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LDEF POLYMERIC MATERIALS: A SUMMARY OF LANGLEY CHARACTERIZATION

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SUMMARY

The NASA Long Duration Exposure Facility (LDEF) enabled the exposure of a wide variety of materials to the low Earth orbit (LEO) environment. This paper provides a summary of research conducted at the Langley Research Center into the response of selected LDEF polymers to this environment. Materials examined include graphite fiber reinforced epoxy, polysulfone, and additional polyimide matrix composites, films of FEP Teflon, Kapton, several experimental high performance polyimides, and films of more traditional polymers such as poly(vinyl toluene) and polystyrene. Exposure duration was either 10 months or 5.8 years.

Flight and control specimens were characterized by a number of analytical techniques including ultraviolet-visible and infrared spectroscopy, thermal analysis, scanning electron and scanning tunneling microscopy, x-ray photoelectron spectroscopy, and, in some instances, selected solution property measurements. Characterized effects were found to be primarily surface phenomena. These effects included atomic oxygen-induced erosion of unprotected surfaces and ultraviolet-induced discoloration and changes in selected molecular level parameters. No gross changes in molecular structure or glass transition temperature were noted.

The intent of this characterization is to increase our fundamental knowledge of space environmental effects as an aid in developing new and improved polymers for space application. A secondary objective is to develop benchmarks to enhance our methodology for the ground-based simulation of environmental effects so that polymer performance in space can be more reliably predicted.

1.0 INTRODUCTION

The 69-month low Earth orbit (LEO) flight and subsequent January 1990 return to Earth of the NASA Long Duration Exposure Facility (LDEF) provided a novel opportunity for the aerospace community to examine the effects of long-term space exposure on a variety of materials. The saga of this remarkable vehicle is continuing to unfold through a series of symposia, workshops, and journal articles (1-5). The 11-ton satellite shown in Figure 1 contained 57 experiments to assess the effects of the space environment on materials, living matter, and various space systems (6). Perhaps as much as 90% of our first-hand knowledge of LEO space environmental effects rests with the LDEF and its contents (7).

The Langley Research Center actively pursued the chemical characterization of polymeric materials which flew on LDEF (8-20). The present paper summarizes almost 5 years of LDEF-related polymer research at this facility. It represents the collective efforts of a number of individuals and organizations in both assembling and analyzing a broad variety of control and exposed specimens.

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The intent of this activity is to increase our fundamental understanding of space environmental effects on polymeric materials and to develop benchmarks to enhance our methodology for the ground base simulation of those effects so that polymer performance in space can be more reliably predicted.

Initial planning for the chemical characterization of LDEF polymeric materials was guided by a number of anticipated environmental effects. Table I, taken from a presentation given at the LDEF Materials Data Analysis Workshop just prior to deintegration activities at the Kennedy Space Center (21), summarizes many of these effects. Modifications to molecular structure and molecular weight, changes in surface chemistry, surface erosion, optical property changes, and a deterioration in various mechanical properties were among more dominant effects to be examined. An analysis plan, summarized in Table II, was developed to address these anticipated effects. Extensive use was planned for selected solution property measurement techniques, spectroscopic analyses, thermomechanical analyses, and techniques to assess surface chemistry. Analytical methods to characterize the molecular level response to environmental exposure, in addition to more obvious physical and mechanical effects, would be emphasized.

Table III lists LDEF polymeric materials assembled for analysis. These materials were provided by several Principal Investigators, and depending on LDEF row and tray location, experienced somewhat different environments. Specimens were exposed for either 10 months or 5.8 years as noted. Materials ranged from early 1980 state-of-the-art graphite fiber reinforced polymer matrix composites, to space films and coatings, high performance polymer films, and more traditional polymers. Representative data obtained on these materials is given in this paper. A more complete data presentation can often be found in accompanying referenced reports.

2.0 EXPERIMENTAL

Most materials identified in Table III were originally obtained from commercial sources. The fabrication, quality control, specimen preparation, and baseline testing of Langley-supplied P1700/C6000, 934/T300, and 5208/T300 composite materials is discussed in references 22 and 23. Polyimide-polysiloxane copolymer films were synthesized under NASA Grant NAG-1-343 with Virginia Polytechnic Institute and State University, Blacksburg, Virginia. Several high performance polyimide films were synthesized in-house (24-26).

As noted in the text, some specimens were exposed for only 10 months while other materials received the full 5.8-year exposure. Specimens exposed for 10 months were inside an Experimental Exposure Control Canister (EECC) (6). The EECC was closed when LDEF was launched. It opened 1 month after deployment and closed 10 months later. Various environmental exposure parameters are included with Figures 1 and 2.

2.1 Instrumental Methods of Analysis

Thermal analyses were conducted using a DuPont 9900 Computer/Thermal Analyzer to process data from a DuPont 943 Thermomechanical Analyzer operating in the expansion mode. The glass transition temperature (T_g) was obtained by noting the point of inflection from the thermogram baseline. Ultraviolet-Visible (UV-VIS) transmission spectra were scanned on a Perkin-Elmer Lambda 4A Spectrophotometer. Infrared spectra were recorded on a Nicolet 60SX Fourier Transform Infrared System (FTIR) using a diffuse reflectance technique (27). X-ray Photoelectron Spectroscopy (XPS) measurements were conducted under NASA Grant NAG-1-1186 at the Virginia Tech Surface Analysis Laboratory, VPI&SU, Blacksburg, VA. Measurements were made on a

Perkin-Elmer PHI 5300 Spectrometer equipped with a Mg K α x-ray source (1253.6 eV), operating at 15 kV/120mA. Scanning Tunneling Microscopy (STM) was performed in air on a NanoScope II instrument (Digital Instruments, Inc., Santa Barbara, CA) using a tungsten tip and G-Head accessory. Specimens were prepared by coating with 5-7 nm of gold-palladium using a Hummer IV sputtering system (Anatech, Ltd., Alexandria, VA). Transmission Electron Microscopy (TEM) analyses were conducted under NASA Contract NAS1-19656 at the Virginia Institute of Marine Science, Gloucester Point, VA. A Cambridge StereoScan 150 (Cambridge Instruments, Deerfield, IL) equipped with an EDAX S150 detecting unit (EDAX International, Inc., Prarie View, IL) performed Scanning Electron Microscopy (SEM) analyses. Various photographic techniques were used to document specimen appearance.

2.2 Solution Property Measurements

Molecular weight measurements for LDEF polystyrene specimens were determined on a Waters 150-C Gel Permeation Chromatograph (GPC) interfaced with a Viscotek (Viscotek Corp., Porter, TX) Model 150R Differential Viscometer (DV). The general technique used to make these measurements has been previously described (28). Experiments were conducted in toluene at 40°C using a Waters 10³/10⁴/10⁵/10⁶Å MicroStyragel HT column bank. The flow rate was 1.0 ml/min. A universal calibration curve was constructed using Polymer Laboratories (Polymer Laboratories, Inc., Amherst, MA) narrow dispersity polystyrene standards. Polyimide films were analyzed at 35°C in 0.0075M LiBr in DMAc. GPC-DV measurements on all polysulfone specimens were determined on a standard Waters Associates chromatograph at room temperature using a 10³/10⁴/10⁵/10⁶Å MicroStyragel HT column bank. The solvent was chloroform.

GPC sample solutions were prepared 1 day prior to analysis by dissolving specimens in the appropriate solvent. The soluble portion was filtered through 0.2 mm PTFE filters before injection into the chromatograph. Insoluble gel was decanted into tared beakers, rinsed several times, and allowed to dry for about 2 hours before placing in an oven at 100°C and drying to constant weight. GPC sample concentrations were then adjusted to correct for removal of insoluble gel. Molecular weight parameters reported are averages obtained from two or three GPC-DV analyses.

2.3 Mechanical Property Measurements

Measurements on 4-ply ($\pm 45^\circ$)_s composite tensile specimens were performed according to ASTM D3039-76. Test specimens were cut to standard dimensions and tapered end-tabs machined from epoxy/glass cloth were adhesively applied prior to integration onto the LDEF experimental tray. A detailed description of composite test specimen preparation and testing is given references 15, 22, and 23.

3.0 RESULTS AND DISCUSSION

A precise orbital orientation was achieved by the LDEF spacecraft. As a result, the environmental exposure a sample received often depended on where it was located on the vehicle. Figure 1 depicts the spacecraft and its flight orientation. The 30 foot long by 14 foot in diameter gravity gradient stabilized structure had 12 sides or rows with 6 experimental trays per row. Additional trays were mounted on the Earth and space-pointing ends (6). The location of polymeric materials in this report will be identified by Tray and Row. For example, B9 identifies a specimen from Tray B on Row 9.

The Row 9 leading edge nominally faced the RAM or velocity vector direction and the Row 3 trailing edge faced the WAKE direction. A detailed analysis of several factors determined that the actual RAM direction was about 8° of yaw from the perpendicular to Row 9 in the direction of Row 10, with 1° of pitch (29). This orientation was sustained throughout flight, from deployment in April 1984 until retrieval in January 1990.

Figure 2 gives additional environmental parameters. The procedure for calculating total atomic oxygen (AO) fluence and equivalent ultraviolet (UV) sun hours may be found elsewhere (30-31). The asymmetrical AO fluence around the vehicle is partly due to the 8° of yaw and a short excursion during which the vehicle received exposure while in the Shuttle payload bay after retrieval. A further discussion of orientation and environments may be found in several references (1, 3, 4, 6).

3.1 Films

The primary environments of concern for polymeric films in low Earth orbit are AO and UV. The most dominant visual effect for exposed films was AO-induced surface erosion which generally resulted in a diffuse or frosted appearance. This visual effect was readily apparent with silvered fluorinated ethylene propylene (FEP) teflon thermal blanket material which provided thermal protection for 17 underlying experiment trays distributed around LDEF. Blankets located near Row 9 were opaque while blankets located near Row 3 remained highly specular. Figure 3 shows on-orbit photographs of F4 and E10 thermal blankets which illustrate this phenomenon. The change from specular to diffuse correlated with the change in AO fluence at various LDEF locations.

Atomic-oxygen-eroded thermal blankets changed from specular reflectors of solar radiation to diffuse reflectors (9). The total reflectance, specular plus diffuse components, which determines solar absorptance (α_s), remained virtually constant. The thermal emissivity (ϵ) was also virtually unchanged. Thus, the α_s/ϵ parameter, which influences equilibrium temperatures for passive thermal control coatings in space, was largely unaffected. This fortuitous result meant that the thermal performance of frosted and specular thermal blankets were probably the same. While surface atomic carbon to fluorine ratios, as determined by XPS, changed with exposure and UV-induced surface crosslinking no doubt occurred, various infrared and thermal analyses failed to detect significant molecular structural changes in the bulk FEP polymer (9).

The AO-induced erosion of films has been described as producing a textured, carpeted, or "christmas tree" morphology (32). Figure 4 gives SEM photomicrographs of the edge of a 5 mil Kapton film specimen which flew on the space end of LDEF at H7. This specimen was oriented such that the AO flow was perpendicular to the film edge and in the plane of the film surface. Figure 4a shows the "christmas tree" morphology associated with the leading edge of this film. The trailing edge, shown in 4b, did not receive direct exposure and remained fairly smooth.

Figure 5 gives the SEM photomicrograph of polysulfone film exposed for 10 months on Row 9 (11). AO exposure for this specimen was essentially orthogonal to the film surface. Evidently, surface contamination partially protected underlying resin from AO to produce the relief pattern apparent in this figure. This phenomenon provides a perspective on the depth of erosion for this 10-month specimen.

The roughened surface dramatically reduced the ultraviolet-visible transmission properties of exposed film. Figure 6 gives before and after UV-VIS spectra between 200 and 600 nm for 5 high performance polyimide films (19). Kapton was included as a reference. The molecular structure of each polyimide is identified in Table IV. All films received 10 months of Row 9 exposure and, thus, experienced the environment summarized in Figure 2d. While some UV and AO degradation of the

polymer molecular backbone no doubt occurred, the decrease in transmittance with exposure is considered to be largely due to physical roughening of the film surface by AO. The uneven surface reflected and/or refracted the impinging radiation and, thus, less light was transmitted.

Scanning Tunneling Microscopy (STM) has proven to be an effective tool for profiling the surface of space-exposed films. Figure 7 shows STM line plots for unexposed and exposed BTDA-ODA and exposed BTDA-ODA-Al³⁺, two high performance polymer films included in a previous study (19). The smooth surface shown in 7a is typical of that observed for other unexposed LDEF specimens. Minor undulations in the x-direction likely resulted from the drawing procedure used during casting when the film was doctored onto a glass plate. The egg-crate-like appearance of exposed BTDA-ODA is also typical of the "christmas tree" morphology observed for several other LDEF films. The mechanism by which polymeric materials develop this conical shape upon exposure to AO is not adequately understood. VUV-induced surface crazing/crosslinking may play a role in this phenomenon.

The BTDA-ODA-Al³⁺ specimen shown in 7c also exhibited erosion but the appearance is different from that observed in 7b for the undoped film. An obvious conclusion is that aluminum ions had an effect on how the film surface responded to the LEO environment. A protective aluminum oxide phase may have formed with exposure. STM has provided insight into the erosion of additional 10-month exposed Row 9 films (10). The technique could not be used on many 5.8-year exposed films on or near Row 9 because the specimens were too rough. The STM probe tip tended to "crash" with the irregular surface of these full-exposure samples. Ten month-exposed Row 9 films received approximately 2.6×10^{20} AO atoms/cm² while 5.8-year exposed Row 9 films received up to 8.99×10^{21} AO atoms/cm². These results suggest the upper limit of directional AO exposure for characterization by the STM technique is intermediate between these two fluences.

Transmission Electron Microscopy (TEM) also proved to be an effective tool for characterizing AO erosion of polymer films. Figure 8 shows TEM photomicrographs of the five experimental polyimide films and Kapton. Prior to analysis, a segment of each film was cast into an epoxy potting resin, the resin cured, and then carefully microtomed. Irregular features emanating from the darkened films are artifacts of this potting procedure. A constant magnification was used for all specimens in Figure 8. The righthand portion of each micrograph in the figure indicates the original thickness of each film. This portion was protected from direct exposure by an aluminum retaining template which held the films in place during exposure. The diminished film thickness due to AO erosion is noted by the lefthand portion. The PMDA-DAF film was partially eroded through. The aluminum ion-containing film shows little effect at this magnification.

