Oda Smith  
Amitava Gupta

Applied Sciences and Microgravity Experiments Section

Jet Propulsion Laboratory  
California Institute of Technology  
Pasadena, CA 91109

### Introduction

Since the earliest flights of the space shuttle (STS I, II and III), it has been recognized that exposure of a wide variety of materials (organic, inorganic and metallic) to the LEO environment has resulted in significant changes in their physical state and/or properties. The observed phenomena have included such things as surface erosion, weight loss, oxidation, changes in absorptivity and emissivity and in some cases even changes in bulk properties (modulus). Over the past few years, literally hundreds of samples have been exposed to the LEO environment on shuttle flights and returned for analysis. Based on the results of these studies it is believed that the observed material degradation is related to the presence of the rarefied atmosphere through which the shuttle flies. In particular, it is postulated that atomic oxygen in the atmosphere is the primary active agent<sup>(1)</sup>. To date, most of the flight experiments have been directed toward material screening activities. Experiments dedicated to elucidating the mechanisms of the observed degradation have been limited, and in a number of cases, potentially valuable information has been compromised or lost completely due to contamination or sample mishandling. Consequently, the underlying mechanisms of the degradation are still largely unknown. In this paper, we will discuss the LEO environment, the critical issues relating to O-atom degradation, some analytical techniques for studying the problem and some preliminary results on mechanisms. The purpose here is not to give all the answers concerning atomic oxygen degradation; rather it is to state clearly the questions and to point in the direction that we believe must be followed in order to find the answers in the most expeditious manner.

### Environment

The LEO environment under consideration is defined by the shuttle orbital flight altitude which generally ranges from 200 to 500 km where the total pres-

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sure is  $\approx 10^{-7}$ - $10^{-8}$  torr corresponding to an atmospheric number density of  $\approx 10^9 \text{ cm}^{-3}$ . The shuttle velocity is  $\approx 8 \text{ km/sec}$  which corresponds to a particle flux of  $10^{14}$ - $10^{15}$  particles/ $\text{cm}^2$ -sec as the vehicle sweeps through the atmosphere. At this altitude, the atmosphere is primarily comprised of ground state ( $O^3P$ ) atomic oxygen ( $\approx 80\%$ ) and molecular nitrogen ( $\approx 20\%$ ). Helium becomes important only at higher altitudes and the ion concentrations are  $10^3$  times lower than neutrals. The velocity of the shuttle is almost an order of magnitude greater than the thermal velocities of the atmospheric gasses; therefore, most gas collisions with the spacecraft occur on the forward or ram surfaces. The kinetic energy of the collisions with atmospheric constituents is high ( $\approx 5\text{eV}$  for O-atoms) resulting from the high vehicle velocity. It is important to understand that a thermal velocity of  $8 \text{ km/sec}$  for O-atoms would correspond to a temperature of  $\approx 60,000\text{K}$ ! Under these conditions, it is not surprising that macroscopic changes in materials have been observed.

### Critical Issues and Approach

Several critical issues related to O-atom interactions with materials have been identified. These include questions like:

- 1) Is the observed loss of material due to ablation or more complex chemistry?
- 2) What is the energy dependence of O-atom interactions with materials?
- 3) Is the degradation dependent on the angle of collision with the atmospheric constituents?
- 4) What is the effect of surface temperature?
- 5) What are the degradation products and what is their energy distribution?
- 6) Are the effects confined to the surface or are changes occurring in the bulk?

Fragmented data exists relating to some of these questions. Clearly, a more structured approach is necessary to come to a final conclusion on these issues. A four point approach including

- 1) carefully planned and executed flight experiments,
- 2) development of ground based capabilities to simulate the LEO environment,
- 3) extrapolation (where possible) of data from conventional atomic oxygen studies, and
- 4) theoretical modeling

is proposed to lead ultimately to a complete mechanistic understanding of the interactions.

The bulk of the efforts in mechanistic investigations to date has involved analysis of flight samples and to a lesser extent, samples exposed to ground based O-atom sources. The techniques applied to study these samples can be divided into two groups, those designed to interrogate the surface and those which can measure bulk properties. Table I lists some of the applicable analytical techniques.

