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NASA FINAL SUMMARY REPORT

TITLE:	**SURFACE ANALYSIS OFLDEF MATERIALS**
GRANT NO:	**NAG-1-1186**
INSTITUTION:	**VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY**
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SUMMARY

The majority of the research accomplished under this grant was summarized in the M.S. thesis of Ms. Holly L. Grammer. Six papers have been presented at technical meetings based on the results obtained in Grammer's thesis. In addition, two refereed papers have been published. Details of the thesis, presentations, and publications are noted below.

The remaining part of the research accomplished under this grant was concerned with the surface analysis of materials originating within four separate groups at NASA - LARC. Details of these projects are also noted below.

Thesis:

**(1) H. L. Grammer, Surface Characterization of NASA-LDEF Materials", M. S. (Chemistry), July 1993.

** This thesis was submitted to NASA - LARC in late 1995 to be issued as a NASA Technical Publication. An Abstract of this thesis is included in the Appendix.

Presentations:

(1) H. L. Grammer, P . R. Young and J. P. Wightman, "X-ray Photoelectron Spectroscopic Analysis of Materials from the NASA-LDEF Satellite", 70th Annual Meeting Virginia Academy of Science, Richmond, VA, May, 1992.

(2) T. F. Cromer, H. L. Grammer, J. P. Wightman, P. R. Young and W. S. Slemp, "Surface Characterization of Selected LDEF Tray Clamps", 2nd LDEF Post Retrieval Symp., San Diego, CA, June, 1992.

(3) H. L. Grammer, P . R. Young and J. P. Wightman, "XPS Analysis of LDEF Materials", 66th Colloid & Surface Science Symp., Morgantown, WV, June, 1992.

(4) H. L. Grammer, J. P . Wightman and P . R. Young, "Surface Characteristics of LDEF Materials", 67th Colloid & Surface Science Symp., Toronto, CANADA, June, 1993.

(5) H. L. Grammer, J. P. Wightman, W. S. Slemp and P. R. Young, "Surface Analysis of Materials from NASA-LDEF Satellite", 3rd LDEF Post Retrieval Symp., Williamsburg, VA, November, 1993.

(6) [Invited] J. P. Wightman, "The NASA - LDEF Satellite - A National Materials Treasure", Virginia Academy of Science, Lexington, VA, May, 1995.

Publications:

(1) T. F. Cromer, H. L. Grammer, J. P. Wightman, P. R. Young and W. S. Slemp, "Surface Characterization of Selected LDEF Tray Clamps", in **LDEF - 69 Months in Space**, A. S. Levine, ed., pp 1015-1022, NASA Conference Publication 3194, Pt 3, NASA, Hampton, VA (1993).

(2) H. L. Grammer, J. P. Wightman, P. R. Young and W. S. Slemp, "Surface Characterization of LDEF Carbon Fiber/Polymer Matrix Composites", in **LDEF - 69 Months in Space**, A. S. Levine, ed., pp 601-612, NASA Conference Publication 3275, Pt 2, NASA, Hampton, VA (1995).

The above papers are included in the Appendix.

Projects:

In addition to the above research on LDEF materials, surface analyses were also done on four separate projects as requested by personnel at NASA-LARC. Details of these projects are noted below.

(1) NASA Technical Contact: Bob Yamaki

Requested Analysis: XPS analysis of EOIM-III carbon/carbon composites

Date: 10/17/94

(2) NASA Technical Contact: John W. Connell

Requested Analysis: XPS analysis of LEO polymer films

Date: 12/12/94

(3) NASA Technical Contact: A. K. StClair/R. L. Kiefer

Requested Analysis: XPS analysis of Ultem films

Date: 6/20/95

(4) NASA Technical Contact: John Stadler

Requested Analysis: XPS analysis of laser components

Date: 7/15/95

The results of each of these projects were summarized in a letter report to the NASA technical contacts listed above.

APPENDIX

H. L. Grammer, "Surface Characterization of NASA-LDEF Materials", M. S. thesis (Chemistry), Virginia Polytechnic Institute and State University, Blacksburg, VA, July 1993.

SURFACE CHARACTERIZATION OF LDEF MATERIALS

by

Holly L. Grammer

Committee Chairman: Dr. James P. Wightman

Chemistry

(ABSTRACT)

The NASA Long Duration Exposure Facility (LDEF), a passive experimental satellite, was placed into low-Earth orbit by the Shuttle Challenger in April 1984. The LDEF spent an unprecedented 69 months in space. The flight and recovery of the LDEF has provided a wealth of information on the long-term space environmental effects of a variety of materials exposed to the low-Earth orbit environment.

Surface characterization of LDEF materials included polymers, composites, thermal control paints, and aluminum: X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), scanning electron microscopy (SEM), and contact angle analysis were used to document changes in both the surface composition and surface chemistry of these materials. Detailed XPS analysis of the polymer systems, such as Kapton®, polyimide polysiloxane copolymers, and fluorinated ethylene propylene thermal blankets on the backside of the LDEF revealed significant changes in both the surface

composition and surface chemistry as a result of exposure to the low-Earth orbit environment. Polymer systems such as Kapton®, polyimide polysiloxane copolymers, and polysulfone showed a common trend of decreasing carbon content and increasing oxygen content with respect to the control sample.

Carbon 1s curve fit XPS analysis of the composite samples, in conjunction with SEM photomicrographs, revealed significant ablation of the polymer matrix resin to expose the carbon fibers of the composite during exposure to the space environment.

