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ON THE LINEARITY OF FAST ATOMIC OXYGEN EFFECTS

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INTRODUCTION

The effect of bombardment of 8 km per second atomic oxygen (AO) experienced by exposed surfaces of satellites in low Earth orbit must be considered in the selection of materials to be used in instruments and functional systems on these satellites. The degree of importance of the effects varies widely depending on the material, the application, and the exposure (fluence of atoms) to which it is to be subjected. Some highly erodible thin polymer film materials might be considered unacceptable on a long-lived space station, but may be perfectly serviceable on a normal shuttle flight. In order to determine the acceptability of a material for a particular environment, a designer must know the relationship between the magnitude of the effect (for example, mass-loss) and the magnitude of the fluence. To determine this relationship, we need data over a useful range of fluence.

Until the return of the Long Duration Exposure Facility (LDEF), the bulk of the data on materials effects was obtained from a few shuttle flights, and the bulk of that data from the flight of experiment Evaluation of Oxygen Interaction With Materials (EOIM-2) on STS-8 in 1983. EOIM-2 obtained a fluence of 3.5×10^{20} atoms cm^{-2}, while the LDEF fluence approached 10^{22} atoms cm^{-2}, or about 30 times greater. Although other flight exposures had been obtained with lower fluences, considerable uncertainty was attached to these results because of the possibility of large relative systematic errors and of other factors such as sweeping angle of attack.

In the future, it is hoped that simulation facilities in the laboratory will allow testing of materials without the necessity of flying them in space. In addition, if the relationship of effect with oxygen fluence is well determined, it should not be necessary to expose a material for an entire mission fluence. In this paper, we shall avoid a comparison of flight data with results from simulators, though that comparison is important for the materials community. The present discussion will be limited to flight data only.

We may divide materials into two broad classes in their reaction with fast AO, according to the nature of their oxide products.

- *Materials with gaseous oxide products.*
  These include carbons of various kinds, and most of the commercially available useful organic polymers (including polyimides, polyesters, polycarbonates, and many others). The class does not include silicon-containing materials such as polysiloxanes. The metal osmium is included, since it appears to readily form the labile oxide O_5O_4 (ref. 1).

If the rate of product-oxide evaporation is rapid compared to the rate of oxygen adsorption, the presumed relationship between erosion and fluence is linear. While such a statement may seem obvious, it should be remembered that from some earlier data such a relation was often far from obvious and "incubation periods" were discussed. To the present day, only preliminary work has been done to investigate the mechanisms of reactions in the hyperthermal regime.

- *Materials with refractory oxide products, or with oxides strongly bound to the substrate surface.*
  Most metals fall into this category; Cu, Ni, Al, Cr, Nb, Ir. (ref. 1). Silver is a member of this class, though a special case since it oxidizes to depths of several microns at ambient temperature. The class also includes nonmetals such as Si and Ge, and compounds such as SiC, Si_3N_4 , and GaAs. In the case of oxidation of materials of this class, the presence of an oxide layer tends to reduce the rate of reaction, so that a rate law is obtained which follows a parabolic or similar function (ref. 2). We shall address this second class elsewhere and limit this present discussion to the evidence for linearity in the first class.

If we examine the data for evidence to support the linearity hypothesis, we must be aware of systematic differences in the data which may affect the conclusions drawn. Such systematic effects may depend on the measurement method, specific material properties, and even mission- or flight-related parameters.

Some experimental factors affecting data comparison include:

- The presence of contaminant films can affect the rate of reaction of oxygen with the substrate. This is particularly true for silicones which form, under the proper conditions, a continuous layer of SiO_2 on the surface. This can occur with thicknesses of only 30 to 50 Å, effectively preventing further reaction with the surface. Such contamination may be produced by poor handling procedures prior to flight, or may occur on orbit.

- Some erodible materials may contain particulates, which, if relatively unreactive, may remain on the eroded surface and reduce reaction efficiency as the erosion proceeds.

- Some materials such as the fully halogenated hydrocarbons may show increased reactivity to oxygen after they have received UV irradiation.

