Effect of Low Earth Orbit Atomic Oxygen Exposure on Epoxy Functionalized Siloxanes

J. W. CONNELL,[1,*] J. V. CRIVELLO,[2] and D. BI[2]

[1] Materials Division, National Aeronautics and Space Administration, Langley Research Center, Hampton, Virginia 23681-0001 and [2] Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180-3590

SYNOPSIS

Epoxy functionalized siloxanes (EFS) are a novel class of UV curable monomers that can be rapidly photopolymerized to give transparent coatings and composites. Thin films of these materials have been subjected to low Earth orbit exposure to atomic oxygen (AO) aboard the space shuttle. It was found that UV cured samples of all four different EFS monomers exhibited excellent AO resistance both to ambient in-flight conditions as well as exposure at 120°C. Based on SEM, STM, XPS, and weight loss data, it was proposed that AO exposure of these materials efficiently produces a thin layer of SiO_x at the surface of the sample. This layer provides a barrier toward further attack by AO. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

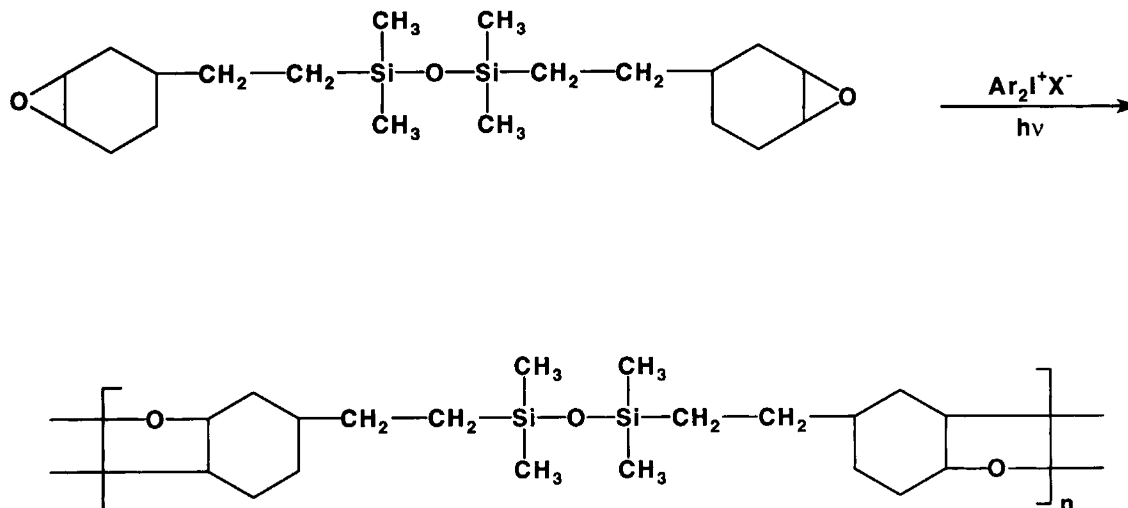
Evaluation of Oxygen Interactions with Materials-III (EOIM-III) is the third in a continuing series of materials exposure experiments flown aboard the space shuttle. The objective of this experiment, which was flown in August 1992 aboard Atlantis (STS-46), was to expose material samples to the low Earth orbit (LEO) environment under controlled temperature conditions. Subsequently, the samples were brought back to Earth for characterization and assessment of environmentally induced effects on a variety of material properties. The samples were mounted on temperature controlled exposure trays and the temperature was monitored during the course of the flight experiment. Most of the epoxy functionalized siloxane (EFS) samples discussed herein were mounted on the 120°C exposure tray only because there was lack of available space on the ambient temperature exposure tray. The temperature fluctuation was recorded as ±10°C during the exposure period.