Figure 9 shows three TEMs at progressively higher magnifications for BTDA-ODA-Al³⁺. The 3675X micrograph given in 9a clearly shows the smooth back and eroded front film surfaces. The arrow to the left in the figure denotes the original uneroded surface. The textured morphology is clearly apparent in 9b and 9c. The survival of small strands of polymer in such a hostile environment, particularly as depicted in Figure 9b, is astonishing.

3.2 Composites

Unprotected composites were also affected by LEO exposure. Figure 10 shows the SEM of T300 carbon fiber reinforced 934 epoxy matrix specimens for two exposures. The 10-month and 5.8-year samples were placed adjacent to each other in the SEM to enable simultaneous analyses. The left side, low magnification photomicrograph shows both exposed surface and surface protected from direct exposure by an aluminum retaining template. The fabric-appearing pattern visible in the micrograph was transferred to the composite surface by a glass cloth peel-ply during processing.

The right side photomicrograph shows a higher magnification SEM of exposed regions of two specimens. Individual carbon fibers apparent with the 10-month composite are no longer distinguishable after 5.8 years.

Table V gives XPS data for control, 10-month, and 5.8-year T300-934 epoxy composites. Surface carbon content increased in the first 10 months of exposure. This probably reflects increased carbon fiber content due to an initial preferential erosion of matrix resin. Oxygen and sulfur did not appear to change significantly. Fluorine on the control likely resulted from release agent used during processing. Fluorine was not detected on exposed composites because this outer surface was eroded away by AO. The increased silicon content with exposure is no doubt due to a well-documented LDEF contamination to be discussed later. Additional chemical characterization including FTIR, TMA, and DSC failed to detect significant differences between the two specimens.

The loss of both resin and fiber is clearly illustrated by the SEM in Figure 11. This figure gives photomicrographs at two magnifications for a 4-ply $[\pm 45^\circ]_s$ 5208/T300 epoxy composite which received 5.8 years of Row 9 exposure. The righthand micrograph shows the interface between the top ply and the second ply in some detail.

As expected, the loss of fiber and matrix due to flight exposure affected selected mechanical properties. Figure 12 and Figure 13 give ultimate tensile strength and tensile modulus for five different composite materials flown on a Langley experiment (15). No major differences are noted between baseline values obtained when the composites were tested in 1983, ground control composites which remained at Langley, and composites which flew on LDEF as flight control specimens, protected from direct exposure. However, specimens which flew exposed experienced a deterioration in tensile strength and tensile modulus. No doubt, more than resin loss contributed to this phenomenon since the thickness loss was not proportional to the loss in tensile properties by rule of mixtures. The P1700/C6000 specimens lost least in thickness and retained more ultimate tensile strength than other specimens. No explanation for this has been found.

PMR-15 and LARCTM-160 are two similar addition polyimides of considerable promise in the early 1980's when LDEF experiments were being designed. Celion 6000 graphite fiber reinforced composites of these polymers were flown on a Row 1 and Row 7 experiment (33). Specimens of these two materials were made available to Langley for chemical characterization. Figure 14 summarizes selected analyses performed on a PMR-15/C6000 composite. Inspection of the TMA thermogram suggests no difference in T_g for control and exposed specimens. Long-term isothermal weight loss also failed to detect significant effects due to exposure. Exposed and unexposed composite specimens were also examined by DR-FTIR spectroscopy. Spectra given in Figure 14 suggest little difference. A new absorption band at 1650cm^{-1} was anticipated for the exposed specimen. This band would have been indicative of oxidation of a methylene group in the polymer molecular backbone. This band along with an accompanying band at 930cm^{-1} had been detected in the spectrum of thermally aged LARCTM-160 composites (27). The two bands are missing in the spectra shown in Figure 14. The band at 1684cm^{-1} is due to the anhydride portion of the polymer backbone and is supposed to be present. Similar FTIR analyses of other LDEF-exposed composites have failed to detect significant molecular level differences as a result of exposure. Figure 15 gives a typical example of spectra obtained for a P1700/C6000 polysulfone composite. Spectra of exposed and protected composite specimens are virtually identical.

One of the unsolved mysteries concerning materials on LDEF were "stripes" and/or "gray ash" associated with selected epoxy matrix composites. This phenomenon was investigated in some detail. Figure 16 gives a photograph of a striped 5.8-year exposed 934/T300 epoxy composite specimen and also SEM photomicrographs of a sample of the gray ash. Projections rising from the composite surface were apparently caused by contamination protecting underlying material from AO attack. The righthand photograph, obtained by overlaying three individual micrographs, shows

graphite fiber presumably sheared off by AO. The gray ash in question is visible at the base of the finger-like projection.

Figure 17 provides additional information on the 934/T300 flight specimen. The upper righthand portion shows a high resolution SEM of the ash. The residue appears to contain crystals on the order of $0.1\mu\text{m}$ in diameter. EDS and XPS analyses on these crystals, given in Figure 17, revealed sulfur to be a significant component. This was an unexpected result. However, sulfur is present in the diaminodiphenylsulfone (DDS) cured epoxy matrix resin. Similar-appearing residues have been noted for DDS-cured 5208 epoxy composites. The exact chemical nature of this sulfur-containing species has not been established; sodium may be a counter ion. XPS data in Table V for another epoxy flight specimen shows no unusual sulfur content. Apparently this analysis was not conducted on an ash-rich portion of the exposed composite.

Figure 18 contains information on a striped 5208/T300 epoxy composite. Optical and SEM micrographs are given at the top of the figure. The slightly recessed dark stripe is on the order of a tow wide. XPS analysis of a 1mm^2 spot size failed to note significant differences between white and dark areas. Why one tow of the epoxy composite behaved differently from adjacent tows has not been adequately explained.

The composites addressed in this paper were uncoated materials. They were intentionally left uncoated in order to maximize the effects of long term LEO exposure. Identical materials protected with thin coatings, such as 1000\AA of nickel followed by 600\AA of silicon dioxide, exhibited outstanding resistance to surface erosion (8, 15, 16). Several additional inorganic coatings were found to be effective in preventing surface degradation (17).

3.3 Glass Transition Temperature

Table VI summarizes glass transition temperature (T_g) measurements conducted on a series of composites and films which flew on LDEF along with selected data obtained on films flown on STS-8 and STS-46 experiments. Exposure duration, row, and tray location are identified in the table. A careful inspection of T_g values for control and flight specimens suggests no significant change as a result of exposure. T_g effects do not appear to be an issue for polymeric materials in LEO, at least for polymers exposed for 69 months or less.

3.4 Solution Property Measurements

Selected solution property measurements have been conducted on several polymeric materials which flew on LDEF. The most extensively studied material is a thermoplastic polysulfone resin designated P1700. Both film and graphite fiber reinforced composites have been examined. Table VII summarizes molecular weight data for P1700 film and composite specimens and Figure 19 gives typical molecular weight distribution curves for 10-month exposed film. All data was obtained by Gel Permeation Chromatography-Differential Viscometry (GPC-DV). Several points concerning these data are evident.

A decrease in solubility was noted in testing control film, then a template-protected specimen cut from around the yellowed edge of a flight specimen, and finally a directly exposed center-cut specimen. This decreased solubility with exposure along with a significant decrease in number average molecular weight (M_n) and increase in weight- and z-average molecular weights (M_w and

M_z) is evidence for chain scission plus crosslinking. This behavior confirms predictions derived from ground-based simulation of space environmental effects on this material (34-38).

Table VII also includes molecular weight data obtained on the top ply of 4-ply composites flown on Row 9 and exposed for 10 months or 5.8 years. Data for the 5.8-year sample reflects no molecular weight change when compared with the control composite while the 10-month exposed specimen suggests the same molecular level trends observed with the film sample. This potentially contradictory observation is best understood by considering the orbit of the spacecraft during its flight. LDEF was deployed in an essentially circular orbit of 257 nautical miles on April 7, 1984 (39). It was retrieved 69 months later at an altitude of 179 nautical miles. Only about 2 months of orbit lifetime remained at retrieval. The atomic oxygen fluence differs greatly at these two altitudes.

Figure 20 is the approximate cumulative percent RAM AO fluence as a function of time. Exact AO exposure for these specimens is given in reference 30. The 10-month specimens were exposed early in the mission when AO fluence was at a minimum. The 5.8-year specimens received significant AO near the end of the mission. As much as 50% of total AO was received during the last 6 months in orbit. The molecular level effects observed after 10 months, primarily related to changes in surface chemistry, had most likely been eroded away by the time the satellite was retrieved. An earlier retrieval from a higher orbit may have provided different results. Subtractive FTIR spectroscopy gave additional insight into the molecular level response of P1700 film to LEO exposure. Since the LDEF specimen was too thick for good quality transmission studies, somewhat poorer quality spectra of control and exposed specimens were obtained by diffuse reflectance (DR). Differences between the two spectra were difficult to establish until they were subtracted. Figure 21 is the result of subtracting the DR-FTIR spectrum of the control film from that of the exposed. A downward inflection in the curve is indicative of a larger amount of a particular species in the exposed spectrum.

The band centered around 3400cm^{-1} is most likely due to -OH. Bands at 1485 and 1237cm^{-1} may also be associated with that group. Reports in the literature have noted the 3400cm^{-1} -OH band for polysulfone film exposed to UV (40) and also to 3-MeV protons (37). Additionally, the loss of the 1385cm^{-1} methyl band was noted in at least one study (40). Methyl does not appear to have been lost in the present study. A diminished -CH₃ content would have resulted in an upward inflection in the subtraction spectrum at 1385cm^{-1} ; no band is present around 1385cm^{-1} in Figure 21.

The presence of -OH has been explained by cleavage of the ether oxygen in the backbone of the polymer followed by abstraction of a proton (37), or by a photo Claisen rearrangement of the ether oxygen to produce an ortho-hydroxy substituted biphenyl linkage (36). We made no determination in this study of the origin of the -OH group.

Solution property measurements were also conducted on polystyrene specimens exposed for 5.8 years on LDEF Row 9 and Row 3. Table VIII gives various molecular weight parameters for these two specimens. Only a slight reduction in M_n was observed with exposure while M_w and M_z increased dramatically. This behavior is indicative of crosslinking and is the predicted response to UV for polystyrene. FTIR and UV-VIS spectra of this polymer will be included in a future report.

Additional solution property measurements were conducted on two polyimide films exposed for 10 months on Row 9. The molecular structure of the two polyimides, 6F-BDAF and 6F-DDSO₂, is included with structures given in Table IV. The two 6F-anhydride polymers were the only potentially soluble polyimides flown on LDEF. Table IX summarizes molecular weight data determined by GPC-DV. Analyses were conducted on a control film, the edge of a flight specimen shielded from direct exposure, and a 10-month exposed specimen cut from the center of the film. All

samples contained residual insoluble material. The insoluble gel was recovered by filtration and dried to constant weight. Analyzed concentrations were then adjusted to account for the insoluble portion.

An inspection of data for 6F-BDAF suggests that various molecular weight parameters were not affected by the 10-month LEO exposure provided by LDEF. In contrast, 6F-DDSO₂ exhibited significant changes at the molecular level. Solubility decreased from 94.5% to 60.9% with exposure. The number average molecular weight (M_n) remained fairly constant while the z-average molecular weight (M_z) doubled. Changes in the polydispersity ratio (M_w/M_n) are also noted for this material. These observations, particularly solubility and M_z behavior, are considered evidence that the 6F-DDSO₂ structure crosslinked during exposure. The z-average molecular weight (M_z) is probably a neglected parameter for evaluating crosslinking in environmentally exposed polymers (41). Figure 22 gives GPC-DV molecular weight distributions for 6F-DDSO₂. They show the broadening with exposure and shift to higher molecular weight documented in Table IX. The molecular weight distributions for control and exposed 6F-BDAF were virtually superimposable. The change in molecular weight for 6F-DDSO₂ is considered primarily a result of VUV damage to the -SO₂- group in the polymer backbone.

3.5 Additional Studies

Polyimide-polysiloxane copolymers. The chemical characterization of a series of polyimide-polysiloxane copolymers which received 10 months of Row 9 exposure also provided molecular level insight into LEO space environmental effects. Preliminary results obtained on these experimental materials have been given in previous reports (10, 13, 18). In general, the films discolored somewhat with exposure but did not exhibit significant weight loss. SEM, STM, and limited XPS data may be found in the referenced reports.

Table X gives detailed XPS results for three different siloxane-containing copolymers. Data for both control and exposed film is included in the table. Several points are made concerning these data. Note the decrease in surface carbon content with exposure and concurrent increase in surface oxygen content. Note also the increase in silicon and that the silicon to oxygen ratio is about 1:2 after exposure. Finally, note the increase in the silicon 2p electron binding energy with exposure from approximately 102 electron volts to 103 eV. This data is consistent with the following interpretation. Upon AO exposure, the surface of these siloxane-containing copolymers eroded to expose silicon atoms. These atoms were initially present as an organically-bound silicon, as evidenced by the 102 eV binding energy. Upon exposure to AO, organic silicon (102 eV B.E.) was oxidized to inorganic silicon (103 eV B.E.), most likely an SiO₂ type of silicate. At this point, further AO erosion was retarded. Inorganic silicates are known to be effective barriers to AO erosion. These observations suggest an exciting potential for designing AO protection into the backbone of certain polymers. This protection could likely be achieved by periodic incorporation of siloxane groups into the molecular structure of the host polymer.

RTV-511 Silicone. Several polymeric materials which flew on a Row 8 experiment were characterized. Figure 23 summarizes selected information on one of these materials, an RTV-511 silicone specimen. SEM revealed topography typical of embrittlement. Surface carbon and oxygen content changed with exposure but silicon did not. The 102.5 eV binding energy for this element for both unexposed and exposed specimens suggests no change in chemical state of Si with exposure. Thermogravimetric analysis included in Figure 23 revealed that the exposed sample exhibited 2-3% less weight loss prior to decomposition than the unexposed sample. Apparently the flight sample had outgassed low molecular weight species while in space. This phenomenon no doubt contributed to the general contamination observed on the LDEF spacecraft.

Contamination. As documented in numerous LDEF publications, much of the vehicle surface was coated with varying amounts of a molecular contamination film commonly referred to as the "nicotine stain." Figure 24 summarizes XPS results obtained on an optical window flown on a Row 9 experiment. One side of the window received 5.8 years of RAM exposure while the reverse side was vented to the inside of the experiment tray. Approximately 20% silicon was detected on the exposed surface while only 3.3% was found on the vented side. The control contained no silicon. The 102.9 eV binding energy for the Si 2p electron indicates that exposed surface silicon was present as inorganic silica/silicate. The 101.9 eV binding energy for the vented side is indicative of organic silicone.