- Erosion rate data may vary systematically depending on the measurement technique. We note the dispersion of values, for example, of the mass-loss rate of Kapton®, obtained by different laboratories after the STS-8 flight. This dispersion has greatly decreased during the period up to the present time. There has also been a convergence of values obtained by stylus-profilometry with those obtained by weighing.

- Reaction rates often show a temperature dependence (ref. 3), and data from different experiments may have been obtained at different temperatures.

- Fluences calculated from orbital parameters and the Man Systems Integration Standard (MSIS) model have varied somewhat depending on some variations of the manner of computation.

COMPARISON OF THE DATA

Though there was a large number of erodible materials exposed on STS-8 (EOIM-2) (1983), and an even larger variety on EOIM-3 in 1992, very few of those polymers were also flown on LDEF. In addition, even if the polymers were present, they may not have been in a condition or form suitable to provide useful erosion data. For example, although much Kapton® was flown on LDEF, in all cases except that of the University of Alabama in Huntsville (UAH) experiment, the thickness was insufficient to withstand total erosion. It should be remembered that not only was the actual LDEF exposure some 5 to 10 times greater than expected, but also that LDEF experiments were delivered and stored before the flight of STS-8 in 1983, even though LDEF was not launched until 1984. Thus, there was no opportunity to apply lessons learned from the earlier flight.

The measurements of erodible polymers obtained from experiment A0114 are shown in Table 1. Calculated reactivities are based on a mission fluence of 9.0×10^{21} atoms cm^{-2}. The measurements were obtained using a Taylor-Hobson Talysurf stylus profilometer, and a sample scan from two separate samples of polystyrene exposed on the LDEF is shown in Figure 1. The actual erosion depth is measured by constructing a line through the peaks and valleys as shown in the figure. Large peaks, or mesa-like regions, are ignored as evidence of erosion-protection caused by contaminants of some kind. It is seen from the example shown that even for extremely rough etched surfaces, and even in the case of total erosions of one-half millimeter, the agreement between different samples of the same material is good. This is also true for multiple scans of different areas of a sample.

Table 1. Erosion depths and rates for polymers measured on LDEF. Experiment A0114 (UAH). All data from samples on Row 9 (leading edge - 8°).

Polymer	Erosion Depth† (μm)	Reaction Rate * 10^{-24} (cm^3 $atom^{-1}$)
Kapton®	260±5	2.89±0.06
Nylon	253±19	2.8±0.2
Polystyrene	375±15	4.17±0.17
PVT	396±27	4.4±0.3
PMMA	566±28	6.3±0.3
Polyethylene	357±21	3.97±0.23
PTFE	33.5±5	0.37±0.06

* Assuming an LDEF fluence for row 9 of 9.0×10^{21} atoms cm^{-2}.

† Errors quoted in parenthesis (except for Kapton®) are simply the RMS roughness of the exposed area. This is usually much rougher than the unexposed.

Some general observations may be made on the results in Table 1. With the exception of polytetrafluoroethylene (PTFE), all the reactivities are the same within a factor of 2 for polymers of widely different chemical nature. Reaction rates may be controlled by an adsorption process involving a precursor step which is largely independent of the nature of the surface. The reaction rates of polystyrene and polyvinyltoluene are very similar, as are their structures (they differ only in that

PVT has a $-CH_3$ group attached to the benzene ring of polystyrene). However, the rate for polyethylene is about the same, even though no benzene ring is present at all. While aromatic structures often confer stability against environmental degradation such as autoxidation or thermal oxidation in normal air, this is not noticeably true in the case of oxidation by fast AO. This is good evidence that surface oxidation is proceeding by different mechanisms in the two cases. The reactivity of PTFE, lower by a factor of 10 than the other polymers listed, is attributed to the failure of the hydrogen-abstraction mechanism for oxidation of this fully fluorinated molecule.

Table 2 compares reactivities of erodible materials which were both flown on STS-8 and on LDEF. Nylon and polyvinyltoluene were not flown on STS-8. Some carbon results are shown here, but do not include the glassy or vitreous isotropic carbons, which were not included on LDEF.