The primary parameters of concern for organic polymeric materials in LEO are degradation due to atomic oxygen (AO) and ultraviolet (UV) radiation. Other parameters that can affect organic polymeric materials such as vacuum, thermal cycling, particulate radiation, and micrometeroids and debris are somewhat less important for short-term LEO space flight experiments. The materials in this flight experiment were exposed to $2.3 \pm 0.1 \times 10^{20}$ oxygen atoms/cm^2 and 30.6 UV sun hours. AO is known from previous space flight experiments, of both short and long duration, to cause substantial erosion and mass loss of organic polymers.[1-4] Certain perfluorinated polymers, such as poly(perfluoropropylene-*co*-tetrafluoroethylene) (FEP Teflon®) have exhibited good resistance to AO in both ground based and space flight exposure experiments. However, simultaneous exposure to AO and UV radiation can dramatically increase the rate of degradation of this material.[5,6] Coatings of inorganic oxides such as aluminum oxide,[7] silicon oxide,[7] chromium oxide,[8] and indium-tin oxide,[9] as well as decaborane-containing polymers,[10] have been shown to protect organic materials from oxygen plasma and/or AO erosion. To provide maximum protection, the coatings need to be ~ 500–2000 Å thick, relatively uniform, and defect free.

UV radiation present in LEO is of sufficient energy to cause organic bond cleavage. Organic polymeric materials can undergo UV induced chain scis-

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 57, 1251–1259 (1995)
© 1995 John Wiley & Sons, Inc. CCC 0021-8995/95/101251-09



Scheme 1 Representative photoinitiated cationic cure of epoxy functionalized siloxane.

sion and crosslinking reactions resulting in darkening, thermal conductivity, optical and mechanical property changes, embrittlement, and loss of strength. These material property changes can dramatically affect spacecraft performance and lifetime.

As a means to improve AO or oxygen plasma resistance, silicon in the form of siloxane groups was incorporated in polyimides as backbone or pendent substituents. Enhancement of oxygen plasma/AO resistance occurs through the formation of inorganic silicon (i.e., silicates/silicon dioxide) species by interacting with AO or oxygen plasma.[3,5,11-18] Other polymers containing silicon, such as poly(carborane siloxane)s, have also exhibited excellent oxygen plasma resistance.[18]

The EFSs flown on this experiment showed very low weight losses after exposure to an oxygen plasma.[19] As expected, the silicon near the surface of the oxygen plasma exposed specimens was converted to silicon oxide upon exposure. The cured resins are derived from epoxy functional monomers that contain a catalytic amount (0.5 mol %) of photoinitiator and cure on UV exposure via a cationic mechanism as shown in Scheme 1.[20]

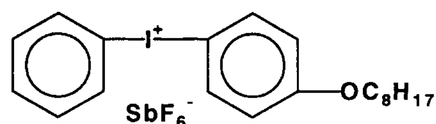
The photoinitiator ($Ar_2I + X^-$) used in these studies was (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate salt with the structure shown in Scheme 2.

The resins are liquids at room temperature and cure very rapidly on exposure to UV radiation at wavelengths from 230 to 250 nm. Once cured, the films are clear, reasonably tough, and relatively colorless at thicknesses of 0.001–0.004 in. Recently, the fabrication of carbon fiber reinforced composites based on the EFS resin systems and electron-beam radiation as a curing medium has been reported.[19] The effects of the LEO exposure on material properties of UV cured EFS resins is discussed herein.

EXPERIMENTAL

Materials

α,ω-Dihydrogen functional oligopolydimethyldisiloxanes were purchased from the Hüls America and Silar Laboratories and distilled prior to use. 3-Vinylbicylclo[4.1.0]heptane (4-vinylcyclohexene oxide) was purchased from the Union Carbide Chemical Co. FEP Teflon® is a product of the DuPont de Nemours Co. $RhCl[(C_6H_5P)]_3$ was obtained from the Alfa Products Division of Morton Thiokol, Inc. The Lamoreaux (octyl alcohol complex of platinum)[21] and Karstedt (platinum complex of 2,4,6,8-tetramethyl - 2,4,6,8 - tetravinylcyclotetrasiloxane) catalysts[22] were gifts of the General Electric Company. The photoinitiator, (4-octyloxyphenyl) phenyliodonium hexafluoroantimonate, was prepared as described previously.[23]



Scheme 2 Chemical structure of (4-octyloxyphenyl)phenyliodonium hexafluoroantimonate salt.