This contamination layer likely had an effect on the behavior of polymeric materials on LDEF. UV probably contributed to the discoloration of contaminated specimens. Upon exposure to AO, the silicon-containing contamination was oxidized from silicone to silicate. The resultant AO-resistant protective layer likely affected the manner in which the material eroded. Contaminated samples probably performed differently than had they not been contaminated.

Post Exposure Effects. The possibility that some LDEF polymeric materials have changed or degraded after the spacecraft was returned to Earth has been raised on several occasions. At the First Post Retrieval Symposium, we reported that two thin films flown on STS-8 in 1983 had changed significantly in appearance since they were initially examined (12). Additional information on these two films was presented at the LDEF Materials Workshop '91 (13). One of the films flown on STS-8, an experimental polyimide designated PMDA-DAF, was reflowed on LDEF. By visual inspection, the exposed area of this film is noticeably more opaque now than it was when the experiment was deintegrated from LDEF in Spring 1990.

Selected Ag/FEP Teflon thermal blanket specimens have changed in appearance with time. Figure 25 shows photographs of a micrometeoroid impact on a thermal blanket flown on Row 11. Both photographs were obtained on an optical microscope at the same magnification. The photograph on the left was taken in April 1990, shortly after the analysis of LDEF materials began at the Langley Research Center. The same specimen area was located and photographed again in November 1991. A careful inspection of the two photographs in Figure 25 will reveal that cracks on the vapor deposited silver side of the thermal blanket material had continued to form and intensify. The aged specimen had also become duller in appearance.

Thus, some polymeric materials no doubt continued to age after environmental exposure. Quantified information is needed to define the chemical and/or mechanical mechanisms associated with this phenomenon. The prudent analyst must be aware that certain characterized effects may have become exaggerated during the interval between when the specimen was returned to Earth and when it was analyzed. In retrospect, Electron Spin Resonance (ESR) should have been used to investigate the formation and lifetime of free radicals which likely contributed to various observed post exposure effects. Including ESR with other characterization techniques outlined in Table II would have strengthened our understanding in this particular area.

3.6 A Perspective

A significant amount of fundamental information has been generated on several polymers which received 10 months or 5.8 years of LEO exposure. For example, Table VII gives molecular weight data on P1700 polysulfone film and composite specimens. Table VIII gives similar data for polystyrene specimens flown on Row 3 and Row 9 of LDEF. Additional unreported molecular weight measurements were conducted on 5.8-year exposed Row 3 poly(vinyl toluene). Polystyrene and poly(vinyl toluene) are two well-characterized polymers. Finally, Table IX contains molecular weight data for two 10-month exposed experimental polyimide films.

All polysulfone, polystyrene, and polyimide specimens were extensively characterized by UV-VIS and FTIR spectroscopy, thermal analysis, SEM, STM, and in most cases, XPS. Thus, a thorough understanding has been obtained of the molecular level response of these polymers to extended LEO exposure. Additional polysulfone and polystyrene data has been obtained on samples flown on recent Space Shuttle experiments.

Can this data be used as a benchmark to calibrate the ground-based simulation of LEO space environmental effects? If effects on materials described in this report can be simulated, then the same conditions can be used to simulate the effects of LEO exposure on new and emerging polymeric materials of current interest for space application. Synergistic and accelerated effects may also then be better understood. Such understanding will significantly enhance our ability to predict the long-term performance of polymeric materials in low Earth orbit.

4.0 CONCLUDING REMARKS

Current studies indicate LDEF to be the definitive source for long-term exposure verification of LEO environmental effects on polymeric materials. A wide variety of materials has been characterized. Exposure to atomic oxygen led to changes in the physical appearance of most flight specimens and reductions in selected mechanical properties. Other environmental effects are considered to be primarily surface phenomena. Changes in various molecular weight parameters, attributed to ultraviolet degradation, were documented for several soluble polymers. Many environmental effects for specimens located on or near Row 9 were lost to increased AO erosion near the end of the LDEF mission. An ubiquitous silicon-containing contamination likely affected the behavior of many polymeric materials. Finally, the possibility that selected LDEF polymers have changed since they returned to Earth in January 1990, was addressed.

The Long Duration Exposure Facility provided a once-in-a-career opportunity for the first-hand examination of effects of long-term space exposure on a variety of polymeric materials. As a result, research on space environmental effects has taken a forward leap past pre-LDEF levels of analytical procedures, data acquisition, modeling, and understanding of degradation mechanisms in low Earth orbit.

ACKNOWLEDGMENT

A significant portion of this research was made possible by the generous contribution of LDEF specimens by a number of individuals. The authors express appreciation to John C. Gregory, The University of Alabama in Huntsville; James B. Whiteside, Grumman Aerospace Corporation; Richard F. Vyhnal, Rockwell International Corporation; Michael G. Grote, McDonnell Douglas Astronautics Company; Ann F. Whitaker and James M. Zwiener, NASA Marshall Space Flight Center; H. Gary Pippin, Boeing Defense and Space Group; Anne K. St. Clair and Bland A. Stein, NASA Langley Research Center.

REFERENCES

1. A. S. Levine, ed.: LDEF-69 Months in Space. First Post Retrieval Symposium, Kissimmee, FL, June 2-8, 1991. NASA CP-3134, Parts 1, 2, and 3.
2. B. A. Stein and P. R. Young, comp.: LDEF Materials Workshop '91. Langley Research Center, Hampton, VA, November 18-21, 1991. NASA CP-3162, Parts 1 and 2.

3. A. S. Levine, ed.: LDEF-69 Months in Space. Second Post Retrieval Symposium, San Diego, CA, June 1-5, 1992. NASA CP-3194, Parts 1, 2, 3, and 4.
4. J. C. Gregory, ed.: LDEF Materials Results for Spacecraft Applications Conference, Huntsville, AL, October 27-28, 1992. NASA CP-3257.
5. L. E. Murr and W. H. Kinard: Effects of Low Earth Orbit. American Scientist, **81**, 152 (1993).
6. L. G. Clark, W. H. Kinard, D. J. Carter, and J. L. Jones, ed.: The Long Duration Exposure Facility (LDEF). NASA SP-473, 1984.
7. T. Stevenson: LDEF Comes Home. Aerospace Composites and Materials, **2(2)** May-June (1990).
8. P. R. Young, W. S. Slemp, W. G. Witte, and J. Y. Shen: Characterization of Selected LDEF Polymer Matrix Resin Composite Materials. SAMPE International Symposium, **36(1)**, 403(1991).
9. P. R. Young and W. S. Slemp: An Analysis of LDEF-Exposed Silvered FEP Teflon Thermal Blanket Material. NASA TM 104096 (1991).
10. P. R. Young, W. S. Slemp, and C. R. Gautreaux: Characterization of Selected LDEF Exposed Polymer Films. SAMPE International Symposium, **37**, 159 (1992).
11. P. R. Young, W. S. Slemp, E. J. Siochi, and J. R. J. Davis: Analysis of a Space-Exposed Thermoplastic Resin. SAMPE Intl. Tech. Conf., **24**, T174 (1992).
12. P. R. Young and W. S. Slemp: Chemical Characterization of Selected LDEF Polymeric Materials. NASA CP-3134, Part 2, 687 (1991).
13. P. R. Young and W. S. Slemp: Characterization of Selected LDEF-Exposed Polymer Films and Resins. NASA CP-3162, Part 1, 1992, 357 (1992).
14. P. R. Young and W. S. Slemp: Space Environmental Effects on Selected LDEF Polymeric Materials. American Chemical Society Book Series 527, Radiation Effects on Polymeric Materials, E. Reichmanis, C. W. Frank, J. H. O'Donnell, eds., ACS, Washington, DC, 1993.
15. W. S. Slemp, P. R. Young, W. G. Witte, and J. Y. Shen: Effects of LDEF Flight Exposure on Selected Polymer Matrix Resin Composite Materials. NASA CP-3134, Part 2, 1149 (1992).
16. P. R. Young, W. S. Slemp, and A. C. Chang: LDEF Polymeric Materials: 10 Months vs. 5.8 Years of Exposure. NASA CP-3194, Part 3, 827 (1993).
17. W. S. Slemp and P. R. Young: LDEF Thermal Control Coatings Post-Flight Analysis. NASA CP-3194, Part 3, 1093 (1993).
18. P. R. Young, W. S. Slemp, and B. A. Stein: Performance of Selected Polymeric Materials on LDEF. NASA CP-3257, 125 (1992).
19. P. R. Young, A. K. St. Clair, and W. S. Slemp: Response of Selected High Performance Films to LEO Exposure. SAMPE International Symposium, **38(1)**, 664 (1993).
20. C. R. Kalil and P. R. Young: Scanning Tunneling Microscopy Analysis of Space-Exposed Polymer Films. 39th Intl. Instrument Symposium, ISA **39**, 445 (1993).
21. B. A. Stein and P. R. Young, comp: LDEF Materials Data Analysis Workshop. NASA CP-10046, 1990.
22. W. G. Witte, Jr.: Manual for LDEF Tensile Tests. NASA TM 87624, 1985.
23. W. G. Witte, Jr.: Baseline Tensile Tests of Composite Materials for LDEF Exposure. NASA TM 89069, 1987.
24. A. K. St. Clair, T. L. St. Clair, and K. I. Shevet: Synthesis and Characterization of Essentially Colorless Polyimide Films. Proceedings of the ACS Division of Polymeric Materials: Science and Engineering, **51**, 62(1984).
25. Aluminum Ion-Containing Polyimide Adhesives. U.S. Patent 4,234,461 to NASA, Aug. 13, 1981.
26. V. L. Bell: Polyimide Structure-Property Relationships. I. Polymers from Fluorene-Derived Diamines. J. Polym. Sci.: Polym. Chem. Ed., **14**, 225(1976).

27. P. R. Young, B. A. Stein, and A. C. Chang: Resin Characterization in Cured Graphite Fiber Reinforced Composites Using Diffuse Reflectance FTIR. National SAMPE Symposium, 28, 824 (1983).
28. P. R. Young, J. R. J. Davis, and A. C. Chang: Molecular Weight Characterization in Advanced Thermoplastic Resins. SAMPE International Symposium, 34(2), 1450 (1989).
29. P. N. Peters, P. L. Whitehouse, and J. C. Gregory: Refinements on the Pinhole Camera Measurements of the LDEF Attitude. NASA CP-3194, Part 1, 3 (1993).
30. R. J. Bourassa and J. R. Gillis: Atomic Oxygen Exposure of LDEF Experiment Trays. NASA CR 189627, Contracts NASI-18224 and NASI-19247, May 1992
31. R. J. Bourassa and J. R. Gillis: Solar Exposure of LDEF Experiment Trays. NASA CR 189554, Contract NASI-18224, February 1992.
32. S. L. Koontz: Atomic Oxygen Effects on Spacecraft Materials-The State of the Art of Our Knowledge. NASA CP-3035, Part 1, 241 (1989).
33. R. F. Vyhnal: The Effects of Long-Duration Space Exposure on the Mechanical Properties of Some Carbon-Reinforced Resin Matrix Composites. NASA CP-3194, Part 3, 941 (1993).
34. J. R. Brown and J. H. O'Donnell: Effects of Gamma Radiation on Two Aromatic Polysulfones. J. Appl. Polym. Sci., 19, 405 (1975).
35. J. R. Brown and J. H. O'Donnell: Effects of Gamma Radiation on Two Aromatic Polysulfones II. A Comparison of Irradiation at Various Temperatures in Air-Vacuum Environments. J. Appl. Polym. Sci., 23, 2763 (1979).
36. S. Kuroda, A. Nagura, K. Horie, and I. Mita: Degradation of Aromatic Polymers III. Crosslinking and Chain Scission During Photodegradation of Polysulfones. Eur. Polym. J., 25(6), 621 (1989).
37. D. R. Coulter, M. V. Smith, F. Tsay, and A. Gupta: The Effects of 3-MeV Proton Radiation on an Aromatic Polysulfone. J. Appl. Polym. Sci., 30, 1753 (1985).
38. B. Santos and G. F. Sykes: Radiation Effects on Four Polysulfone Films. SAMPE Technical Conference, 13, 256 (1981).
39. R. L. O'Neal and E. B. Lightner: Long Duration Exposure Facility-A General Overview. NASA CP-3134, Part 1, 3 (1991).
40. B. D. Gesner and P. G. Kelleher: Thermal and Photooxidation of Polysulfone. J. Appl. Polym. Sci., 12, 1199 (1968).
41. D. J. T. Hill, D. A. Lewis, J. H. O'Donnell, P. J. Pomery, C. L. Winzor, D. J. Winzor, and A. K. Whitaker: Recent Advances in the Radiation Chemistry of Polymers. First Pacific Polymer Conference, Maui, December 12-15, 1989. Pacific Polymer Preprints, 1, 67 (1989).

TABLE I. ANTICIPATED ENVIRONMENTAL EFFECTS FOR LDEF POLYMERIC MATERIALS

Chemical

- Modification to molecular structure
- Molecular weight/distribution change
- T_g /crystallinity effects
- Formation of volatile/degradation products
- Changes in surface chemistry

Physical

- Resin loss/erosion
- Dimensional changes (CTE ...)

Optical

- Change in transparency
- α_s/ϵ
- Contamination

Mechanical

- Deterioration in strength, modulus, toughness ...

TABLE II. RECOMMENDED CHARACTERIZATION

Chemical

Solution property measurements

- Gel permeation chromatography (GPC)
- Low Angle Laser Light Scattering (LALLS)
- Differential Viscometry (DV)
- Osmometry
- GPC/LALLS, GPC/DV
- High Pressure Liquid Chromatography (HPLC)

Spectroscopy

- Fourier transform infrared spectroscopy
- UV-VIS-NIR
- Mass Spectroscopy (SIMS)
- Magnetic resonance
- Thermal emittance

Physical

Thermal/thermomechanical

- Thermomechanical Analysis (TMA)
- Dynamic Mechanical Analysis (DMA)
- Differential Scanning Calorimetry (DSC)
- Thermogravimetric Analysis (TGA)

Surface Analysis

- X-Ray Photoelectron Spectroscopy (ESCA)
- Energy Dispersive Spectroscopy (EDAX)
- Scanning Electron Microscopy (SEM)
- Scanning Tunneling Microscopy (STM)

Objective: Molecular level response to environmental exposure

TABLE III. LDEF POLYMERIC MATERIALS

Composites:

- ^aP1700/C6000 Polysulfone
- ^a934/T300 Epoxy
- ^a5208/T300 Epoxy
- ^bPMR-15/C6000 Polyimide
- ^bLARC-160/C6000 Polyimide

^eHigh Performance Polymers:

- Polyimide-Polysiloxane Copolymer
- BTDA-ODA Polyimide
- BTDA-ODA-Al³⁺ Doped polyimide
- 6F-DDSO₂ Soluble polyimide
- 6F-BDAF Soluble polyimide
- PMDA-DAF Polyimide

^gPolyetheretherketone (PEEK)

Films:

- ^aFEP Teflon
- ^cSilvered FEP Teflon
- ^aKynar Fluorocarbon
- ^aP1700 Polysulfone
- ^{a,d}Kapton Polyimide

[†]Traditional Polymers:

- Polystyrene
- Polyvinyl toluene
- Polytetrafluoroethylene
- Polymethylmethacrylate
- Nylon
- Polyethylene terephthalate

^gVarious Silicones

^gPolyurethane

Source: ^a W. Slemp, PI, Expts. A0134/S0010 (B9).