Surface characterization of anodized aluminum tray clamps, which were located at regular intervals over the entire LDEF frame, has provided the first results to evaluate the extent of contamination with respect to position on the LDEF. The XPS results clearly showed that the amount and state of both silicon and fluorine contamination were directly dependent upon the position of the tray clamp on the LDEF.

in **LDEF - 69 Months in Space**, A. S. Levine, ed., pp 1015-1022, NASA Conference Publication 3194, Pt 3, NASA, Hampton, VA (1993).

SURFACE CHARACTERIZATION OF SELECTED LDEF TRAY CLAMPS

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SUMMARY

The surface characterization of chromic acid anodized 6061-T6 aluminum alloy tray clamps has shown differences in surface chemistry depending upon the position on the LDEF. Water contact angle results showed no changes in wettability of the tray clamps. The overall surface topography of the control, trailing edge(E3) and leading edge(D9) samples was similar. The thickness of the aluminum oxide layer for all samples determined by Auger depth profiling was less than one micron. XPS analysis of the tray clamps showed significant differences in the surface composition. Carbon and silicon containing compounds were the primary contaminants detected.

INTRODUCTION

One of the tasks of the MSIG (Materials Special Investigation Group) is the detailed analysis of the chromic acid anodized 6061-T6 aluminum alloy tray clamps. These tray clamps were located at regular intervals over the entire LDEF frame and were exposed to varying amounts of atomic oxygen and vacuum ultraviolet radiation.

A detailed study of the relatively small but statistically significant changes in the optical properties of 228 anodized clamps has been reported [1]. However, there has been no systematic study reported of the effect of low-earth orbit (LEO) environment on the surface chemistry of these clamps.

The objective of this work was to document changes in the surface chemistry of tray clamps taken from different locations on LDEF. Surface characterization of the anodized aluminum clamps using contact angle measurements, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), Auger electron spectroscopy (AES), and x-ray photoelectron spectroscopy (XPS) is reported.

EXPERIMENTAL

The surface analytical techniques used in the characterization of the surface of the seven anodized aluminum tray clamps (control and six flight) are described below. Tray clamps were cut manually to prevent heating of the sample as well as possible contamination of the surface when cutting. Typical sample sizes were 13mm x 13mm. Surface characterization techniques were used in the following order due to the nondestructive/destructive aspects of the analyses: XPS, SEM/EDS and AES. Water contact angle measurements were made to evaluate the wettability of the aluminum surface using a Rame-Hart 100-00115 NRL goniometer equipped with a video monitor. Different samples were used for the contact angle measurements.

Surface topography was examined by scanning electron microscopy using an ISI-SX-40 microscope operating at 20kV beam voltage. Near surface/bulk (1-5mm) elemental analysis was performed using a Tracor Northern energy dispersive spectrometer. Auger electron spectroscopy-depth profiling was performed on a Perkin-Elmer PHI-610 spectrometer operating at an electron beam voltage/current of 3kv/0.05mA and an argon ion beam voltage/current of 4kV/20mA. X-ray photoelectron spectroscopy was performed utilizing a Perkin-Elmer PHI 5400 spectrometer equipped with a Mg Ka X-ray source (1253.6eV), operating at 15kV/120mA.

The flight samples were located at the following positions on the LDEF: E3 (trailing edge), B4 (near trailing edge), D7 (near leading edge), D9 (leading edge), H9 (space end), and G2 (earth end).

RESULTS/DISCUSSION

Contact Angle

Water contact angle measurements were used to evaluate the wettability of the clamp surface. The results are listed in Table I. An average water contact angle of 62° was calculated for the seven samples independent of location. The high water contact angles on the clamps are indicative of low energy surfaces such as polymers [2]. A near zero contact angle would be expected for a clean anodized aluminum surface [3]. As shown by the results, no changes in wettability of the clamps were observed due to exposure to the low-earth orbit environment.

Scanning Electron Microscopy/Energy Dispersive Spectroscopy

SEM photomicrographs of the control, leading (D9) and trailing (E3) edge samples are shown in Figure 1. The overall surface topography of the three samples is similar. No significant change in the surface topography was evident for the leading compared to the trailing edge samples.

Energy dispersive spectroscopy(EDS) is a near surface/bulk elemental analysis technique. The EDS results for the tray clamps are listed in Table II. An average composition of fifty-two weight percent aluminum and forty-eight weight percent oxygen was determined for the three samples. These results are consistent with the calculated weight percent of aluminum(53%) and oxygen(47%) for Al_2O_3. Aluminum and oxygen were the only elements detected by EDS in the sampling depth of 1-5mm.

Auger Electron Spectroscopy

Auger depth profiling was used to determine the thickness of the oxide layer on five of the clamps. The depth profile of the space end (H9) sample is shown in Figure 2 which is representative of the other samples. The thickness of the aluminum oxide layer was calculated at the time when the oxygen and aluminum signals cross. Aluminum with an oxide layer of known thickness was used as a standard to determine the sputtering rate. Aluminum oxide thickness values are listed in Table III. The average thickness of 0.82 mm is consistent with the results of Plagemann [1] who concluded from SEM measurements that the oxide thickness was <1mm. The range in oxide thickness from 0.6 to 1.0 mm for the trailing edge (E3) and space end (H9) samples respectively can not be attributed to the LEO environment but in fact may be a result of variation in the anodization conditions.