Monomer Characterization

Routine infrared (IR) spectra were obtained on a Buck Scientific Model 500 spectrometer. Gas chromatographic analyses were performed on a Hewlett–Packard HP-5890 Gas Chromatograph equipped with 72 in. × 0.125 in. OV-17 phenylsilicone columns and a flame ionization detector. ^1H- and ^{13}C-NMR spectra were obtained using a Varian XL-200-MHz Spectrometer at room temperature in $CDCl_3$ solvent. Elemental analyses were performed by Quantitative Technologies (Whitehouse, NJ).

EFS

The EFS were synthesized from the corresponding H-functional siloxanes by reaction with 3-vinyl-7-oxabicyclo[4.1.0]heptane in the presence of a platinum or rhodium catalyst as previously described.[20,24] The following procedures are typical of the preparative methods used for the synthesis of all the EFS monomers and oligomers whose chemical structures are shown in Figure 1.

Preparation of 1,3-Bis[2-(3{7-oxabicyclo[4.1.0]heptyl})ethyl]tetramethyldisiloxane (EFS-1)

A solution of 64 g (0.52 mol) 3-vinyl-7-oxabicyclo[4.1.0]heptane in 50 mL *n*-hexane was placed in a 300-mL, three-necked, round-bottom flask equipped with a thermometer, addition funnel, reflux condenser, and magnetic stirrer. To the solution 3 drops of the Lamoreaux catalyst were added and then 33.55 g (0.25 mol) of 1,1,3,3-tetramethyldisiloxane were added dropwise via the addition funnel. The reaction mixture was cooled to control the exothermic reaction. During the course of the reaction, periodic samples were taken and the infrared spectrum was recorded. The reaction was deemed complete (approx. 2 h) when the 2100-cm^{-1} band ascribed to the Si—H bond had completely disappeared. The solvent and excess epoxide starting material were removed under 0.10 mm Hg vacuum. There were obtained 82 g (95% yield) of product diepoxide EFS-1.

ANAL. Calcd for $C_{20}H_{38}O_3Si_2$: C, 62.83%; H, 9.95%. Found: C, 62.64%; H, 9.72%.

