

## AN XPS STUDY OF SPACE-EXPOSED POLYIMIDE FILM

Myung Lee, William Rooney, and James Whiteside

Grumman Corporate Research Center  
Bethpage, New York 11714  
Phone: (516)575-2354; Fax:(516)575-7716

## SUMMARY

X-ray photoelectron spectroscopy was used to assess changes induced in the surface chemistry of Kapton H (Du Pont Trademark) polyimide strips exposed to the low Earth orbit environment at the space-end of the LDEF satellite on Experiment A0133. Results from flight specimens are compared to material cut from the same lot and stored at room temperature under standard atmospheric conditions. One notable difference was a nearly two-fold increase in surface oxygen (atom-percent composition) for specimens exposed to the direct space environment as compared to controls. In addition, space exposed specimens contained distinct silicon peaks (2p 103.2 eV and 2s 154.2 eV) in their spectra. These peaks were absent in control spectra. It is likely that the increase in oxygen is associated with the silicon. This is in agreement with reports of widespread silicon contamination throughout the LDEF satellite.

## INTRODUCTION

Initial studies of Kapton H (Du Pont Trademark) polyimide film exposed to the low Earth orbit (LEO) space experiment on LDEF Experiment A0133 revealed no significant differences in bulk physical-chemical properties when compared to either ground or space control specimens despite the fact that space exposed specimens suffered significant weathering with surface erosions of approximately 8.0  $\mu\text{m}$  (1). It has been proposed that the primary mechanism of polyimide degradation in LEO involves the interaction with high velocity atomic oxygen. Damage induced by atomic oxygen is largely localized at the surface of the polyimide and it is likely that the surface is continually refreshed by a sputtering type mechanism. Therefore, techniques that measure primarily bulk physical-chemical properties are unlikely to have the sensitivity to detect changes localized at the surface.

X-ray photoelectron spectroscopy (XPS) has been used to detect changes induced in the surface chemical composition of polyimide films exposed to reactive oxygen atmospheres. Egitto and coworkers (2) observed an increase in the relative amount of high binding energy peaks in the carbon 1s spectrum of a polyimide exposed to a pure oxygen plasma in an Earth based reactor. A report by Golub et al. (3) describes an increase in surface oxygen concentration for polyimide specimens that had been exposed to

oxygen in either an earth based rf plasma reactor or LEO space environment for a short duration (ca. 40 hrs) during shuttle mission STS-8.

In this communication we report results from an XPS study of Kapton H polyimide films exposed to the LEO for approximately 5.8 years during the LDEF mission.

## METHODS

Kapton H polyimide sheets with a thickness of 127  $\mu\text{m}$  (5 mil) were obtained from Du Pont. Three unique specimen groups were analyzed. Two groups were recovered from the LDEF satellite (space end, bay H row 7) and one group remained in storage at room temperature under Earth ambient atmosphere. Of the two groups recovered from the LDEF satellite, one group had direct exposure to the LEO space environment and the other was protected from the direct space exposure by 0.32 cm butted aluminum plate. We shall refer to the former as space exposed and the latter as space control specimens. The material that remained on Earth will be referred to as ground control. The LDEF experiment A0133 module and specimens have been described in detail elsewhere (1).

Prior to XPS all specimens were placed in a room temperature trichloroethylene ultrasonic bath for ten minutes to remove labile surface contaminants. Following the ultrasonic bath the specimens were dried in a stream of nitrogen gas and placed in the XPS chamber for analysis. The chamber was evacuated to a base pressure of  $2 \times 10^{-10}$  torr. All spectra were acquired on a Leybold AG XPS spectrometer at room temperature using a non-monochromatic Mg K-alpha (1253.6 eV) x-ray as the excitation source produced by a power supply operating at 12 kV and 10 mA. Survey spectra were acquired from 0-1260 eV for qualitative analysis. Semi-quantitative analysis was performed on elemental scans obtained over the energy ranges of 95-160 eV, 274-296 eV, 396-406, and 520-540 eV for silicon, carbon, nitrogen and oxygen, respectively. Peaks were fitted using software provided by Leybold AG with relative intensities determined using photoemission sensitivity factors provided by the manufacturer.

## RESULTS

Representative XPS survey spectra obtained from ground control, space control, and space exposed specimens are presented in panels a, b, and c of Figure 1. All three specimens contain carbon, nitrogen and oxygen as the principal constituents at the surface. The XPS 1s peaks of these constituents appear in Figure 1 at about 285 eV, 400 eV and 533 eV, respectively. Auger peaks associated with oxygen (KVV1, ca. 748 eV and KVV2, ca. 769 eV) and carbon (KLL, ca. 995 eV) also are apparent. A striking observation is the appearance of peaks at about 103.2 and 154.2 eV in spectra obtained from space exposed specimens; peaks that are not present in either ground or space control spectra. We assign these peaks to silicon  $2p_{1/2}$  and 2s, respectively. Also evident is an increase in the relative intensity of the oxygen peak in the spectrum of the space exposed specimen (Figure 1c) compared to spectra obtained from controls. The peak at about 230 eV in Figure 1b (indicated by asterisk) is from Mo substrate.