X-Ray Photoelectron Spectroscopy

The XPS results shown in Table IV for the LDEF tray clamps are reported as binding energy (B.E.) in eV and atomic concentration (A.C.) in %. All photopeaks were referenced to the C 1s photopeak taken at 285.0 eV. The largest amount (53%) of carbon-containing organic contamination was detected on the control sample. However, significant quantities of this same contamination were found on all the LDEF tray clamps. There is no discernible correlation of the surface atomic concentration of carbon with clamp position. This carbon contamination as determined by XPS is indicative of a hydrophobic surface and is consistent with the high water contact angles determined on the same surfaces (see Table I). If the control surface were clean, the expected atomic concentration of aluminum and oxygen for a 1mm aluminum oxide (Al_2O_3) surface layer would be 40% and 60% respectively; and, the O/Al atomic concentration ratio would be 1.5. The fact that the atomic concentration of aluminum is only 11% is prima facie evidence that an ultra-thin layer of carbon-containing organic contamination covers the aluminum oxide surface. The thickness of these contamination layers cannot be more than 5 nm otherwise no aluminum signal would have been detected. The fact that the O/Al ratio is nearly 3 also suggests that this contamination layer contains oxygen in addition to carbon. It is recognized that some of the excess oxygen is probably associated with the silicon which was also detected on the control sample. The sources of the small quantities of nitrogen, sulfur and sodium detected on the control sample were not identified.

It is noteworthy that the silicon content of all flight samples exceeded that of the control sample form 4 to 16 times. Thus, these XPS results further support the case for extensive silicon contamination of the LDEF clamps [4]. Again, there was no discernible correlation of the surface atomic concentration of silicon with clamp position. On the other hand, there was definitive shift in the binding energy of silicon on the clamps (D7, D9, H9,G2) which received a higher atomic oxygen fluence compared to those clamps (E3, B4, control) receiving a lower atomic oxygen fluence. This definitive shift in binding energy of $1.1_8 \pm 0.1_7$ correlates to a change in the state of silicon contamination. The organo-silicon (lower B.E.) material contained in the contamination on the clamps subjected to a higher atomic oxygen fluence was converted to an inorganic-silicon (higher B.E.) or silicate type material. Such an effect of atomic oxygen on organo-silicon material has been noted previously [5].

The fluorine contamination detected on all the flight samples is in the form of inorganic fluorine (fluoride) with a binding energy of 686 eV. In contrast, the binding energy of fluorine in a fluoropolymer is approximately 689 eV. The fluorine contamination present in the ion

form may be a result of the degradation effects of vacuum ultraviolet radiation on the carbon-fluorine bonds of fluoropolymers such as fluoroethylene propylene copolymer (FEP) on the backside of the satellite.

Trace amounts of sulfur, nitrogen and sodium contamination were present on the majority of the flight samples as well as the control. The source of the contamination may be a result of preflight or post flight handling.

ACKNOWLEDGEMENTS

The authors (T.F.C., H.L.G. and J.P.W.) acknowledge the support of this research under NASA Grant NAG-1-1186.

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TABLE I

WATER CONTACT ANGLES ON LDEF TRAY CLAMPS

SAMPLE LOCATION	θw
Control	61°
E3	64°
B4	66°
D7	63°
D9	66°
H9	63°
G2	54°

TABLE II

ENERGY DISPERSIVE ANALYSIS OF LDEF TRAY CLAMPS

SAMPLE	ALUMINUM (wt%)	OXYGEN (wt%)
Control	54.	46.
E3	53.	46.
D9	49.	50.

TABLE III

THICKNESS OF OXIDE LAYER ON LDEF TRAY CLAMPS

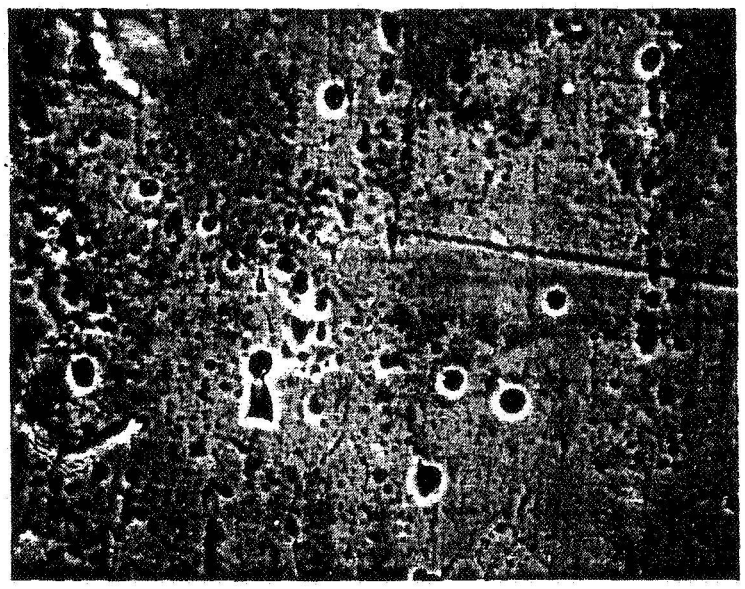
SAMPLE	τ(nm)
Control	785
E3	1005
D9	865
H9	765
G2	665