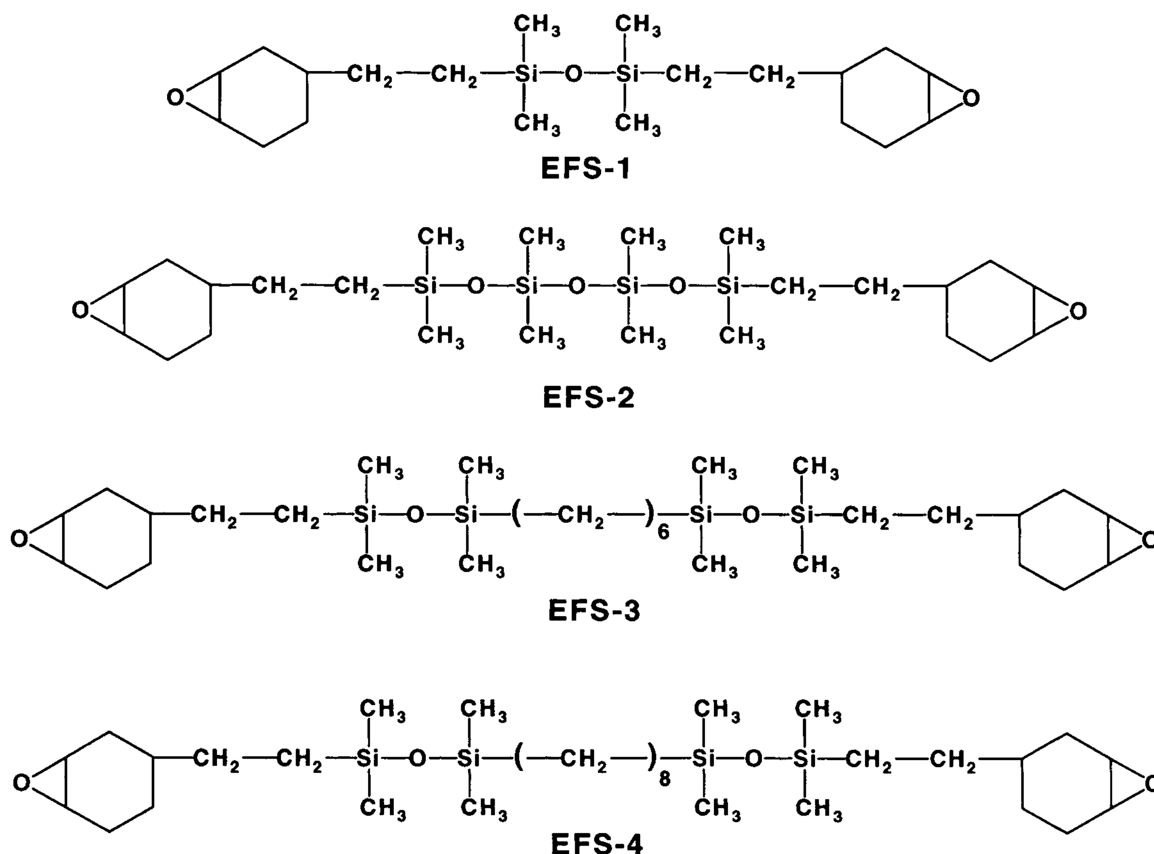


Figure 1 Chemical structures of epoxy functionalized siloxane (EFS-1) monomers prior to curing with a UV source.

Synthesis of Epoxy Functional Oligomer EFS-4

A solution of 13.65 g (0.1 mol) of 1,1,3,3-tetramethyldisiloxane and 6.20 g (0.05 mol) of 3-vinyl-7-oxabicyclo[4.1.0]heptane in 80 mL of toluene were placed in a 250-mL round-bottom flask equipped with a magnetic stir bar and a reflux condenser. To the solution there was added 1–2 drops of the Karstedt platinum catalyst. The reaction mixture was heated at 50–55°C for 3 h and then cooled to room temperature. Approximately 5 mg of 2-mercaptobenzothiazole was added to deactivate the hydrosilation catalyst and the solvent and unreacted starting material were removed *in vacuo*. There were obtained 12.4 g of crude product (95% yield). The product was fractionally distilled to give the desired monoepoxide, 1-[2-(3{7-oxabicyclo[4.1.0]heptyl}) ethyl]-1,1,3,3-tetramethyldisiloxane, having a boiling point of 65°C at 0.3 mm Hg (6.9 g, 56% yield). ^{1}H-NMR ($CDCl_3$, 200 MHz); δ (ppm) 4.64 (*m*, Si—$\underline{H}$); 0.138 (*d*, $HSi(C\underline{H}_3)_2$); 0.027 (*s*, O—$Si(C\underline{H}_3)_2$); 0.51–0.42 (*m*, Si—$C\underline{H}_2$); 2.15–0.72 (*m*, CH_2—$C\underline{H}_2$—C$\underline{H}$—). ^{29}Si-NMR (C_6D_6, 40 MHz); δ (ppm) 10.42 (*s*, $HSi(CH_3)_2$—O); −6.408 (*s*, O—*Si*—$(CH_3)_2$—CH_2).

ANAL. Calcd for $C_{12}H_{26}O_2Si_2$: C, 55.76%; H, 10.14%. Found: C, 55.75%; H, 10.24%.