^b R. Vyhna, PI, Expt. A0175 (A1 and A7).

^c LDEF MSIG (various LDEF locations).

^d J. Whiteside, PI, Expt. A0133 (H7).

^e W. Slemp and A. St. Clair, PI, Expt. S0010 (B9).

^f J. Gregory, PI, Expt. A0114 (C9/C3).

^g A. Whitaker, PI, Expt. A0171 (A8).

TABLE IV. MOLECULAR STRUCTURE OF 10-MONTH EXPOSED POLYIMIDE FILMS

SAMPLE	STRUCTURE	COLOR
6F-BDAF		pale yellow
6F-DDSO ₂		colorless
PMDA-DAF		reddish-yellow
BTDA-ODA		yellow
BTDA-ODA-Al ³⁺	BTDA-ODA + Al(acac) ₃	brownish-yellow
KAPTON		yellow

TABLE V. XPS ANALYSIS OF 934/T300 COMPOSITES

Photopeak	Control	10-Month Exposed	5.8-Year Exposed
C 1s B.E. ^a (eV)	285.0 ... 292.3 ^c	283.6 ... 289.7	283.9 ... 288.5
A.C. ^b (%)	68.9	73.3	72.1
O 1s B.E. (eV)	531.5/532.7/533.9	531.3 ... 534.0	531.1/532.5/534.8
A.C. (%)	18.1	18.8	19.7
S 2p B.E. (eV)	168.4	168.6	170.0
A.C. (%)	1.1	0.8	0.9
N 1s B.E. (eV)	399.9	399.6	400.6
A.C. (%)	3.4	5.5	0.8
Si 2p B.E. (eV)	103.2	103.7	104.0
A.C. (%)	1.0	0.9	6.4
Na 1s B.E. (eV)	1072.2	—	—
A.C. (%)	2.0	NSP ^d	—
F 1s B.E. (eV)	689.3	—	—
A.C. (%)	5.5	NSP	NSP

^a Binding Energy.

^b Atomic Concentration.

^c Multiple Peaks.

^d No Significant Peak.

TABLE VI. GLASS TRANSITION TEMPERATURE*

Composite	Exposure Condition	T _g , °C		Film/Resin	Exposure Condition	T _g , °C	
		Control	Exposed			Control	Exposed
P1700/C6000	1	164	164	P1700	1	184	184
P1700/C6000	2	171	171	P1700	5	185	185
PMR-15/C6000	3	343	342	PET	6	85	86
LaRC-160/C6000	4	356	357	PEN-2,6	7	131	131
5208/T300	2	214	215	6F-BDAF	1	259	255
934/T300	1	202	209	6F-DDSO ₂	1	270	273

Exposure Conditions:

1. 10-Month LDEF, Row 9, Tray B
2. 5.8-Year LDEF, Row 9, Tray B
3. 5.8-Year LDEF, Row 7, Tray A
4. 5.8-Year LDEF, Row 1, Tray A
5. STS-46 EOIM-III, 40 hr RAM
6. 5.8-Year LDEF, Row 3, Tray C
7. STS-8 EOIM-II, 40 hr RAM
8. 5.8-Year LDEF, Row 8, Tray A

PMDA-DAF	1	331	—
BTDA-ODA	1	271	269
BTDA-ODA-AP ⁺	1	295	290
PEEK	8	164	166
Polystyrene	5	99	97
Polystyrene	6	92	93
Polyvinyl toluene	6	85	85
Polymethyl-methacrylate	6	119	119

*Thermomechanical Analysis

TABLE VII. MOLECULAR WEIGHT OF LDEF-EXPOSED P1700 SPECIMENS

Film	¹ Solubility	² M _n	M _w	M _z	M _w /M _n	³ IV
Control	100	18,100	53,600	92,600	2.97	0.48
10 month, edge	96	12,700	73,500	183,000	5.77	0.47
10 month, center	87	12,500	90,900	326,000	7.27	0.49
Composite	% Resin					
Control, top ply	30.3	15,800	57,400	100,600	3.62	0.43
10 month, top ply	27.5	14,300	61,200	115,600	4.28	0.39
5.8 year, top ply	32.9	15,400	57,300	99,800	3.71	0.45

¹ Solubility in Chloroform, %

² All molecular weight in grams/mole

³ Intrinsic viscosity, dL/g

TABLE VIII. MOLECULAR WEIGHT OF LDEF-EXPOSED POLYSTYRENE

Experiment	Origin	Sample	¹ Solubility	² M _n	M _w	M _z	M _w /M _n	³ IV
LDEF, Row 3	⁴ UAH, 30 mil	Control	95	79,900	289,900	754,200	3.63	0.68
		Exposed	95	65,700	410,500	1,422,000	6.25	0.77
LDEF, Row 9	⁴ UAH, 30 mil	Control	100	69,300	310,000	1,099,900	4.47	0.74
		Exposed	90.6	57,600	474,500	1,903,000	8.24	0.85

¹ Solubility in Toluene, %

² All molecular weight in grams/mole

³ Intrinsic viscosity in dL/g

⁴ University of Alabama in Huntsville, John C. Gregory, PI.

TABLE IX. MOLECULAR WEIGHT OF LDEF-EXPOSED POLYIMIDE FILMS

SAMPLE	¹ SOLUBILITY	² M _n	M _w	M _z	M _w /M _n	³ I.V.
6F-BDAF						
Control	98.8	85,600	218,000	710,000	2.54	0.829
		87,500	218,000	659,000	2.49	0.816
⁴ Edge	98.7	76,500	212,000	767,000	2.77	0.846
		84,000	225,000	800,000	2.68	0.805
⁵ Center	96.8	80,500	219,000	651,000	2.72	0.824
6F-DDSO₂						
Control	94.5	66,900	181,000	438,000	2.70	0.715
		46,500	176,000	407,000	3.79	0.732
⁴ Edge	86.8	80,700	302,000	904,000	3.74	1.048
		76,200	309,000	966,000	4.06	1.042
⁵ Center	60.9	41,800	306,000	1,110,000	7.32	0.619
		52,200	274,000	802,000	5.25	0.598

- ¹ Solubility in DMAc. %
- ² All molecular weight in grams/mole
- ³ Intrinsic Viscosity, dL/g
- ⁴ Shielded from direct exposure
- ⁵ 10-month direct exposure

TABLE X. XPS ANALYSIS OF 10-MONTH EXPOSED POLYIMIDE-POLYSILOXANE COPOLYMERS

PHOTOPEAK	PIPSX-6		PIPSX-9		PIPSX-11	
	CONTROL	EXPOSED	CONTROL	EXPOSED	CONTROL	EXPOSED
C 1s B.E. ^a (eV)	285.0/287.6/288.7	285.0/286.1	284.7	284.6	285.0/286.5/288.6	283.7 ... 287.8 ^c
A.C. ^b (%)	57.5	15.5	54.4	16.8	69.2	19.0
O 1s B.E. (eV)	532.6	532.9/533.8	532.5	533.0	532.2/533.7	532.7/533.8
A.C. (%)	23.4	53.8	23.7	52.4	19.2	53.0
N 1s B.E. (eV)	400.1	—	—	—	400.4	—
A.C. (%)	1.6	NSP ^d	NSP	NSP	2.5	NSP
Si 2p B.E. (eV)	102.6	103.8	102.2	103.4	102.2	103.6
A.C. (%)	17.6	27.1	21.6	30.8	9.2	28.0
F 1s B.E. (eV)	—	—	—	—	—	—
A.C. (%)	NSP	—	—	—	NSP	NSP
Na 1s B.E. (eV)	—	1073.1	—	—	—	—
A.C. (%)	—	2.1	—	—	—	—
Cl 2p B.E. (eV)	—	200.1	—	—	—	—
A.C. (%)	—	1.3	—	—	—	—

^a Binding Energy

^b Atomic Concentration

^c Multiple Peaks

^d No Significant Peak

LDEF IN ORBIT

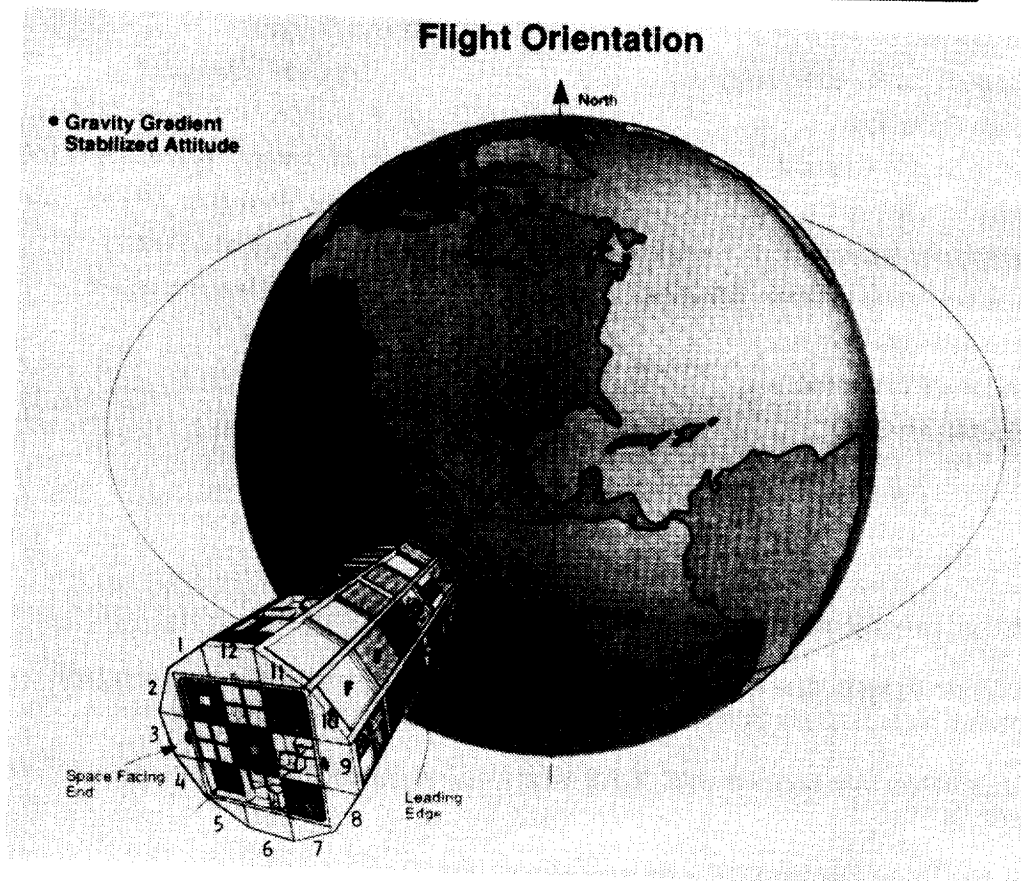
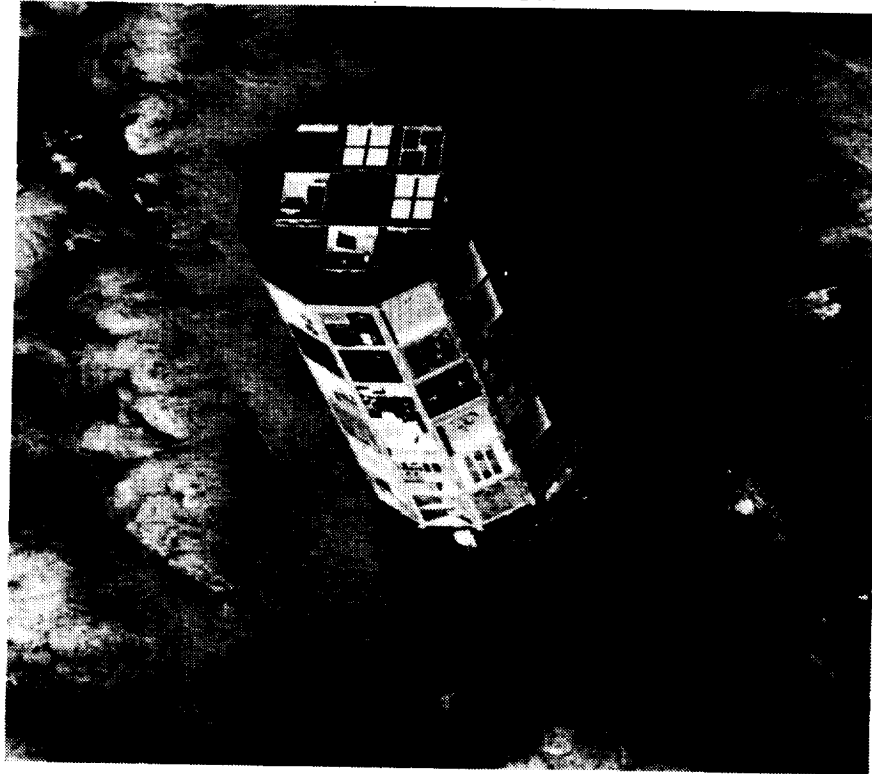
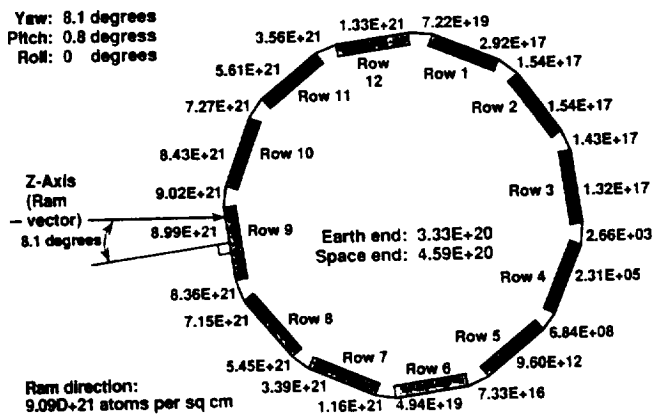
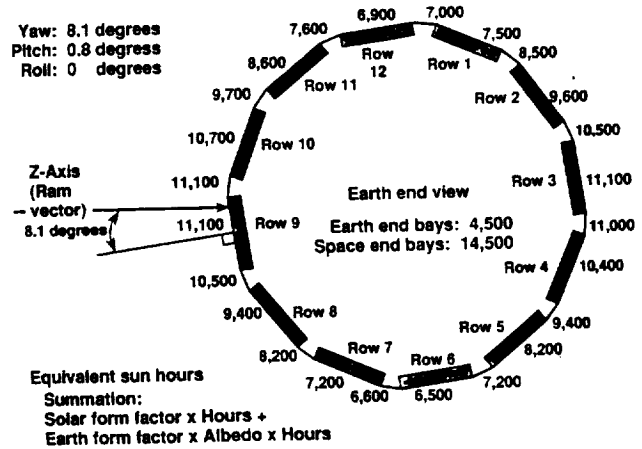


Figure 1. The LDEF and flight orientation.