TABLE IV

XPS ANALYSIS OF LDEF TRAY CLAMPS

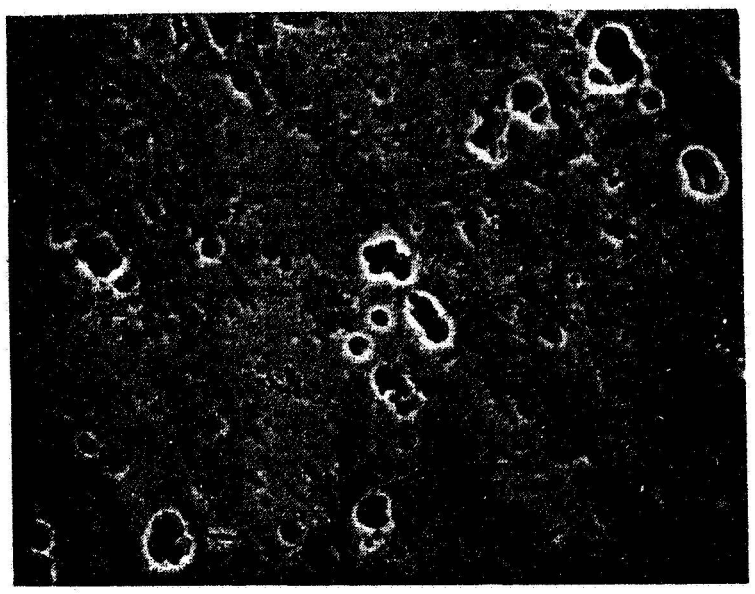
	SAMPLES						
PHOTOPEAKS	Control	E3	B4	D7	D9	H9	G2
C1s A.C. (%)	53.2	27.8	28.0	16.5	20.7	16.6	30.0
B.E. (eV)	285.0	285.0	285.0	285.0	285.0	285.0	285.0
Al2p	11.4	17.6	15.8	17.0	4.9	15.8	8.2
	74.6	74.7	74.6	74.6	74.8	74.6	74.7
O1s	31.0	46.8	47.2	53.4	51.1	52.4	43.5
	532.2	532.3	533.1	532.4	533.0	532.5	532.6
Si2p	1.4	6.0	6.1	10.5	22.6	11.0	13.1
	102.2	102.1	102.2	103.2	103.6	103.3	103.4
N1s	1.8	0.6	1.3	0.3	--	0.3	1.4
	399.9	400.2	400.2	400.6		400.1	400.4
S2p	0.6	0.3	0.4	0.3	--	0.9	--
	169.0	169.5	169.6	169.6		169.5	
Na1s	0.7	0.6	0.7	0.7	--	1.4	1.5
	1072.2	1072.8	1073.0	1072.8		1072.9	1072.7
F1s	--	0.3	0.5	1.5	0.7	1.5	2.4
		686.3	686.4	686.1	686.5	686.5	686.6

CONTROL 0.5 KX



E3 0.5 KX

FIGURE 1: SEM PHOTOMICROGRAPHS OF LDEF TRAY CLAMPS.



D9 0.5 KX

FIGURE 1: CONCLUDED.

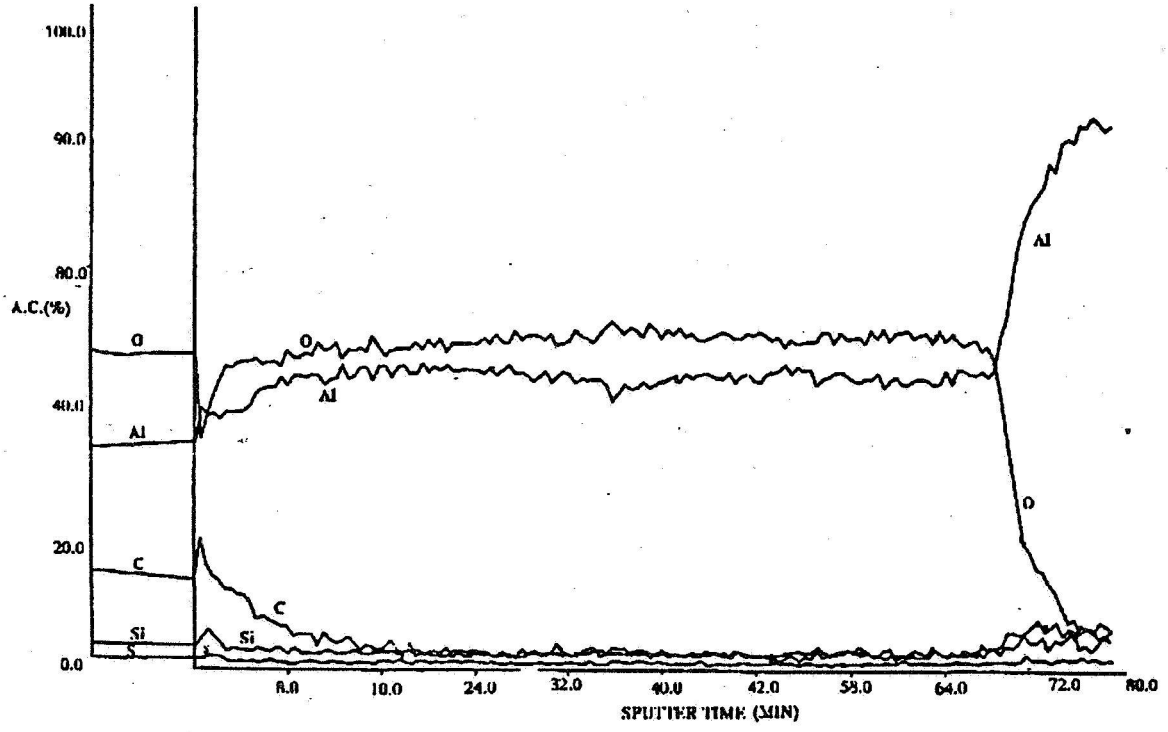


FIGURE 2: AUGER DEPTH PROFILE OF LDEF TRAY CLAMPS.

in **LDEF - 69 Months in Space**, A. S. Levine, ed., pp 601-612, NASA Conference Publication 3275, Pt 2, NASA, Hampton, VA (1995).