Combined in a 50-mL round-bottom flask equipped with a magnetic stirrer, reflux condenser, and thermometer were placed 11.0 g (0.01 mol) of 1,7-octadiene freshly distilled from CaH_2, 5.16 g (0.02 mol) of 1-[2-(3{7-oxabicyclo[4.1.0]heptyl}) ethyl]-1,1,3,3-tetramethydisiloxane, 10 mL of dry tetrahydrofuran (THF) and 2.78×10^{-3} g (0.01 mol %) of $RhCl[(C_6H_5)_3P]_3$. The reaction mixture was heated to reflux (70–80°C) in an oil bath. After 6 h at reflux, the IR spectrum showed complete consumption of the starting materials by the absence of a band at 2160 cm^{-1} (Si—H band). The solvent was removed on a rotary evaporator leaving 6.08 g (97% yield) of the desired difunctional epoxy terminated oligomer EFS-4. ^{1}H-NMR ($CDCl_3$); δ (ppm) 3.11 (*m*, 4H, O—C$\underline{H}$—epoxy); 2.20–0.78 (*m*, 30H, —$C\underline{H}_2$—cyclic); 0.46 (*m*, 8H, —$C\underline{H}_2$—Si); 0.01 (*s*, 24H, $C\underline{H}_3$—Si).

ANAL. Calcd for $C_{32}H_{66}O_4Si_4$: C, 61.34%; H, 10.45%. Found: C, 61.22%; H, 10.41%.

Thin Film Photopolymerizations

Solutions of the diepoxide monomers and oligomers containing 0.5 mol % of (4-octyloxyphenyl) phenyliodonium hexafluoroantimonate as the photoinitiator were prepared. The solutions were spread as (0.001–0.003 in. thick) films onto glass plates using a drawknife and photopolymerization was carried out by exposure to UV irradiation for 10–20 s using a 200-W GE H3T-7 medium pressure mercury arc lamp. The distance of the films from the lamp was approximately 10 cm. Following polymerization, the films were carefully removed from the glass plates using a razor blade.

In-Flight Exposure to AO

Free-standing thin films were prepared as described above and characterized prior to integration onto the EOIM-III experimental platform. Both control and flight experiment specimens were taken from the same piece of film. Both control and flight specimens for the 120°C exposure experiment were thermally treated for 24 h at 120°C under vacuum prior to integration on the exposure platform. Shortly after the return of space shuttle Atlantis to Earth, the film specimens were deintegrated from the exposure platform and stored in a dessicator until they were weighed. The control films were stored in a desiccator and were analyzed concurrently with the postflight specimens. The characterization data determined on the flight specimens presented herein is relative to that of the control specimens that had been stored on Earth for ~ 2 years.

Polymer Film Characterization

UV-visible (UV-VIS) transmission spectra were recorded on a Perkin–Elmer Lambda 5 spectrometer. IR spectra were obtained by diffuse reflectance on a Nicolet Magna-IR System 750 spectrometer (DR-FTIR). Scanning tunneling microscopy (STM) was performed in air on a Nanoscope II instrument (Digital Instrument, Inc., Santa Barbara, CA) using a tungsten tip and G-Head accessory. Specimens were prepared by coating with 5–8 nm of gold-palladium using a Hummer IV sputtering system (Anatech, Ltd., Alexandria, VA). A Cambridge Stereoscan 240 (Cambridge Instruments, Deerfield, IL) scanning electron microscope (SEM) was used to obtain SEM photomicrographs of Au-Pd coated specimens. Glass transition temperature (T_g) determinations were conducted on a DuPont 9900 Computer/Thermal Analyzer-Model 943 Thermomechanical Analyzer (TMA) at a heating rate of 5°C/min.