Additional chemical information can be obtained through spectral deconvolution of peaks obtained during individual elemental scans. The two silicon peaks of the space samples were baseline resolved and each could be well fitted with a single component. Likewise, the single nitrogen peak of all specimens was well fitted with a single component. This is in contrast to the carbon and oxygen peaks of all specimens that exhibited substantial fine structure and required peak deconvolution. The results of

spectral deconvolutions were used to extract semiquantitative surface composition. The chemical information from the XPS elemental scans for ground control and space exposed specimens is collected in Table 1. The binding energy data for both specimen groups has been referenced to carbon 1s (C-C) at 284.6 eV. The values in parenthesis in Table 1 represent elemental fractional contributions.

## DISCUSSION

Parameter extraction from XPS spectra yields information on electronic binding energies and intensities. Binding energy provides information on chemical state and peak intensity provides information on stoichiometry. The binding energies extracted from the ground control specimen were within 0.2 eV of values reported by other workers (2,3). The space exposed specimens had binding energies that were consistently shifted to higher values, typically by 0.5 eV, relative to the ground control specimen. This could be due to differences in surface charging between the samples since the values in Table 1 were not chemical shift referenced. We have data that demonstrates differences in the surface charging profiles for these three specimen groups (4). However, referencing to carbon 1s at 284.6 eV, as has been done in Table 1, brings all binding energies into excellent agreement with previous reports.

The composition of the ground control polyimide determined from XPS is in fair agreement with expected values. However, consistent differences between measured and expected values were obtained. In particular, carbon and nitrogen were deficient by six and two atom percent, respectively. Oxygen, on the other hand, was in excess by about seven atom percent. Assuming that sensitivity factors provided by the manufacturer are correct for the XPS spectrometer, differences could be attributed to non-ideal surface stoichiometry possibly including strongly adsorbed H<sub>2</sub>O. As expected three carbon peaks, two oxygen peaks and a single nitrogen peak were extracted from the XPS spectra obtained from all polyimide specimens. The ratios of intensities obtained from the various sub-peaks of ground control specimens are essentially in agreement with values reported by other workers (2,3).

In comparison to the control specimens the space exposed specimens had a greatly enriched surface concentration of oxygen as determined from XPS. It is likely that the increase in oxygen for the space exposed specimens is associated with silicon containing surface contaminants deposited during the LDEF mission, since silicon peaks were always observed in XPS spectra of space exposed specimens showing greatly increased oxygen. Furthermore, the binding energy of the silicon (2p<sub>1/2</sub> 103.5 eV and 2s 154.5 eV) indicates direct silicon-oxygen chemical bonding apparently very similar to SiO<sub>2</sub> or a silicon sub-oxide (5). This is in agreement with the binding energy of Si deposited on Kapton at the leading edge of the LDEF satellite as reported by Young and coworkers (6). It is interesting to note that an XPS spectrum obtained from a space exposed region that was shielded from the atomic oxygen showed only a trace of silicon (spectrum not shown). Infrared and EDS data from our lab (1) and from others (7) indicates that in addition to silicon, organics are also present in the surface contaminants. However, it does appear that most of the increased oxygen is associated with silicon. Assuming an SiO<sub>2</sub> stoichiometry most of the 15-20 atom percent increase in oxygen can be accounted for with a 7-10 atom percent of silicon. In addition, the ratio of carbon sub-peaks to total carbon does not change appreciably between ground control and space exposed specimens. The contaminants have been attributed to satellite outgassing followed by condensation and activation in the energetically (uv, AO, e-, etc.) rich LEO environment. It is interesting to note that these contaminants were not removed by trichloroethylene in the ultrasonic bath and appear to be strongly associated with the Kapton surface.

## ACKNOWLEDGMENTS

Dr. Richard DeIasi directed the design and integration of Experiment A0133. We thank Jerry DeCarlo for assisting in the collection and processing of XPS data.