Table 2. Comparison of erosion yields from LDEF experiment A0114 with previous data from STS-8 and STS-41g.

Material	Erosion Yields†; $cm^3 \times 10^{-24}$ (oxygen atom)$^{-1}$	
	LDEF Value (this work)	Prior Value
Kapton®	2.89±0.06	3.00**
PTFE (or FEP)	0.37±0.06	0.1–0.5
polyethylene	3.97±0.23	3.32–3.74
PMMA	6.3 ±0.3	4.91*
polystyrene	4.17±0.17	1.7
Carbon; (HOPG)	1.04	0.6*
Carbon; pyrolytic polycrystalline	0.61	0.58

*Indicates UAH measurement on STS-8. Other values are from tabulations of others' data by JSC and LeRC.

**Error not quoted, may be 10 to 20 percent.

†Erosion yields for LDEF are based on a preliminary fluence of 9.0×10^{21} atoms cm^{-2}.

The comparison in data in the case of Kapton® is particularly noteworthy because of the large number of reactivity measurements that have been reported from STS-8 and elsewhere (though not by our group). The details of the UAH LDEF Kapton® measurement are reported elsewhere (ref. 4). This value $(2.89 \pm 0.06) \times 10^{-24}$ cm^3 $atom^{-1}$ is within 3 percent of the normally quoted value of 3.0 based on many measurements. The reactivity of Kapton® is usually quoted without errors, but these might reasonably be about ±10 percent. It is interesting to note that the silicone contamination known to be present on LDEF (and indeed on all shuttle-borne vehicles) does not seem to affect the linearity of the erosion. Perhaps the silicones aggregate upon adsorption or oxidation, or perhaps adsorption is low on these materials. It is, however, well known that if a continuous film of SiO_2 is actually formed, such a film is very effective in preventing oxidation by fast AO.

The fluorinated polymer flown on A0114 was a commercial grade bulk PTFE. The measured rate of $(0.37 \pm 0.06) \times 10^{-24}$ cm^3 $atom^{-1}$ is within the range of reported prior values for PTFE and FEP at lower fluences.

Our value for polyethylene from LDEF is a little higher than the range of values reported by others from STS-8. (We did not include polyethylene on our STS-8 experiment). However, the values are still within experimental errors. Our value for PMMA of $(6.3\pm0.3)\times10^{-24}$ cm^3 $atom^{-1}$ is higher than our own STS-8 value (4.91) and considerably higher than the tabulated values of others. In the case of polystyrene (which we did not fly on STS-8), the difference is even greater from the reported values of others. These other values were obtained by weighing, a technique which underestimates the erosion rate if nonerodible contamination is present.

SUMMARY AND CONCLUSIONS

In general, agreement is good between erosion rates or reactivities obtained from the LDEF experiment AO114 and prior flight data obtained at much lower mission fluences. Agreement is particularly satisfactory in the case of Kapton®, for which the prior data base is large and which is often used as a reference material for comparing erosion rates obtained in terrestrial simulators. Within experimental errors, LDEF and STS-8 reactivities are also in good agreement for PTFE, polyethylene, PMMA (Lucite) (our values), and pyrolytic polycrystalline graphite. Our LDEF value for PMMA and polystyrene is about twice that of earlier data at lower fluences obtained by weighing. The value for HOPG or "single-crystal" graphite obtained from LDEF appears high, but we note that there was only one small sample of this material available.

Polymers consisting only of C, H, O, and N show reactivities which are both independent of fluence and remarkably similar to each other despite great differences in chemical structure. Low reactivities are exhibited by polymers (e.g., graphite, PTFE) for which the H-abstraction process by fast oxygen is not possible.

On the other hand, reactivities higher than average are shown by materials like PMMA, which is known to depolymerize, or "unzip" readily upon heating, and by CR-39 (ref. 1) which has a high oxygen content to begin with.

Erosion measurements by stylus profilometry of these highly erodible materials does not appear to be affected by surface silicone contamination occurring during shuttle flights.