SURFACE CHARACTERIZATION OF LDEF CARBON FIBER/POLYMER MATRIX COMPOSITES

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SUMMARY

XPS (x-ray photoelectron spectroscopy) and SEM (scanning electron microscopy) analysis of both carbon fiber/epoxy matrix and carbon fiber/polysulfone matrix composites revealed significant changes in the surface composition as a result of exposure to low-Earth orbit. The carbon 1s curve fit XPS analysis in conjunction with the SEM photomicrographs revealed significant erosion of the polymer matrix resins by atomic oxygen to expose the carbon fibers of the composite samples. This erosion effect on the composites was seen after 10 months in orbit and was even more obvious after 69 months.

INTRODUCTION

One of the tasks of the MSIG (Materials Special Investigation Group) is the detailed analysis of LDEF composites. Stein presented a summary of the findings of the LDEF materials studies on polymer-matrix composites and noted that atomic oxygen causes surface degradation of uncoated composites but that thin inorganic coatings prevent atomic oxygen erosion [1]. George and Hill [2] using SEM reported a similar highly eroded topography for both epoxy matrix and polysulfone matrix/carbon fiber composites due to reaction with atomic oxygen. A lack of resin on the exposed (leading edge) surfaces was determined by infrared spectroscopy. Sulfur present in the curing agent of the epoxy resin and sulfur in the polysulfone backbone was presumed to react with atomic oxygen to produce sulfate species on the exposed surfaces of both composites.

Measured decreases in the thickness of epoxy and polysulfone matrix/carbon fiber composites on the leading edge have been reported by Slemp et al.[3] in the range of 75 - 115 mm. Whitaker et al. [4] noted that the measured thickness decrease for the polysulfone matrix (110 mm) was about 50% greater than for the epoxy matrix (70 mm). It was also noted that erosion due to atomic oxygen was much greater for the matrix resin than for the carbon fibers. A detailed XPS study of poly(arylacetylene) matrix/carbon fiber composites on the leading edge has been reported by Mallon et al. [5]. The presence of inorganic silicon at 103.5 eV was noted on the exposed surface.

The objective of the present work was to document changes in the surface chemistry of composite samples taken from LDEF. Surface characterization results obtained using x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) are reported. These results

are a part of a larger study [6] where surface characterization techniques were used to examine polymer films and aluminum tray clamps taken from LDEF.

EXPERIMENTAL

Materials

An epoxy matrix composite (934/T300) and a polysulfone matrix composite (P1700/C6000) were studied. The epoxy and polysulfone matrix resins were produced by Fiberite and Union Carbide, resp. The T300 and C6000 carbon fibers were produced by Union Carbide and Celanese, resp. A control and two flight samples exposed for 10 and 69 months of each composite were studied. The flight samples were located on Tray B, Row 9 of the LDEF. The flight samples were cut from larger panels processed at the NASA - Langley Research Center using prepreg manufacturer's specifications. Control samples were cut from the same panel as the flight specimens. The control samples remained at the NASA - Langley Research Center in a low humidity environment.

Procedures

Extreme care was used when preparing the composite samples for surface characterization. Lint free nylon white gloves from Fisher Scientific Company were used to prevent sample contamination. The gloves, prior to use, were washed in solvent grade hexane, also obtained from Fisher Scientific, to remove any silicon contamination. The gloves were then subsequently washed with soap and water and allowed to dry. Scotch Magic Tape® was used to secure samples for XPS and SEM analysis. Preparation of the composites for XPS and SEM analysis required cutting of the samples using an Exacto-knife. Typical sample dimensions were 13 mm x 13 mm.

Analysis Techniques

XPS (x-ray photoelectron spectroscopy) analysis was performed on a Perkin-Elmer PHI 5400 spectrometer with a magnesium Ka achromatic X-ray source (1253.6 eV) operated at 15 keV and 400 watts with an emission current of 30 mA. The spectrometer was calibrated to the $4f_{7/2}$ photopeak of gold. Atomic concentrations were determined using PHI software, version 3.0. Curve fitting was carried out by using PHI software, version 3.0. All photopeaks were fitted with Gaussian curves. The peak positions, indicative of the type of chemical functionality present, were assigned using known literature values [7]. The various peak positions were held at a constant value and were referenced to the C1s photopeak characteristic of adventitious carbon-containing organic species taken at 285.0 eV. The full width at half maximum for the C1s photopeaks was held constant at 1.70 eV. Curve fit photopeaks contributing less than 5% to the total carbon content were neglected.

SEM (scanning electron microscopy) photomicrographs were obtained using an International Scientific Instrument ISI SX-40 scanning electron microscope operated at a beam voltage of approximately 20kV. All samples were sputtered for approximately two to three minutes with gold to reduce charging.

RESULTS/DISCUSSION

The surface analysis results for the two composites are discussed separately.