RESULTS AND DISCUSSION

The chemical structures of the EFS monomers prior to cure via UV radiation are presented in Figure 1. Typically, polymeric film samples that have been eroded by AO exhibit a diffuse or frosted appearance easily detected by visual examination. However, visual inspection of the LEO exposed EFS films revealed no evidence of frosting and the specimens remained transparent. The initial weights, and weight losses of the films after LEO exposure are presented in Table I. For comparative purposes, the weight loss data for FEP Teflon® on EOIM-III is included. The samples were either 1.0 or 0.5 in. in diameter and 0.001–0.003 in. thick. Consequently, the initial weights varied considerably. The EFS films were exposed at 120°C only, with one exception (EFS-1), due to limited available space on the ambient exposure tray. In general, the EFS films exhibited weight losses after 120°C exposure comparable to that exhibited by FEP Teflon® after ambient exposure (Table I). The initial sample weights are included in Table I. The ambient LEO exposed film from EFS-1 was brittle and broke apart during deintegration, thus the weight loss could not be obtained. However, the pieces were large enough to perform other analyses. The weight losses exhibited by the EFS films were similar or less than that of FEP Teflon®, with one exception. Unlike FEP Teflon®, these materials do not undergo linear weight loss rates due to the formation of a silicon oxide coating upon exposure to AO. The overall trend exhibited by the weight loss data correlates well with observations from other analyses such as STM and X-ray photoelectron spectroscopy (XPS) discussed later in this section.

UV-VIS Spectroscopy

The films were analyzed by UV-VIS spectroscopy to assess any LEO environmental induced changes in optical transparency. Relative to siliconless organic polymers exposed to AO,[25-28] the EFS films exhibited only minor reductions in optical transmission after LEO exposure (Fig. 2). These minor reductions in optical transmission are likely due to the slight amount of surface roughening that occurred as a result of the reaction of the silicon with AO. In contrast, most organic polymers exhibit dramatic reductions in optical transparency after AO exposure. No visible darkening of the samples were observed. Because the amount of UV exposure was low, most of the observed changes are probably due to AO exposure. The effects of higher doses of UV radiation on these materials is not presently known. The organically bound silicon (siloxane) was oxidized to inorganically bound silicon (silica/silicate) by AO (see XPS section). The thin SiO_x layer subsequently provided protection from further AO attack; consequently the optical transparency was not significantly degraded. Silicon oxide is known to be an excellent protective barrier to AO erosion and is utilized for that purpose on spacecraft in LEO. The chemical transformation of siloxane-containing materials to silicon oxide upon exposure to AO or an oxygen plasma has been known and utilized in the microelectronics industry for some years.[29] This phenomenon has also been observed with other silicon-containing materials flown on several space flight exposure experiments.[25,30-32]

IR Spectroscopy

Selected representative specimens were examined by FTIR spectroscopy. Because control and exposed films were too thick for high quality transmission spectra, somewhat lower quality diffuse reflectance spectra were obtained. Differences between control and exposed samples were difficult to assess by visual examination of the spectra. However, subtle differences could be detected by subtracting the two spectra.

The result of subtracting the exposed EFS-1 spectra from that of the control is presented in Fig-

Table I Weight Losses of Films after Exposure at 120°C in LEO

Film Sample	Exposure Area (in^2)	Initial Weight (mg)	Weight Loss (mg)	Weight Loss (%)
EFS-1	0.196	8.37	0.36	4.3
EFS-2	0.785	31.27	0.01	0.032
EFS-3	0.785	30.48	0.21	0.69
EFS-4	0.785	43.55	0.11	0.25
FEP Teflon® [a]	0.196	15.60	0.03	0.19

[a] Exposed at ambient temperature.