(a) Atomic Oxygen Fluence Summary



(b) Equivalent Sun Hours Summary



(c) Integrated 5.8-Year Parameters

Thermal Cycles:
~34,000 (-20 to 160°F, $\pm 20^\circ$)

Particulate Radiation:
 e^- and p^+ : 2.5×10^5 rad
Cosmic: <10 rad

Micrometeoroid and Debris:
34,336 Impacts (0.5mm - 5.25mm)

Vacuum: 10^{-6} - 10^{-7} torr

Altitude/Orbital Inclination:
255-180 nm/28.5°

(d) Selected 10-Month Parameters

Atomic Oxygen:
 2.6×10^{20} atoms/cm²

UV Radiation: ~2,300 hrs

Thermal Cycles: ~4,900 (-20 to 140°F)

Particulate Radiation: $\sim 4 \times 10^4$ rad

Micrometeoroid and Debris:
No Visual Impacts on Test Specimens

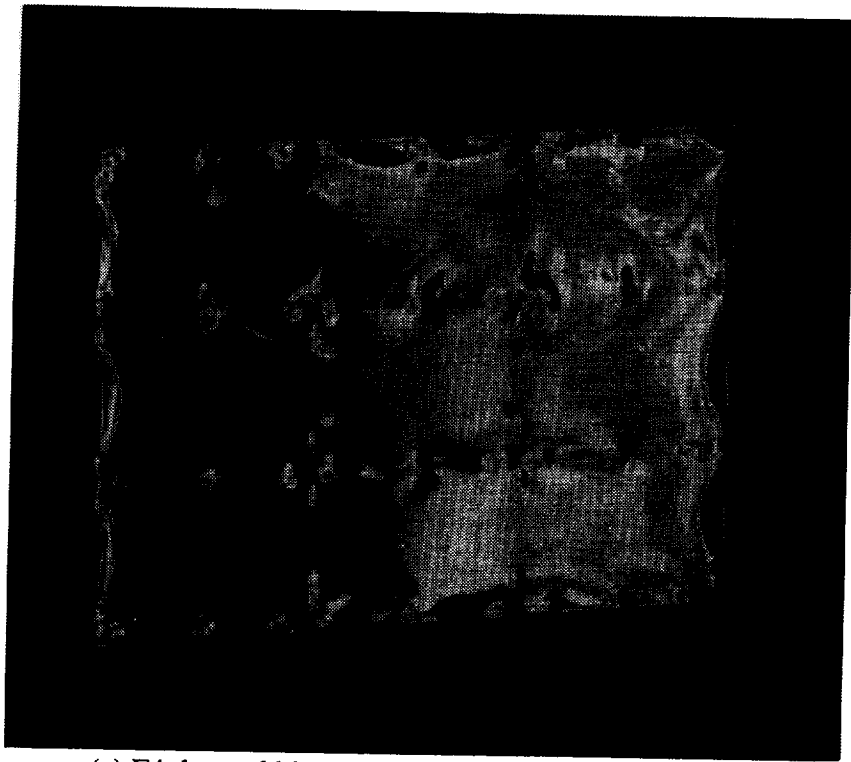
Figure 2. LDEF environmental exposure parameters.

(a) atomic oxygen fluences at end of 5.8-year mission for all row, longeron, and end-bay locations including the fluence received during the retrieval attitude excursion (30).

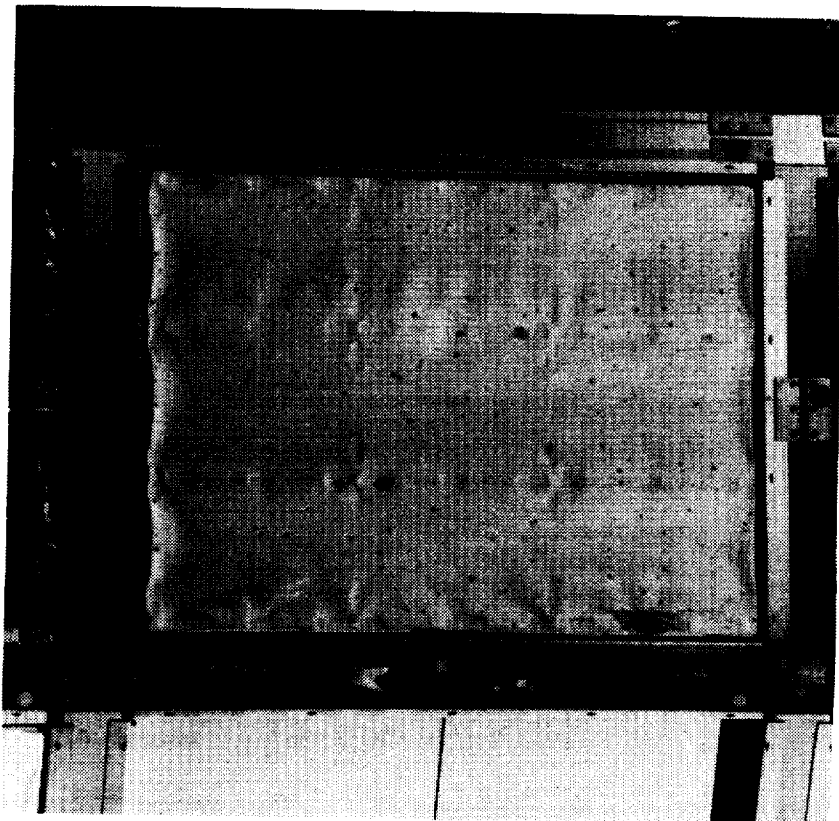
(b) equivalent sun hours at end of 5.8-year mission for each row, longeron, and end-bay location (31).

(c) additional integrated 5.8-year exposure parameters.

(d) selected 10-month exposure parameters.



(a) F4 thermal blanket



(b) E10 thermal blanket

Figure 3. On-orbit retrieval photographs of (a) F4 and (b) E10 silvered FEP teflon thermal blankets.

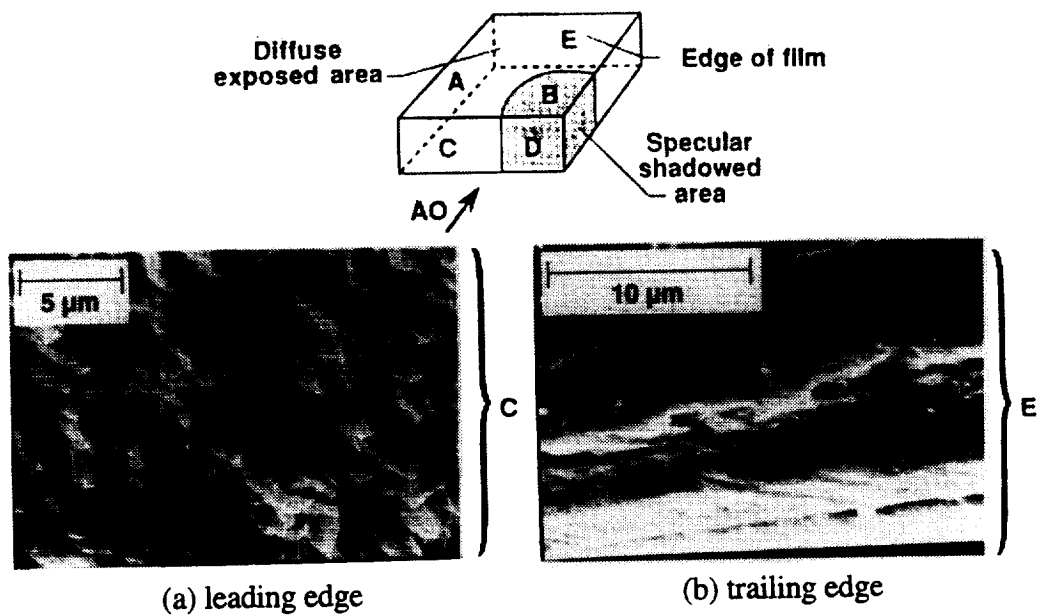


Figure 4. SEM photomicrographs of exposed Kapton film.

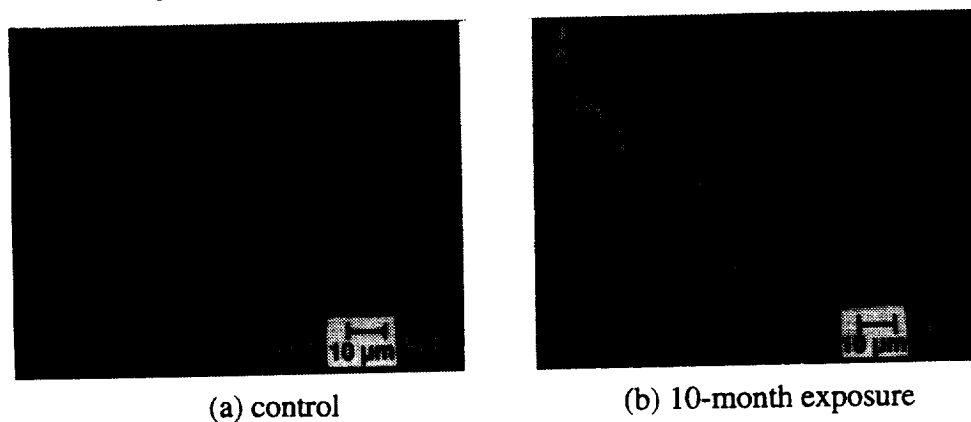


Figure 5. SEM photomicrographs of control and 10-month exposed polysulfone film.

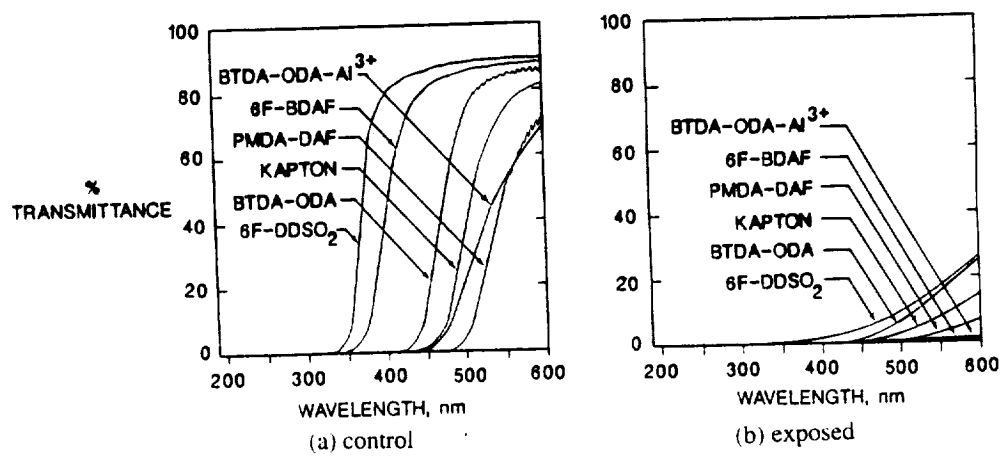
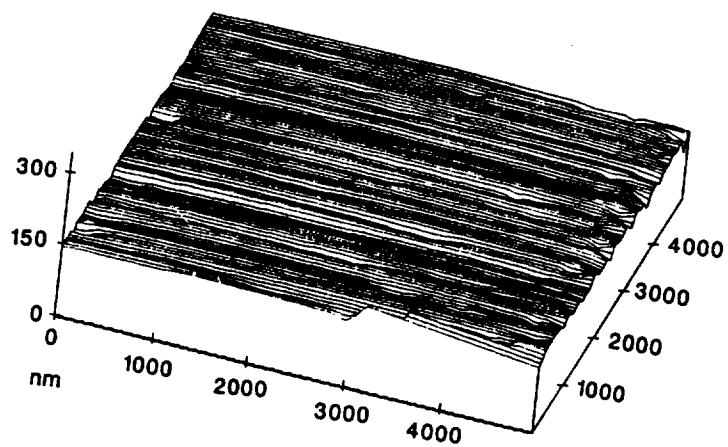
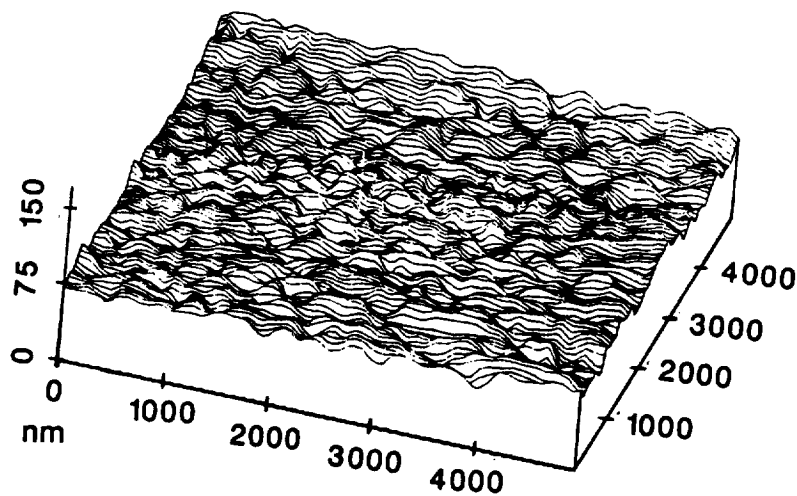


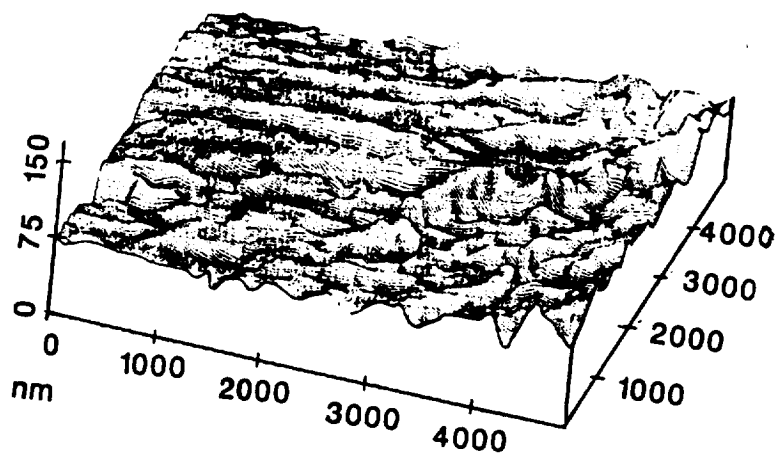
Figure 6. UV-VIS spectra of 10-month exposed polyimide films.