## REFERENCES

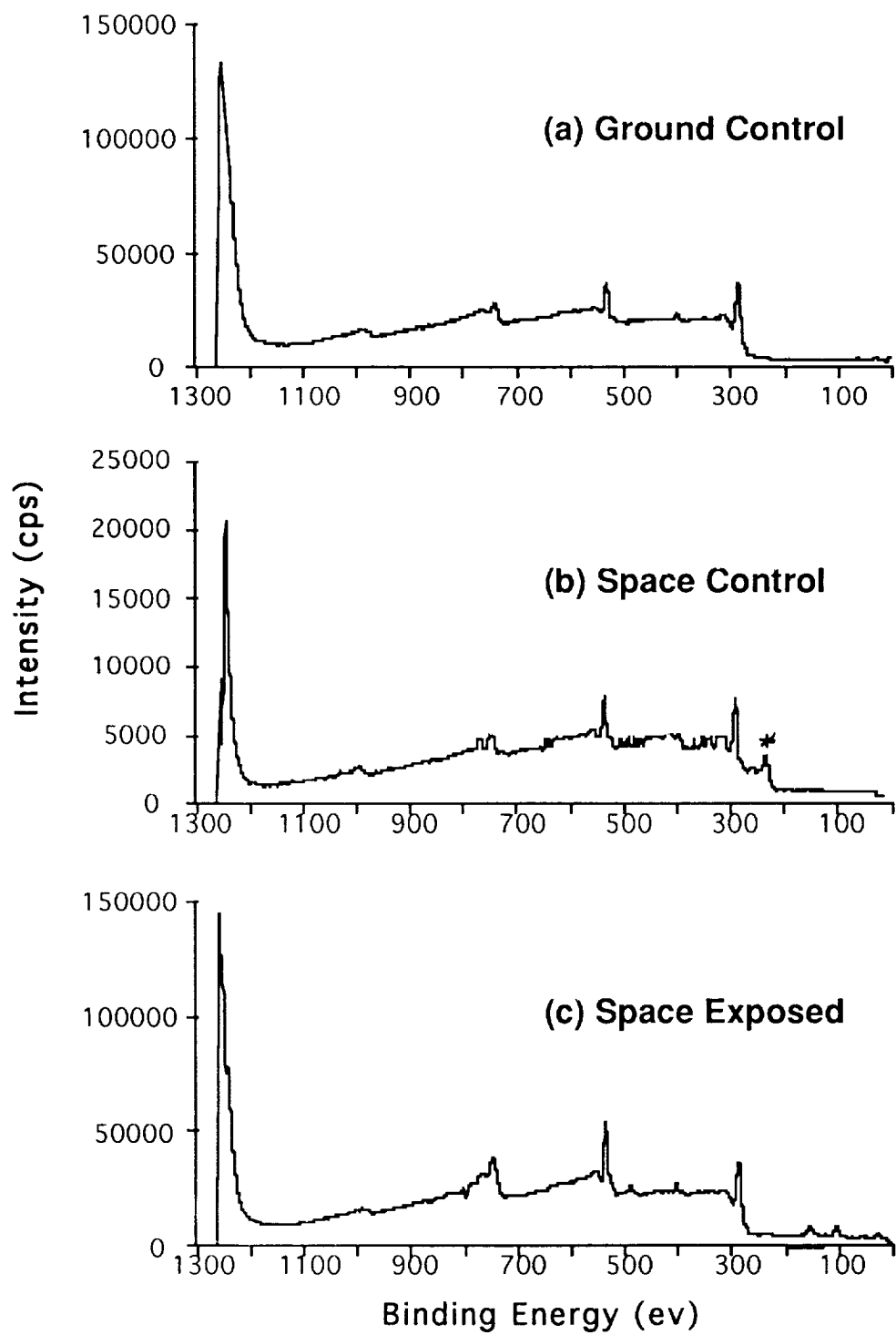
1. Whiteside, J.B.; Giangano, D.; Heuer, R.L.; Kamykowski, E.; Kesselman, M.; Rooney, W.D.; Schulte, R.; and Stauber, M.: LDEF Conference Proceedings, Kissimmee Florida, June 1991
2. Egitto, F.D.; Emmi, F.; Horwath, R.S.; and Vukanovic, V.: *Journal of Vacuum Science Technology B* 3 893 (1985)
3. Golub, M.A.; Wydeven, T.; and Cormia, R.D: *Polymer Communications* 29 285 (1988)
4. Walters, W.S: private communication (1991)
5. Briggs, D; and Seah, M.P., eds: *Practical Surface Analysis 2<sup>nd</sup> Edition Volume 1: Auger and Photoelectron Spectroscopy* Wiley, 1990
6. Young, P. R.; Slemp, W.S.; Witte, Jr., W.G.; and Shen, J.Y.: 36th International SAMPE San Diego CA, April 15-18 1991
7. Young, P. R.; Slemp, W.S.; and Gautreux, C.R.: 37th International SAMPE Anaheim CA, March 9-12 1992

## FIGURE LEGENDS

Figure 1. XPS survey spectra for ground control, space control and space exposed Kapton specimens. The asterisk in panel b (ca. 230 eV) indicates contamination by Mo substrate.

Table 1. Summary of XPS Results

	ground control		space exposed	
	B.E. (eV)	atom %	B.E. (eV)	atom %
<b>Si 2s</b>			154.3	8.8
<b>C 1s</b>	284.6	28.1(0.40)	284.6	20.1(0.40)
	285.7	34.1(0.48)	285.6	24.6(0.50)
	288.6	<u>8.2(0.12)</u>	288.6	<u>5.0(0.10)</u>
<i>subtotal</i>		70.3(1.00)		49.7(1.00)
<b>N 1s</b>	400.7	4.9	400.7	0.82
<b>O 1s</b>	532.4	17.4(0.70)	532.5	17.2(0.42)
	533.7	<u>7.3(0.30)</u>	533.3	<u>23.6(0.58)</u>
	<i>subtotal</i>		24.7(1.00)	



**Figure 1.** XPS survey spectra for ground control, space control and space exposed Kapton specimens