Atomic Composition

The XPS results for the surface composition of the control, 10- and 69-month flight samples are shown in Table I. Elemental photopeaks are listed in the first column followed by the binding energy (in eV) and atomic concentration (in %) for each element. Carbon, oxygen, and nitrogen are expected for an epoxy composite which has a resin-rich surface. For example, the XPS composition of a BASF epoxy composite has been determined [8] to be 67.5% carbon, 14.2% oxygen, and 2.2% nitrogen in reasonable agreement with the present results for the control sample. The organo-fluorine photopeak at 689.3eV present on the composite surface most likely resulted from the transfer of a fluorinated release agent used in the fabrication of the composite. Moyer and Wightman [9] reported a 30% organo-fluorine content on the surface of a carbon fiber/polyimide composite. It is noted that the control sample has a 1.1% silicon characteristic of inorganic silicon at 103.2eV but the source is not identified. The small amounts of sodium (2.0%) and sulfur (1.1%) are not identified although Mallon et al. [5] have reported similar concentrations of minor contaminants on carbon fiber/polymer matrix composites.

As shown in Table I, the surface composition of the 10- and 69-month samples parallels that of the control which might appear at first to be a surprising result. The O/C atomic ratios were essentially the same for the three samples. However, some significant changes were observed. The loss of organo-fluorine was obvious for the two flight samples compared to the control. It is assumed that exposure to atomic oxygen results in the formation of volatile fluorine-containing species. Silicon contamination of LDEF samples is widely reported [1]. It is only noted that the 69-month sample has the highest silicon content (6.3%) with a binding energy characteristic of inorgano-silicon. It is well established that organo-silicon compounds when subjected to atomic oxygen are converted to inorgano-silicon containing materials [5].

Curve Fit Analysis

The results of the curve fit analysis for the three samples are summarized in Table II. Significant differences are observed in the carbon 1s curve fit region for the three samples showing different contributions (percentages) as well as different types of carbon functionality under the carbon 1s envelope. Although the atomic compositions of the three samples were similar (see Table I), the types of carbon functionality for each sample are very different. These results reinforce the necessity of curve-fitting photopeaks obtained in XPS measurements. Information obtained from proper curve fitting procedures is useful and critical in describing the surface chemistry of materials.

The carbon 1s photopeak of the control sample revealed a resin rich surface. The carbon 1s photopeak (C2) corresponding to hydrocarbon functionality accounted for 55.7% of the total carbon. The carbon-oxygen functionality (peaks C3, C4 and C5) accounted for 38.0% of the total carbon.

A dramatic shift in the curve fit analysis is seen for the 10- and 69-month flight samples. In both cases, a new major photopeak (C1) appeared with a binding energy of 283.7 eV assigned to a graphitic type carbon [10]. The appearance of the graphitic type carbon is a direct result of the degradation/erosion of the epoxy matrix to expose the carbon fibers of the composite. The curve fit analysis supports the argument that significant erosion of the epoxy matrix occurred within the first ten months of exposure in low Earth orbit.

The degradation/erosion of polymer matrix composite samples flown on the LDEF, particularly on the leading edge, has been discussed previously [11]. Here, atomic oxygen reaction results in polymer bond breaking and subsequent molecular fragmentation leading to erosion of the materials.

SEM Photomicrographs

The SEM photomicrographs of the control, 10- and 69-month flight samples are shown in Figure 1. Three very different surface topographies are observed in Figure 1 and support the results obtained from the XPS curve fit analysis.

The SEM photomicrograph of the control sample (see Fig. 1A) shows an apparent resin rich surface. The weave pattern seen on this control sample is not the weave pattern of the carbon fibers within the composite but rather the impression left from the scrim cloth used in the consolidation of the composite.

The SEM photomicrograph of the 10-month flight sample (see Fig. 1B) suggests some erosion of the matrix resin. The curve fit analysis of the 10-month flight sample showed carbon functionality that is consistent with the presence of both resin and carbon fiber. Photopeaks C2 - C5 for the 10-month flight sample are attributed to the resin since these photopeaks were also observed in the control sample. However, photopeaks C3-C5 have been reported for carbon fibers [12]. On the other hand, photopeak C1 is uniquely assigned to the carbon fibers. This significant photopeak, accounting for 46% of the total carbon signal, was absent in the control sample.

The SEM photomicrograph of the 69-month flight sample (see Fig. 1C) shows significant continued erosion of the matrix resin. The 69-month flight sample exhibits similar topography as reported previously for composite samples from the LDEF [2]. The carbon 1s curve fit analysis for the 69-month flight sample again suggests that the surface composition results from a combination of both resin and carbon fibers. However, the contribution of the C1 photopeak would suggest the composition is predominantly due to carbon fibers. The SEM photomicrographs are consistent then with the XPS curve fit analysis for the control, 10- and 69-month flight samples.

The SEM photomicrographs and the curve fit analysis support the degradation/erosion of the epoxy matrix within the first 10 months of the mission as well as further degradation for the remaining 59 months. Tennyson [13] reported that an atomic oxygen fluence of 1.33×10^{21} atoms/cm^2 on Row 12 was sufficient to erode the epoxy layer and a portion of the reinforcing graphite fibers. The epoxy samples discussed in the present study were located on the leading edge (Row 9) of the LDEF where the atomic oxygen fluence was 8.99×10^{21} atoms/cm^2. Thus, the higher atomic oxygen fluence for Row 9 would facilitate the degradation/erosion of the matrix to expose the carbon fibers as seen in Figure 1.