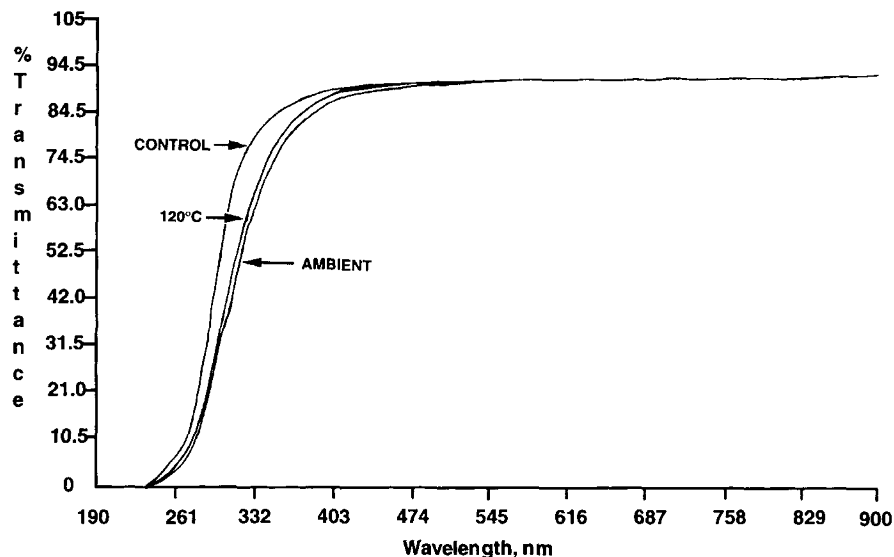


Figure 2 UV-VIS overlay spectra of cured epoxy functionalized siloxane (EFS-1) before and after LEO exposure.

ure 3. An upward inflection is indicative of a higher concentration of a particular functional group in the control specimen. Although differences in DR-FTIR subtraction spectra were generally not dramatic, several trends were noted.

The exposed EFS polymers exhibited less aliphatic character with loss of methyl bands around 2970 cm^{-1}. Film thinning was also observed with exposure as evidenced by an upward inflection in subtraction spectra of most specimens. The band around 3350 cm^{-1} in the exposed film is presumably due to moisture absorption (hydration) of the SiO_x surface that formed upon AO exposure.

Surface Analysis

The silicon-containing films exhibited no discernible differences between exposed and control samples by

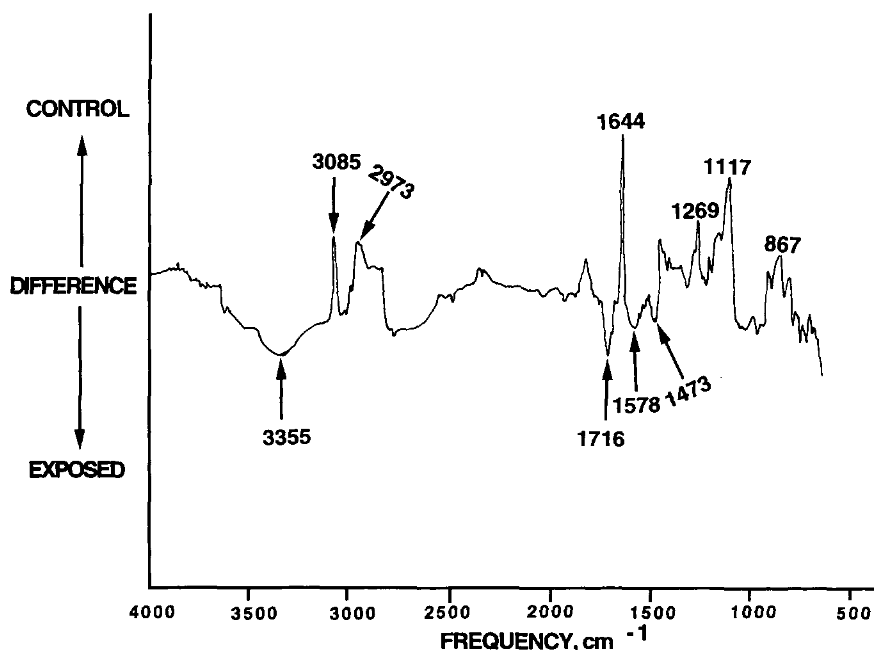


Figure 3 DR-FTIR subtraction spectrum of cured epoxy functionalized siloxane (120°C exposed sample spectrum minus control spectrum).