TABLE I. EXPERIMENTAL METHODOLOGY FOR ANALYSIS OF EXPOSED SAMPLES

<u>SURFACE TECHNIQUES</u>	<u>BULK TECHNIQUES</u>
• SEM	• WEIGHT LOSS MEASUREMENTS
• SURFACE ENERGY ANALYSIS	• TRANSMISSION FTIR
• ESCA	• SOL-GEL STUDIES
• FTIR-ATR	• HPLC
• RAMAN SPECTROSCOPY	• STRESS-STRAIN MEASUREMENTS
• UV-VISIBLE REFLECTANCE SPECTROSCOPY	• DYNAMIC MECHANICAL RESPONSE

### O-Atom Effects on Polymers

In the early stages of the investigation of O-atom effects on polymers, a key question to be answered was whether the observed loss of material was due to simple ablation or if more complex chemistry was going on. If the mechanism is ablative, then all organics should show approximately the same erosion rate. If more complex chemistry is involved, then the erosion rates should be material specific. There is now considerable evidence that the latter is the case. Table II shows reaction efficiencies for a number of polymers determined from O-atom fluence calculations<sup>(2)</sup>. The data clearly show that the erosion rates vary by more than two orders of magnitude in going from Teflon® to Mylar®. Furthermore, it is known that metals which form volatile oxides (i.e., osmium) suffer serious erosion as compared to those which do not. Both of these facts point clearly to a chemically based mechanism for erosion.

If indeed chemistry is occurring on the surface, it is important to understand what the reactions are. The study of the reactions of atomic oxygen with organic molecules has been carried out extensively for many years. It is known for example that the interaction of <sup>3</sup>P oxygen with hydrocarbons generally results in hydrogen abstraction while <sup>1</sup>D oxygen usually undergoes insertion. Unfortunately, these data are for low energy O-atom reactions. It is not understood what the effect of 5eV of translational energy will have on

TABLE II. REACTIVITY OF ATOMIC OXYGEN AND MATERIALS

MATERIAL	REACTION EFFICIENCY ( $10^{-24}$ cm <sup>3</sup> /IMPINGING ATOM)
TEFLON <sup>®</sup>	< 0.03
25% POLYSILOXANE-POLYIMIDE	0.3
POLYVINYLIDENE FLUORIDE	0.6
CARBON	1.2
POLYSTYRENE	1.7
KAPTON <sup>®</sup>	3.0
POLYETHYLENE	3.7
MYLAR <sup>®</sup>	3.9

the reaction pathways. Preliminary results by Arnold, et al<sup>(3)</sup> suggest a significant effect of translational energy on erosion of Kapton<sup>®</sup>.

Predicting reaction pathways on the basis of thermodynamics is not a foolproof method. For example, the enthalpies of several reactions of O(<sup>3</sup>P) with aromatic hydrocarbons are shown in Figure 1. The results of molecular beam experiments on reactions of O(<sup>3</sup>P) with benzene are shown in Table III<sup>(4)</sup>. It is seen that the formation of the phenoxy radical is highly favored over the formation of phenol even though the latter is far more thermodynamically stable. Two other relevant pieces of information can be gleaned from this data. First, there is an obvious effect of collision energy on the products, although the conditions still represent very low energies (.1-.3eV) compared to the LEO environment. Secondly, there is a significant isotope effect observed when perdeuterobenzene is used. This again points to the chemical nature of the interactions.

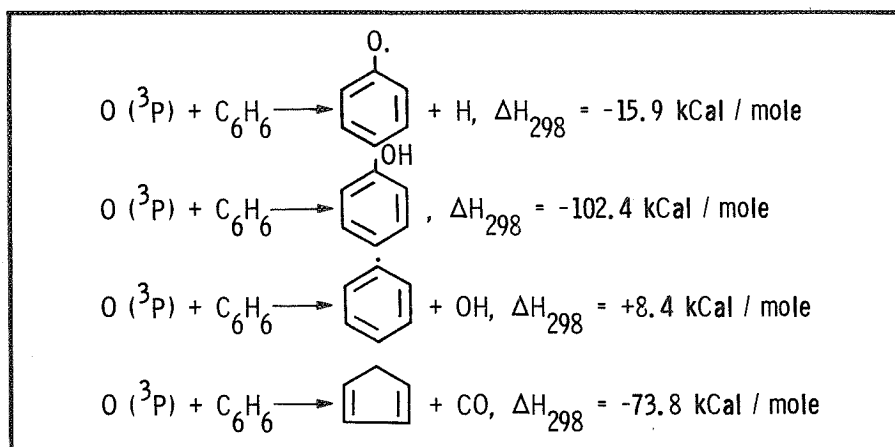


Figure 1. Energetics of several alternate reaction pathways between supersonic beams of O(<sup>3</sup>P) atoms and benzene