P1700/C6000 Polysulfone Composite

Atomic Composition

The XPS results for the surface composition of the control, 10- and 69-month flight samples are shown in Table III. Carbon, oxygen, and sulfur are expected for a polysulfone composite which has a resin-rich surface. For example, the XPS composition of a polysulfone film has been determined [14] to be 82% carbon, 15% oxygen, and 3.0% sulfur. Although the concentrations of carbon and sulfur are in good agreement, the sulfur concentration for the composite sample is considerably lower than expected. The organo-fluorine photopeak at 688.9 eV present on the control composite surface most likely resulted from the transfer of a fluorinated release agent used in the fabrication of the composite. This is similar to the concentration of organo-fluorine noted and discussed above for the control epoxy composite.

The control sample has a 1.2 atomic % silicon characteristic of organo-silicon at 102.4 eV but the source is not identified. The sources of the small amounts of aluminum (1.6%) and calcium (1.3%) are

also not identified. George and coworkers [11] have reported similar concentrations of minor contaminants on P1700 polysulfone/T300 composites.

As shown in Table III, the oxygen content of the 10- and 69-month samples differs significantly from that of the control sample. The O/C atomic concentration ratio increases from 0.19 (control) to 0.36 (10 month) to 2.08 (69 months) in sharp contrast to the constancy of the same ratio for the epoxy composite. George et al. [11] have also reported a trend of decreasing carbon content and increasing oxygen content for flight composite samples compared to control composite samples. The loss of organo-fluorine was obvious for the two flight samples compared to the control as was the case for the epoxy composites.

It is noted that the 69-month sample again has the highest silicon content (17.3%) with a binding energy at 103.7 eV characteristic of inorgano-silicon. A similar result was observed on the 69-month epoxy composite. George et al.[11] also reported an increase in silicon content for the flight samples. A possible SiO_X non-volatile contamination layer on the 69-month flight sample is consistent with the observed increase in the oxygen and silicon contents as well as the shift in the binding energy of the silicon 2p photopeak.

Sulfur is noted on the two flight samples at a higher concentration than for the control and closer to the value of 3.0% expected for neat polysulfone. However, the binding energy increased from 167.9 eV (organo-sulfur) for the control to 169.75 eV (inorgano-sulfur) for the two flight samples. The conversion of organo-sulfur to inorgano-sulfur in the presence of atomic oxygen has been documented [2]. The sources of the small amounts of aluminum (1.9%), calcium (0.1%), and sodium (0.8%) are not identified.

The appearance of nitrogen in both the 10-month and 69-month samples and its absence in the control sample may be due to uncovering of the PAN-based carbon fibers following matrix erosion by atomic oxygen. The nitrogen content of PAN-based T300 carbon fibers as determined by XPS has been reported [15] as 2.1% in fair agreement with the value of 1.1% observed in the present work.

Curve Fit Analysis

The carbon 1s curve fit analysis of the control and two flight samples is shown in Table IV. The curve fit analysis of the control sample again revealed a resin rich surface. Hydrocarbon functionality corresponds to 91% of the total photopeak area. The remaining area corresponds primarily to carbon-oxygen functionality.

The curve fit analysis of the 10-month flight sample showed a three-fold decrease in the hydrocarbon functionality and a two-fold increase in the carbon-oxygen functionality. The appearance of the C1 photopeak at 283.5 eV is taken as supporting evidence the carbon fibers were uncovered as the polysulfone matrix resin was eroded by reaction with atomic oxygen. This is the same striking result as was obtained for the epoxy composite.

The curve fit analysis for the 69-month polysulfone composite shows some difference from the epoxy composite. Carbon-oxygen functionality accounted for 50% of the total carbon content for the polysulfone composite compared to only 9% for the epoxy composite. No definitive conclusion is drawn from this result.

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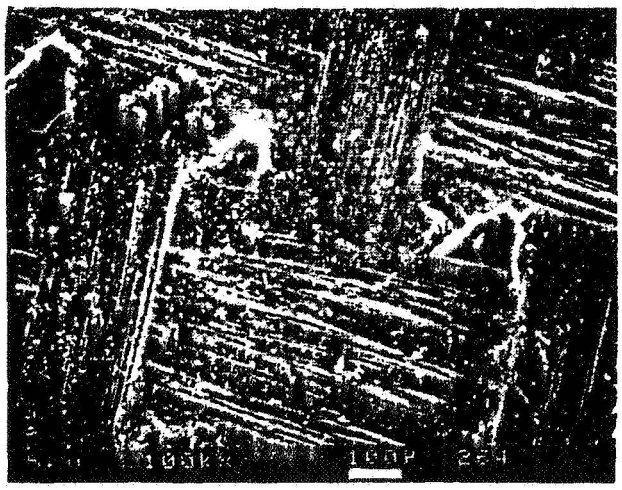
(A)



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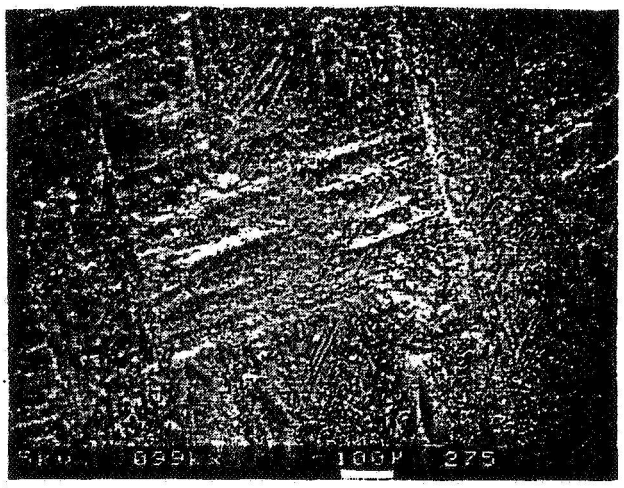