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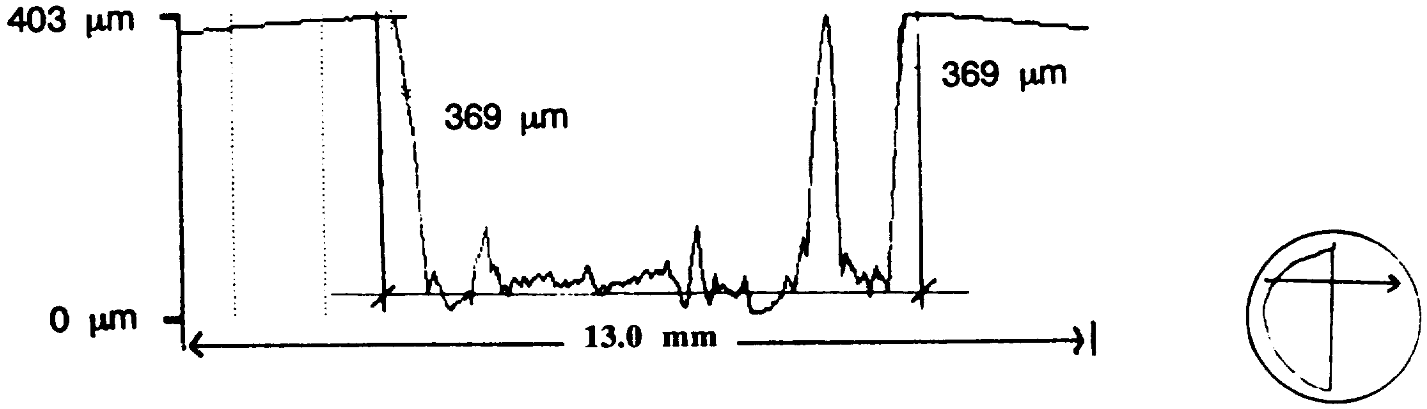
a) Sample C9H-12 Polystyrene.



b) Sample C9-47 Polystyrene.

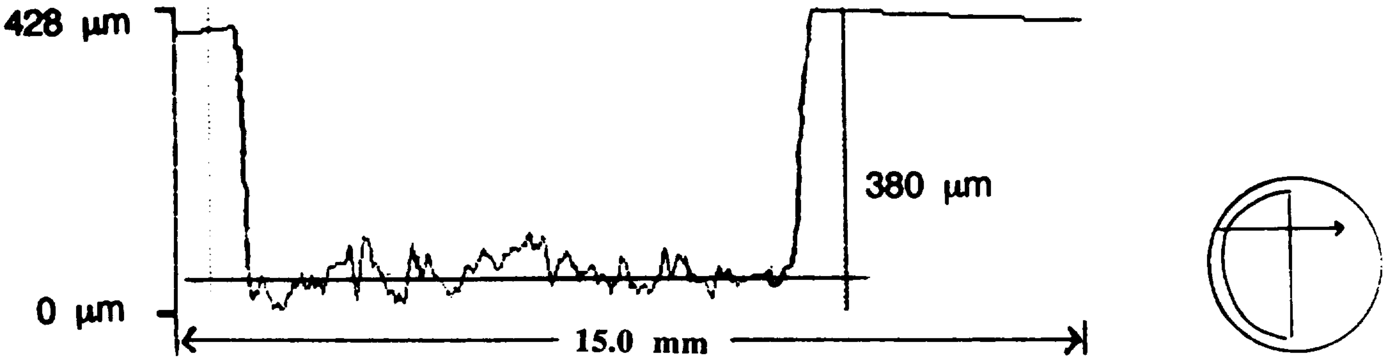


Figure 1. Taylor-Hobson Talysurf profilometry scans of two polystyrene solid samples exposed on the C0 leading surface of LDEF (experiment AO114).

The diagram to the right of each scan shows the physical location of the trace across the 1-in samples. The inverted D-shaped portion of the sample was that exposed to fast oxygen atoms, while the surrounding portion was protected with a mask. Each horizontal scan is about 1/2 inch in length. The different vertical scale should be noted. In spite of considerable roughness induced after prolonged etching, repeated scans in different portions of these samples yield an etch value reproducible to about 5 percent.