TABLE III. OBSERVED REACTIONS OF O ATOMS WITH BENZENE

REACTION	PRODUCT	COLLISION ENERGY	
		0.28 eV	0.11 eV
$O + C_6H_6$	$C_6H_5OH$	16%	< 5%
	$C_6H_5O\cdot + H\cdot$	84%	> 95%
$O + C_6D_6$	$C_6D_5OD$	50%	15%
	$C_6D_5O\cdot + D\cdot$	50%	85%

If specific chemistry is going on at the surface of materials, then the question is whether effects will be transmitted to the bulk. Stress-strain measurements have been made on several materials returned from the STS 8 flight. Figure 2 shows this data for PMMA and Udell 1700 Polysulfone®. Clearly, the modulus of the PMMA is unchanged while behavior of the polysulfone is altered considerably after exposure. The question of UV irradiation contributing to this behavior has been investigated in this laboratory, and the results indicate that UV alone cannot be responsible, although potential synergistic effects of UV with O-atoms have not been investigated.

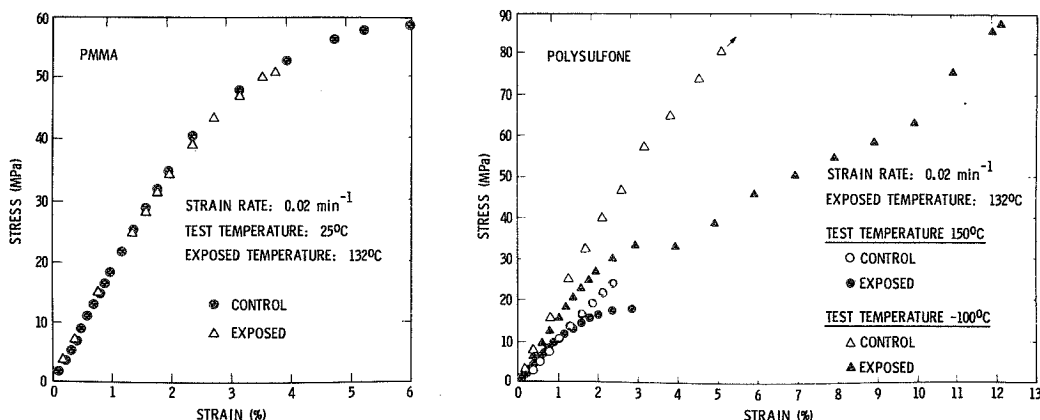


Figure 2. Stress-strain curves for thin ( $\approx 5$  mil) films of PMMA and Polysulfone exposed to the LEO environment on STS-8

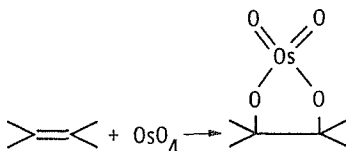
A further indication of bulk material involvement comes from a study of polyethylene (PE) and polyether-etherketone (PEEK) of varying degrees of crystallinity. Samples of both PE and PEEK were prepared from the melts in two ways. One set was fast quenched while the other set was slowly cooled, resulting in otherwise identical samples of lower and higher crystallinity respectively. In both cases, the samples with the higher crystallinity displayed significantly lower erosion rates when exposed to the oxygen atom source at Physical Sciences, Inc.<sup>(5)</sup> The variation of sensitivity with morphology probably is a sign that diffusion of either the O-atoms themselves or some intermediate is occurring from the surface into the bulk. Slower diffusion of small molecules into the crystalline phase as compared to the amorphous phase in semicrystalline polymers is well known. If diffusion is an important process, then one would expect to see significant temperature effects on the degradation. This has not been observed to date; however, the issue is still open to some debate.

### Polyethylene - Case Study of a Flight Experiment

The level to which O-atom interaction mechanisms are understood at this time can be seen by looking at the results of flight exposure studies performed on polyethylene. Thin films flown on the STS-8 shuttle flight showed a weight loss of  $\approx 1.3 \text{ mg/cm}^2$ . Exposure on this flight was for 40 hours and corresponded to a fluence of  $\approx 3 \times 10^{20}$  O-atoms/cm<sup>2</sup> which yields a reactivity of  $\approx 4.3 \times 10^{-24}$  gm/impinging atom or  $\approx 3.9 \times 10^{-24}$  cm<sup>3</sup>/impinging atom. The rate of volatiles leaving the surface can be estimated if an assumption is made about their average molecular weight. Volatile products might be expected to be things like CO, CO<sub>2</sub>, H<sub>2</sub>O, or CHO which would give an average molecular weight of  $\approx 30$  gm/mole. Using this value and the measured weight loss data, a value of  $\approx 2 \times 10^{14}$  molecules/cm<sup>2</sup>-sec can be determined for the rate of volatiles leaving the surface.