(a) BTDA-ODA unexposed



(b) BTDA-ODA exposed



(c) BTDA-ODA-Al³⁺ exposed

Figure 7. STM analysis of BTDA polyimide films.

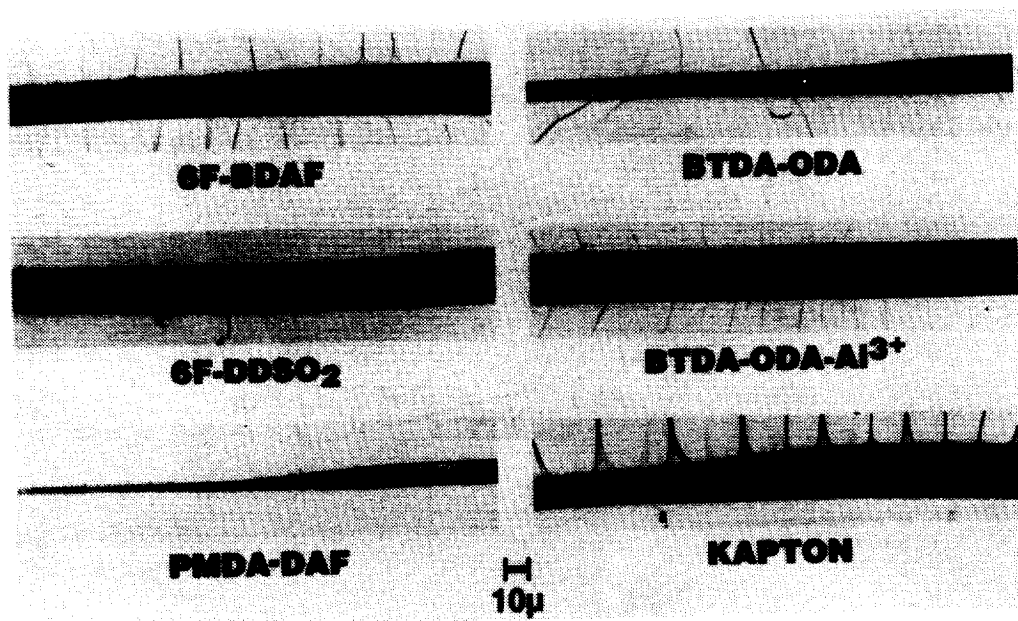


Figure 8. TEM analysis of exposed polyimide films (770X).

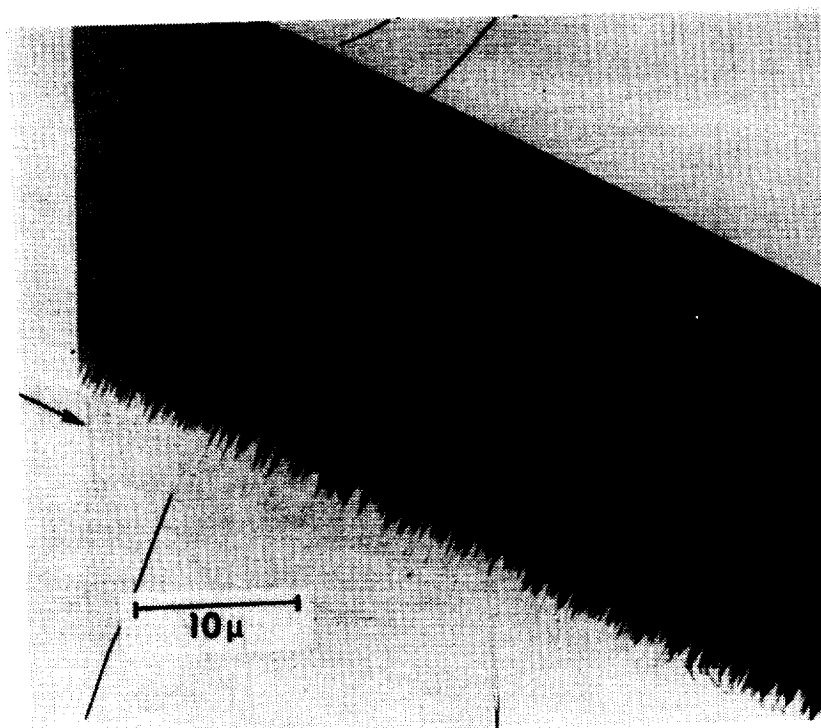


Figure 9a. TEM of exposed BTDA-ODA-Al³⁺ (3675X).

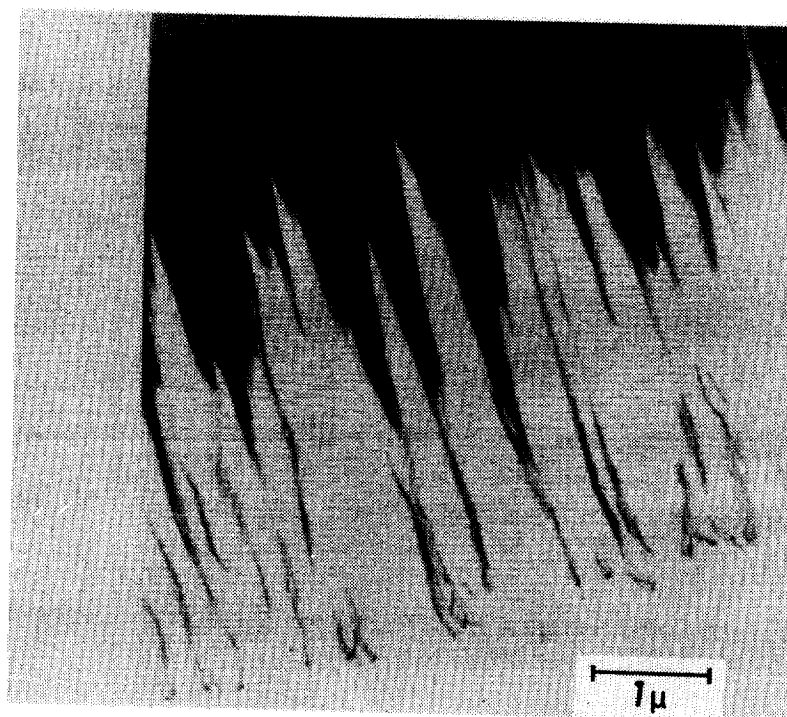


Figure 9b. TEM of exposed BTDA-ODA-Al³⁺ (25,200X).

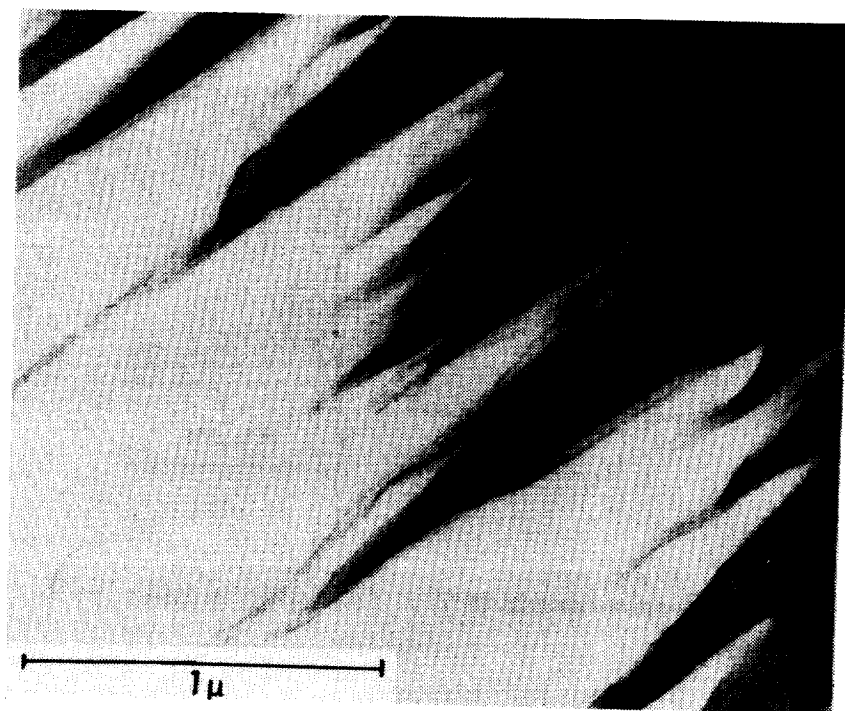


Figure 9c. TEM of exposed BTDA-ODA-Al³⁺ (81,375X).

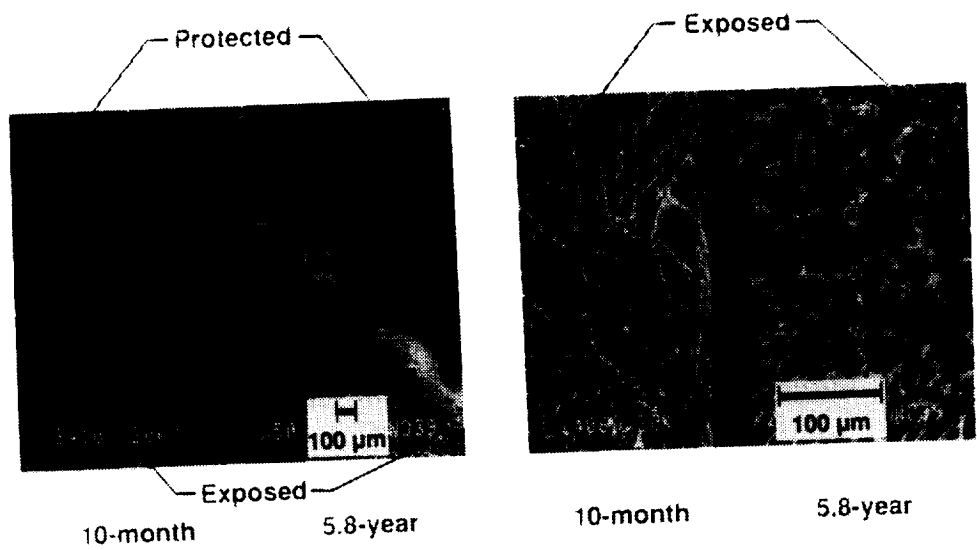


Figure 10. SEM photomicrographs of 934/T300 epoxy/graphite composites after 10-month and 5.8-year LDEF exposures.

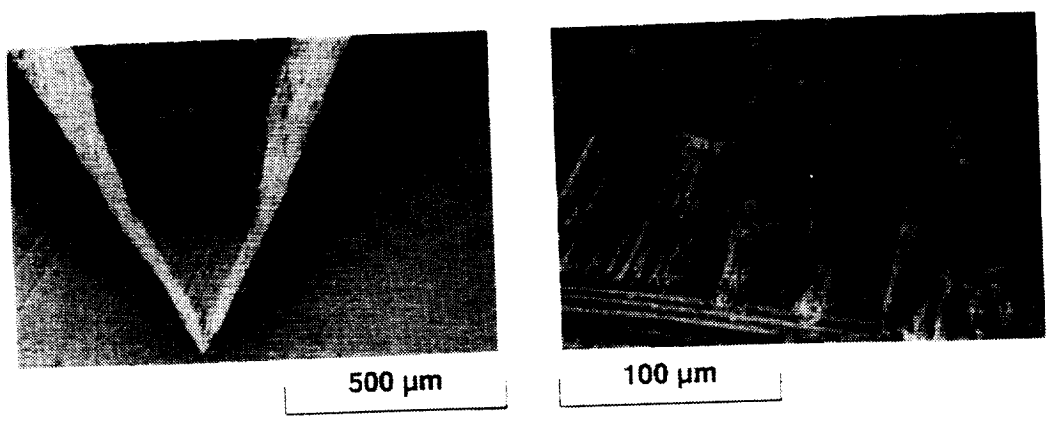


Figure 11. SEM photomicrographs of 5208/T300 epoxy/graphite $[\pm 45]_s$ composite after 5.8-year exposure.

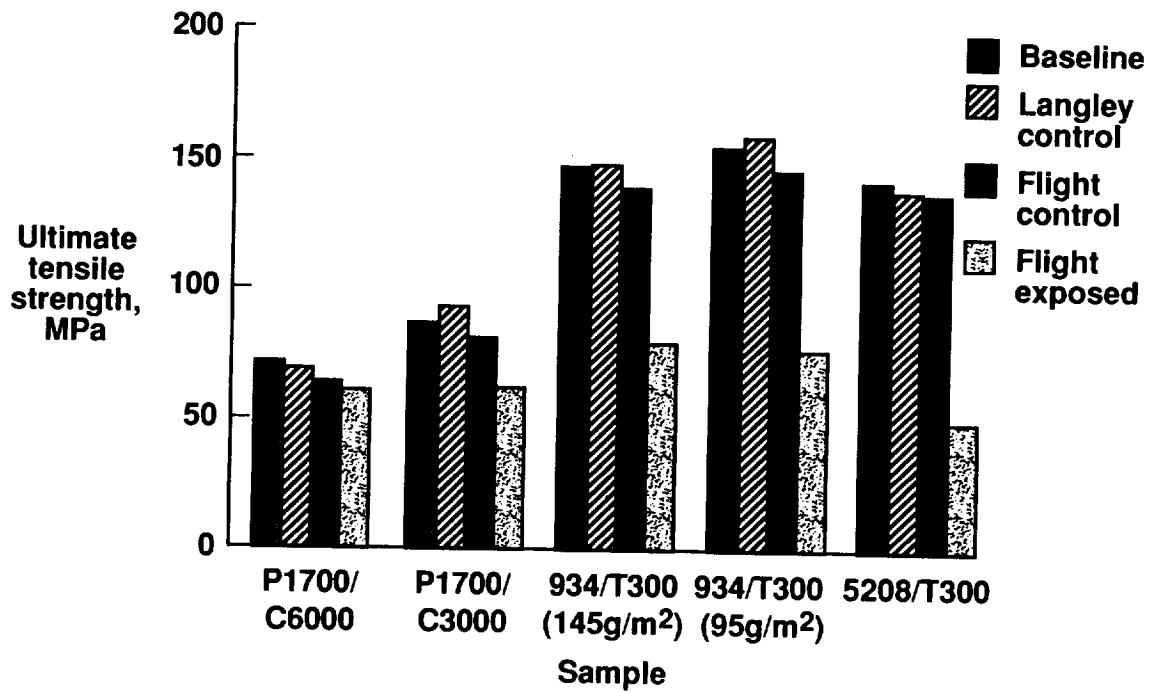


Figure 12. Effects of 5.8 years of LDEF flight exposure on tensile strength of composite materials.