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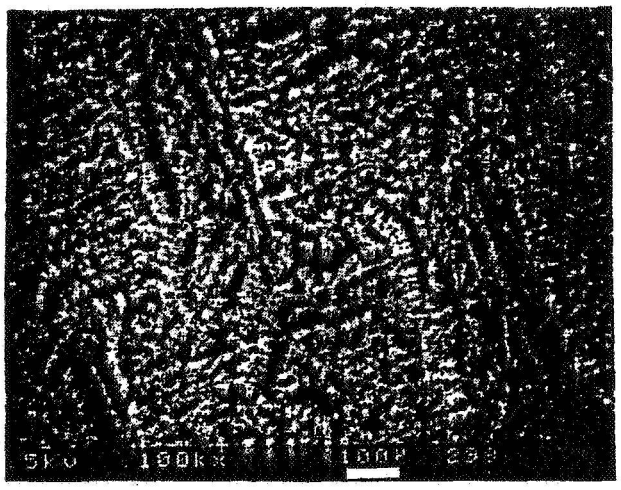

FIGURE 1: SEM PHOTOMICROGRAPHS OF 934/T300 EPOXY COMPOSITE SAMPLES

(A) CONTROL (B) 10 MONTH (C) 69 MONTH.

TABLE I: XPS ANALYSIS OF 934/T300 EPOXY COMPOSITES

CONTROL

PHOTOPEAK	BINDING ENERGY(eV)	ATOMIC CONC(%)
C 1s	285.0	68.8
O 1s	532.6	18.1
N 1s	399.9	3.4
F 1s	689.3	5.5
Si 2p	103.2	1.1
Na 1s	1072.2	2.0
S 2p	168.4	1.1

10 MONTH

PHOTOPEAK	BINDING ENERGY(eV)	ATOMIC CONC(%)
C 1s	285.0	73.3
O 1s	531.9	18.7
N 1s	399.6	5.5
F 1s	688.2	0.2
Si 2p	103.7	0.8
Na 1s	1071.9	0.5
S 2p	168.4	0.8

69 MONTH

PHOTOPEAK	BINDING ENERGY(eV)	ATOMIC CONC(%)
C 1s	285.0	72.0
O 1s	533.3	19.6
N 1s	400.6	0.8
F 1s	nsp*	--
Si 2p	104.0	6.3
Na 1s	nsp	--
S 2p	170.0	0.8

*nsp-no significant peak

TABLE II: CARBON 1s CURVE FIT ANALYSIS OF 934/T300 EPOXY COMPOSITES

CONTROL

PHOTOPEAK	BINDING ENERGY(eV)	% AREA	CARBON TYPE
C2	285.0	55.7	C-H
C3	286.3	25.0	C-O
C4	287.8	7.8	C=O
C5	289.4	5.2	O-C=O

10 MONTH

PHOTOPEAK	BINDING ENERGY(eV)	% AREA	CARBON TYPE
C1	283.6	46.4	graphitic
C2	285.0	30.8	C-H
C3	286.6	11.8	C-O
C4	288.1	7.3	C=O

69 MONTH

PHOTOPEAK	BINDING ENERGY(eV)	% AREA	CARBON TYPE
C1	283.9	49.8	graphitic
C2	285.0	38.9	C-H
C3	286.4	8.6	C-O

TABLE III: XPS ANALYSIS OF P1700/C6000 POLYSULFONE COMPOSITES

CONTROL

PHOTOPEAK	BINDING ENERGY(eV)	ATOMIC CONC(%)
C 1s	285.0	76.9
O 1s	532.1	14.5
S 2p	167.9	0.4
F 1s	688.9	4.1
Al 2p	74.7	1.6
Ca 2p	347.6, 351.1	1.3
Si 2p	102.4	1.2

10 MONTH

PHOTOPEAK	BINDING ENERGY(eV)	ATOMIC CONC(%)
C 1s	285.0	67.0
O 1s	531.2	24.5
S 2p	168.4	2.4
Si 2p	102.0	2.3
Al 2p	73.8	1.9
Na 1s	1071.3	0.8
N 1s	398.2	1.1

69 MONTH

PHOTOPEAK	BINDING ENERGY(eV)	ATOMIC CONC(%)
C 1s	285.0	25.0
O 1s	533.1	51.9
S 2p	169.6	2.9
Si 1s	103.7	17.3
N 1s	400.6	1.2
Ca 2p	348.5, 352.0	0.1

TABLE IV: CARBON 1s CURVE FIT ANALYSIS OF P1700/C6000 POLYSULFONE COMPOSITES

CONTROL

PHOTOPEAK	BINDING ENERGY(eV)	% AREA	CARBON TYPE
C 2	285.0	90.8	C-H
C 3	288.9	2.8	O-C=O

10 MONTH

PHOTOPEAK	BINDING ENERGY(eV)	% AREA	CARBON TYPE
C 1	283.5	53.3	graphitic
C 2	285.0	27.1	C-H
C 3	286.1	12.2	C-O

69 MONTH

PHOTOPEAK	BINDING ENERGY(eV)	ATOMIC CONC(%)	CARBON TYPE
C 1	283.6	22.4	graphitic
C 2	285.0	18.6	C-H
C 3	286.6	33.3	C-O
C 4	288.0	12.4	C=O
C 5	289.5	4.7	O-C=O