The identification of the volatiles leaving the surface is yet to be determined. As of now, the only clues that are available concerning the nature of the chemistry occurring comes from analysis of the exposed surface of the films. Table IV shows the results of ESCA analysis on control and exposed samples.

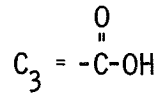
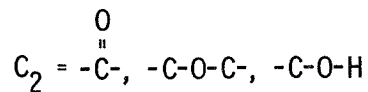
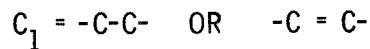
Clearly, the exposed surface is highly oxidized. Unfortunately, ESCA is not capable of distinguishing between all types of oxides. What can be seen is that there are both CO groups (ketones, ethers and/or alcohols) and COO groups (acids) on the surface. There are apparently no esters remaining on the exposed surface. It is also of interest to determine if significant olefin formation occurs on the surface. To answer this question, control and exposed samples were treated with osmium tetroxide which quantitatively adds to olefins according to the reaction below.



ESCA analysis of the treated surfaces of control and exposed polyethylene showed only a slight increase in osmium binding in the exposed sample (0.3% to 0.6%) thus indicating that olefin formation is not a major process in the case of polyethylene.

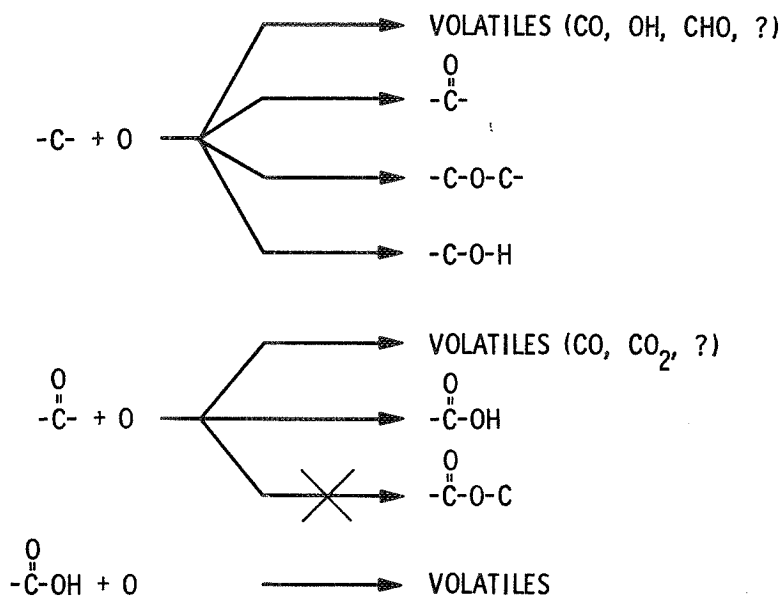
TABLE IV. ESCA ANALYSIS OF POLYETHYLENE SURFACE

	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	O
THEORETICAL	100.0	--	--	--
CONTROL	99.2	--	--	0.8
EXPOSED	81.5	4.5	3.1	9.9



From the results described above, a strawman degradation model has been developed for O-atom degradation of polyethylene. Such a model is shown in Scheme I. It is likely that the pristine polyethylene surface undergoes primary oxidation resulting in both volatiles and surface oxides. Subsequently, there are secondary oxidation processes resulting in further volatilization and secondary oxide formation. Probably, an equilibrium among the surface oxides is rapidly achieved and maintained as erosion occurs. This is borne out by the fact that analysis of polyethylene samples from several shuttle flights shows similar surface chemistry.

Clearly, a great deal is yet to be understood about the mechanisms of O-atom attack on materials. A considerable effort involving further flight experiments, ground based simulation and theoretical modeling is the only way to achieve this understanding. The results of such an effort will have profound effects on future LEO technology by providing the means to do reliable life prediction and to choose or develop stable materials for that harsh environment.



Scheme I

References

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3. G. S. Arnold, D. R. Peplinski and F. M. Cascarano, "Translational Energy Dependence of the O-Polyimide Reaction," AIAA Paper 85-7016-CP, November, 1985.
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5. For a description of the beam source see: R. H. Krech and George Caledonia, Int. SAMPE Tech. Conf. Ser., "Materials for Space," 18, 752 (1986).