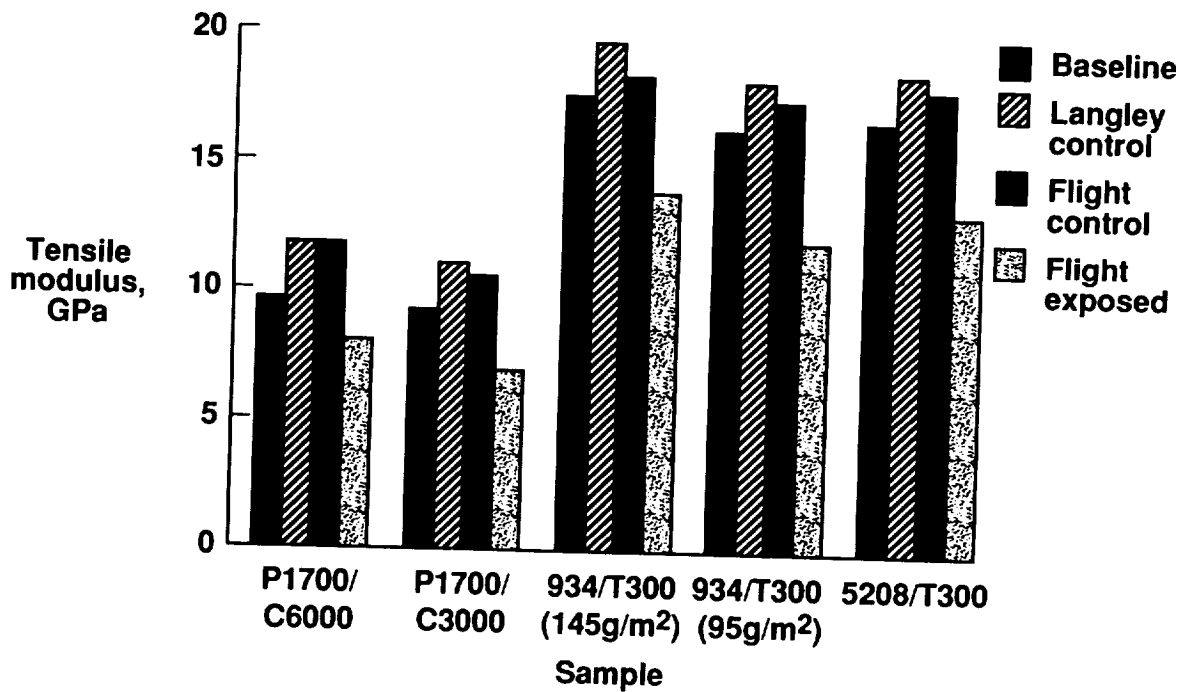


Figure 13. Effects of 5.8 years of LDEF flight exposure on tensile modulus of composite materials.

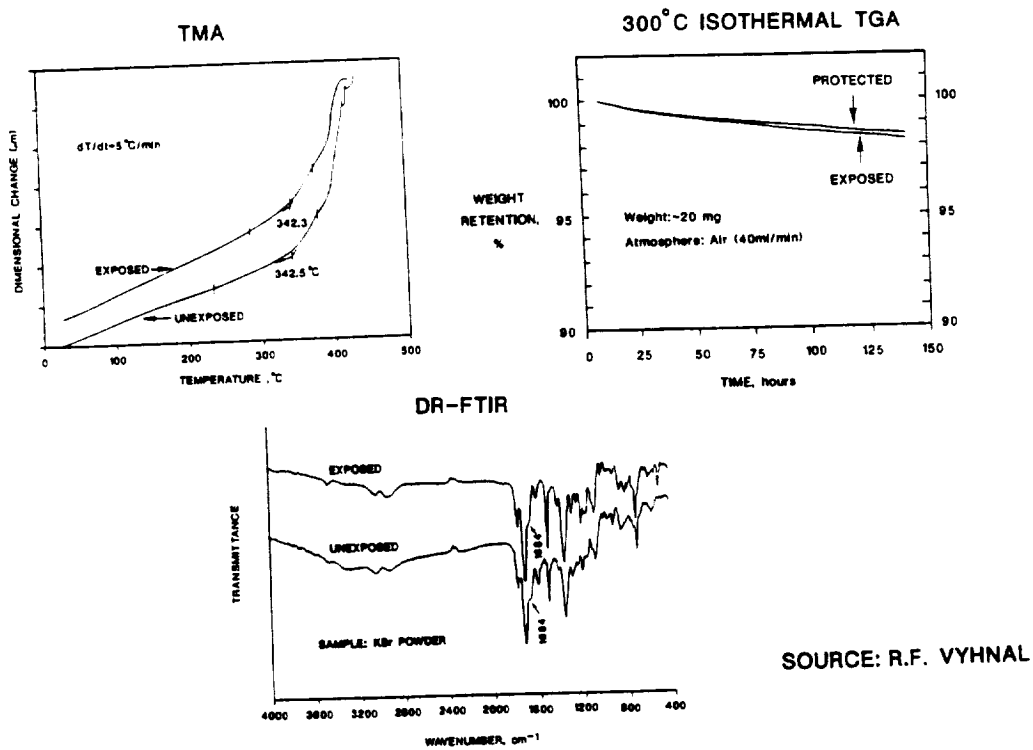


Figure 14. Characterization of PMR-15/C6000 polyimide composites.

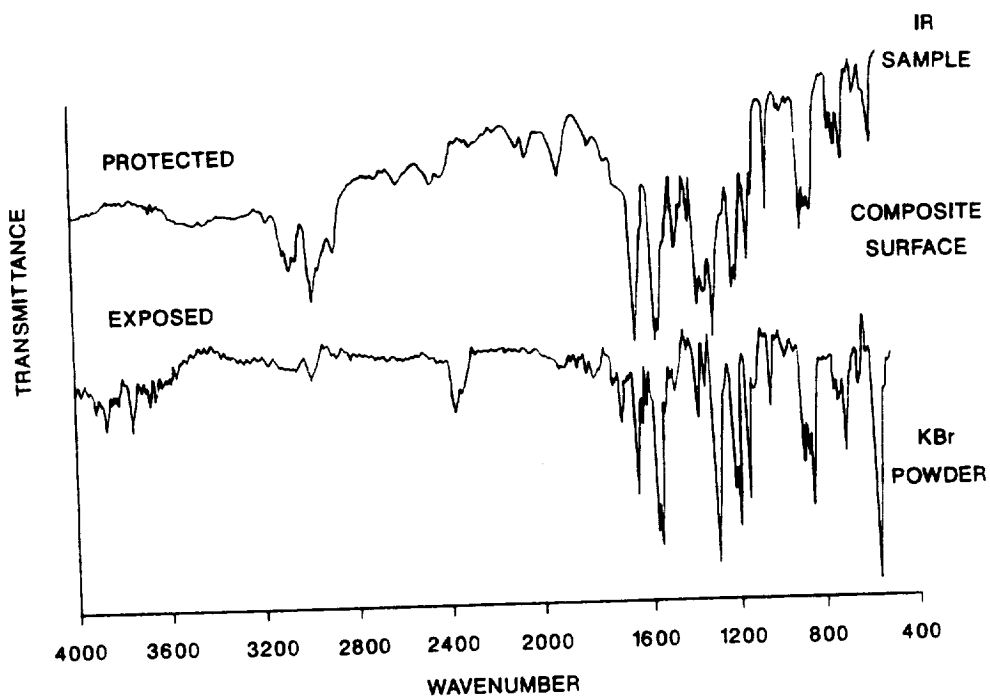


Figure 15. DR-FTIR spectra of LDEF-exposed P1700/C6000 polysulfone composite.

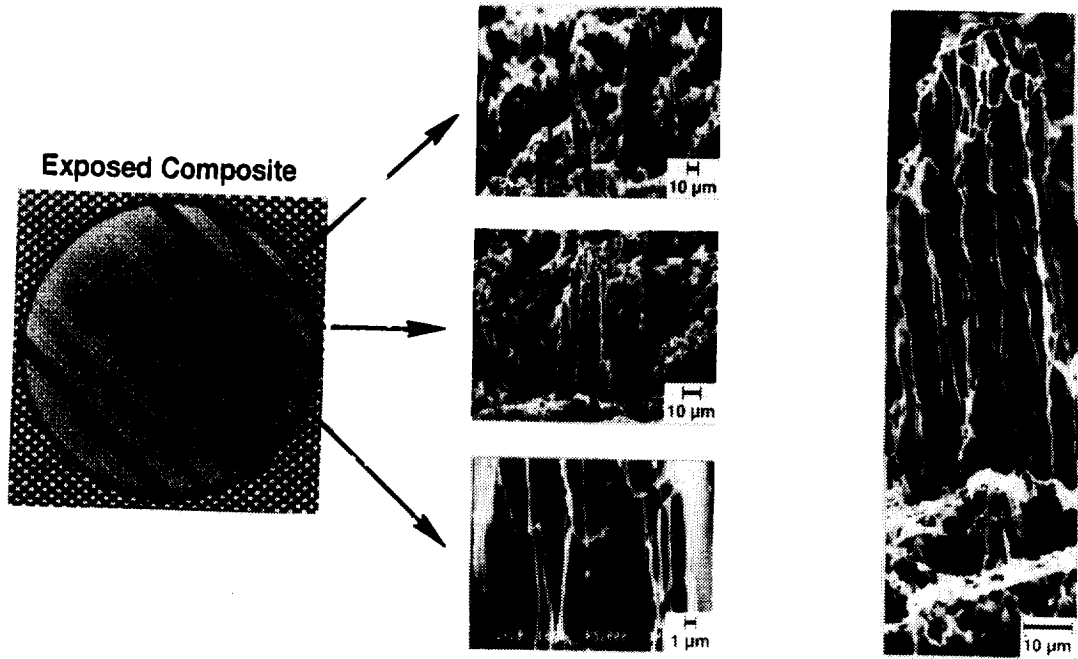


Figure 16. Photograph and SEM photomicrographs of 5.8-year exposed 934/T300 epoxy composite.

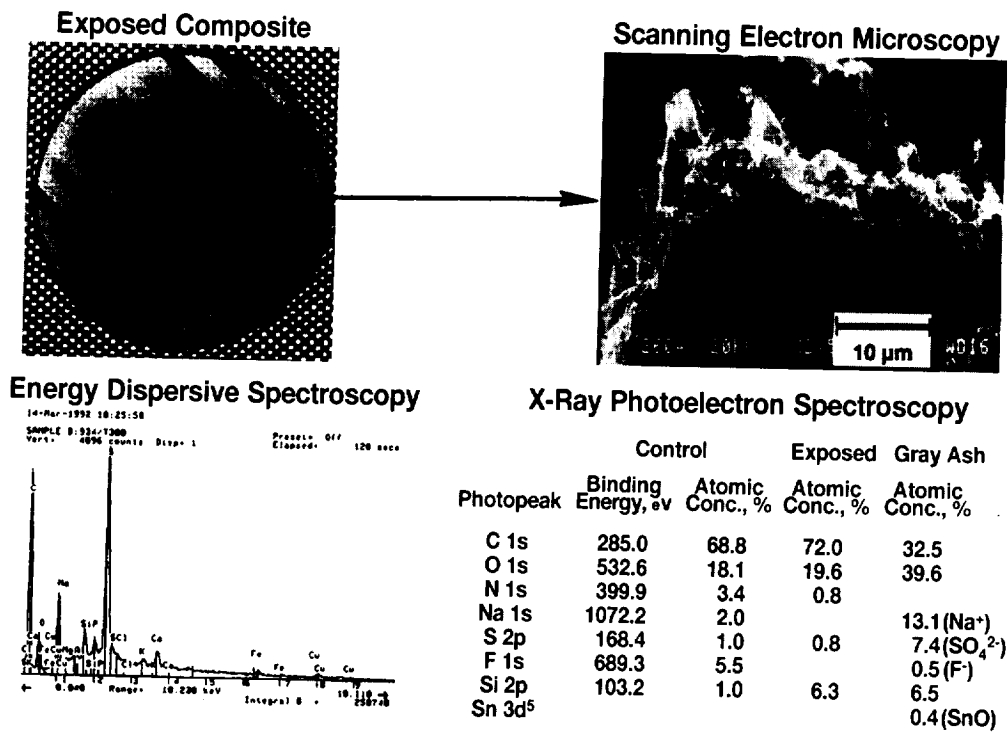


Figure 17. Characterization of 934/T300 epoxy composite.

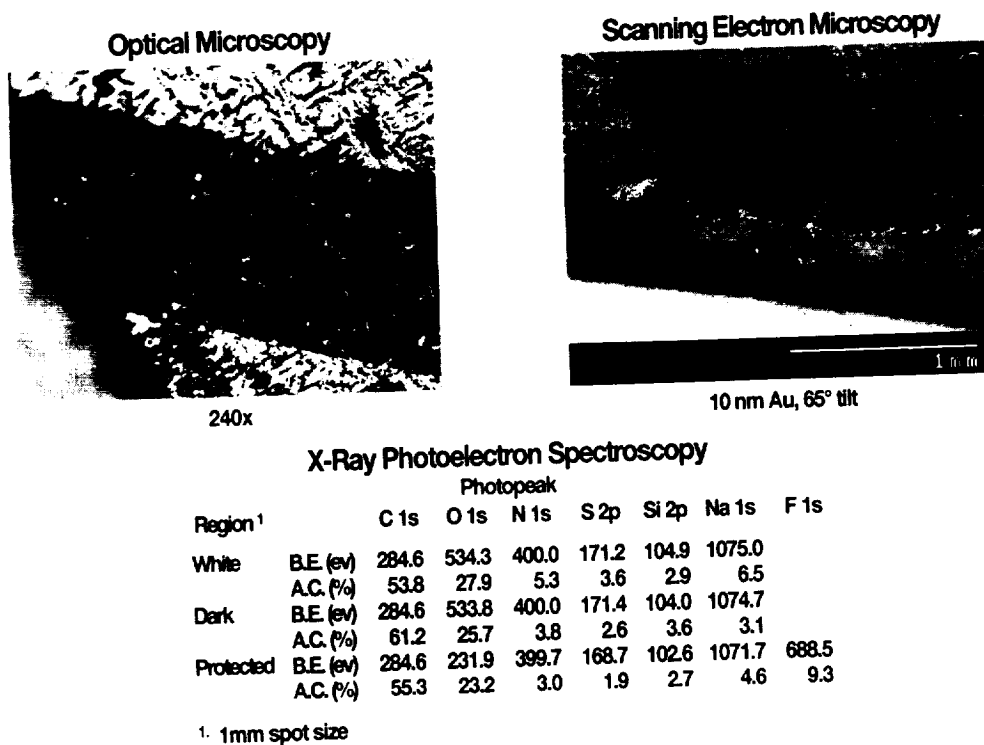


Figure 18. Characterization of 5208/T300 epoxy composite.

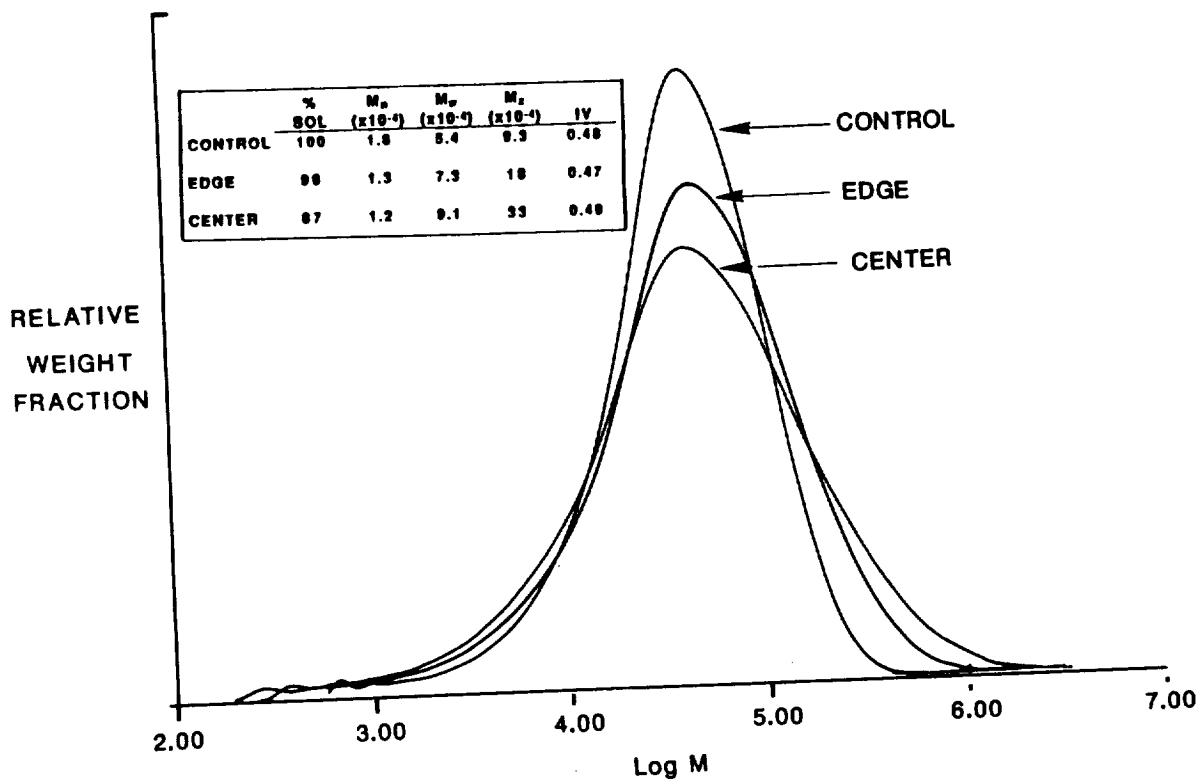


Figure 19. GPC-DV molecular weight distribution of 10-month exposed polysulfone film.

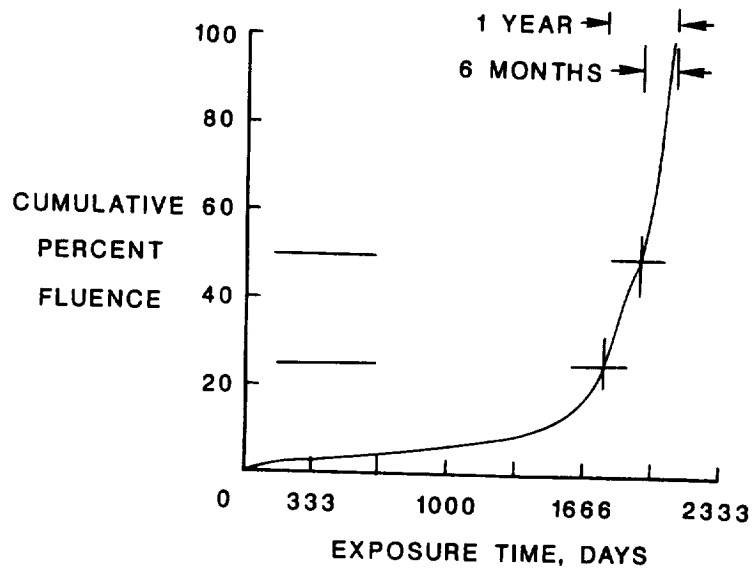


Figure 20. Approximate LDEF cumulative atomic oxygen fluence as a function of exposure time.

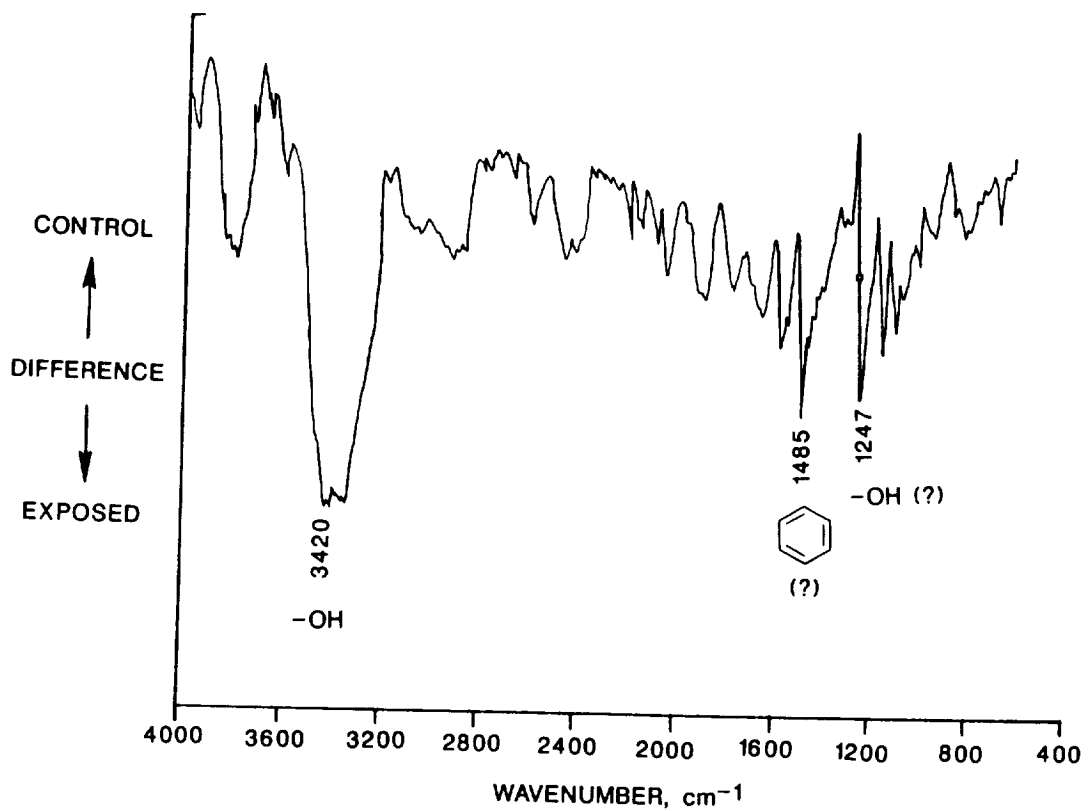


Figure 21. DR-FTIR subtraction spectrum of 10-month exposed polysulfone film.

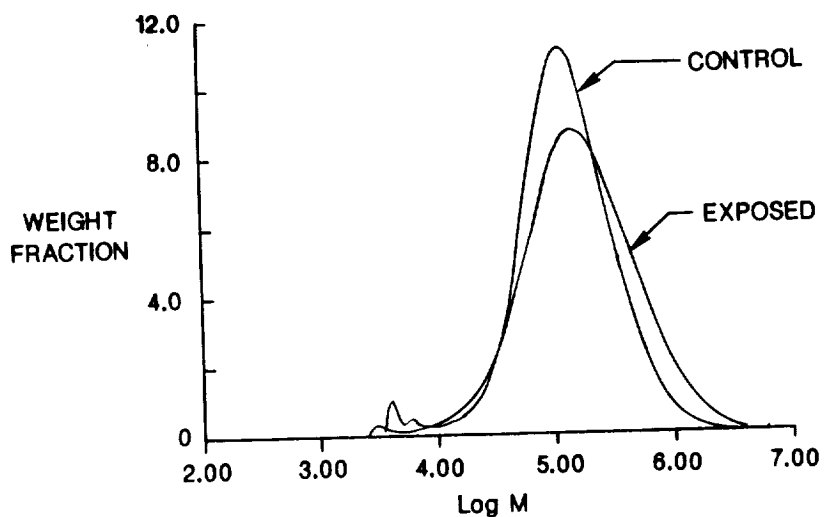
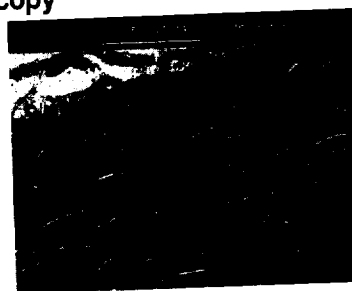
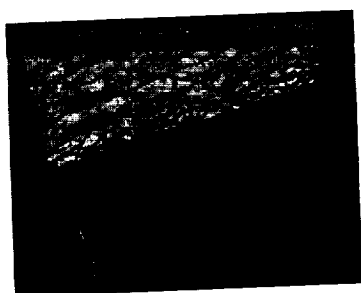
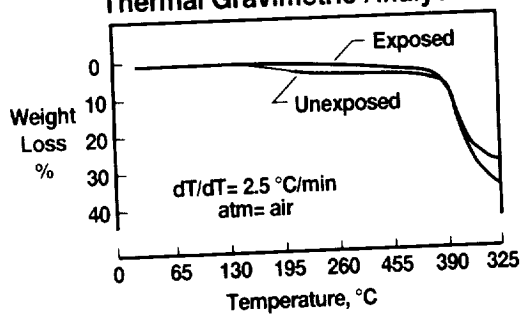


Figure 22. GPC-DV molecular weight distribution of 10-month exposed 6F-DDSO₂ film.

Scanning Electron Microscopy



Thermal Gravimetric Analysis



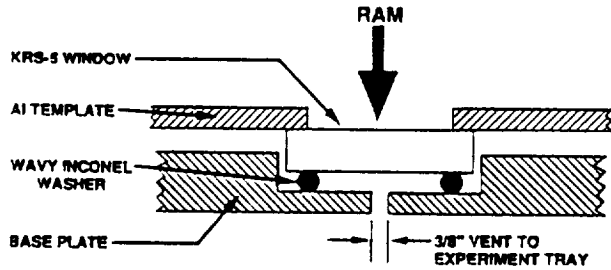
X-Ray Photoelectron Spectroscopy

Sample		C1s	O1s	Si2p
Unexposed	¹ B.E.	285.0	532.6	102.5
	² A.C.	56.0	21.8	22.2
Exposed	B.E.	285.0	532.7	102.5
	A.C.	49.9	28.3	21.8

1. Binding Energy, eV
2. Atomic Concentration, %

Figure 23. Characterization of RTV-511 silicone.

EXPERIMENT DESIGN

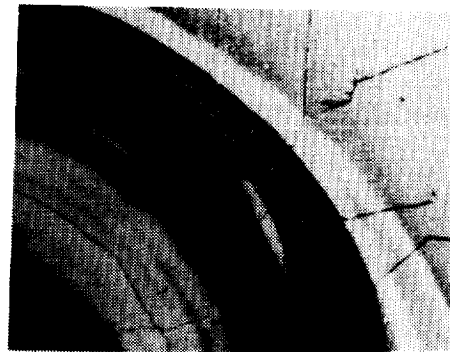


X-RAY PHOTOELECTRON SPECTROSCOPY

Photo Peak	Binding Energy (eV)	Atomic Conc. (%)
DIRECT EXPOSURE SIDE		
C 1s	284.6	15.8
O 1s	529.3/532.5	54.5
Tl 4f 7, 5	118.0/122.3	9.2
I 3d 5, 3	618.7/630.2	9.5
Si 2p	102.9	20.0
NO DIRECT EXPOSURE (VENTED)		
C 1s	284.8	36.1
O 1s	529.5	36.3
Tl 4f 7, 5	118.6/123.1	23.2
I 3d 5, 3	618.7/629.5	1.1
Si 2p	101.9	3.3
CONTROL		
C 1s	284.6/286.5	42.2
O 1s	533.0	21.7
Tl 4f 7, 5	118.3/122.7	25.8
I 3d 5, 3	619.0/630.5	10.1
Si 2p



April 1990



November 1991

Figure 25. Photographs of micrometeoroid impact on Ag/FEP teflon thermal blanket (100X).