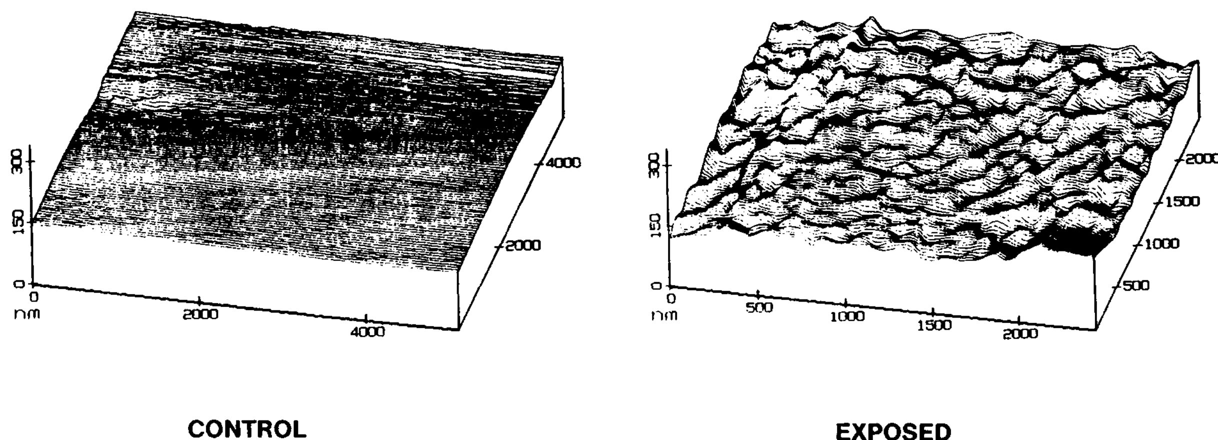


Figure 4 STM lineplots of cured epoxy functionalized siloxane (EFS-4) before and after LEO exposure.

optical microscopy and only minor differences were observed by SEM. However, analyses by STM indicated that some surface erosion did occur. The STM line plot of EFS-4 is presented in Figure 4. STM line plots of the LEO exposed film exhibit the beginnings of the egg-crate-like pattern seen previously in AO exposed polymer films.[33] Presumably, initial AO erosion occurs until a sufficient layer of SiO_x is formed from the reaction of the oxygen atoms with the silicon. This initial erosion is most likely responsible for the slight changes observed in the optical transparency of exposed specimens. Once this layer is formed, the erosion rate is reduced dramatically.

XPS

XPS was performed at Virginia Polytechnic Institute and State University (NASA Langley Grant NAG1-1186). Representative samples of control and exposed EFS films were analyzed using XPS. The results of XPS analyses of EFS-1 and EFS-2 are presented in Tables II and III, respectively. EFS-1 was exposed to LEO at both ambient temperature and 120°C. Both ambient and 120°C exposed samples exhibited increases in the binding energies of the oxygen 1s and silicon 2p electrons relative to that of the control sample. In addition, the concentration of both oxygen and silicon near the surface of the LEO exposed samples increased significantly. The ratio of oxygen to silicon in the LEO exposed samples was ~ 2 : 1. These changes are consistent with the formation of SiO_x on the surface of the LEO exposed samples. LEO exposed samples of EFS-1 were contaminated with a small amount of nitrogen from an unknown source. It is unlikely that this contamination played a significant role in the behavior of this material.

The XPS data for EFS-2 (Table III) exhibited the same general trends as those described for EFS-1. The increases in binding energies and atomic

Table II XPS Results for EFS-1

Photopeak	Control	Ambient Exposed	120°C Exposed
C1s			
Binding energy, eV	284.6	284.6	284.6
Atomic concn, %	65.9	38.7	18.3
O1s			
Binding energy, eV	532.1	532.8	533.1
Atomic concn, %	19.5	38.5	53.1
N1s			
Binding energy, eV	0.0	399.0	399.5
Atomic concn, %	0.0	1.4	0.5
Si2p			
Binding energy, eV	101.8	103.7	103.2
Atomic concn, %	14.6	21.4	28.2

Table III XPS Results for EFS-2

Photopeak	Control	120°C Exposed
C1s		
Binding energy, eV	284.6	284.6
Atomic concn, %	64.3	27.1
O1s		
Binding energy, eV	532.2	533.2
Atomic concn, %	19.6	49.6
Si2p		
Binding energy, eV	102.1	103.9
Atomic concn, %	16.1	23.3

concentrations are consistent with AO induced organosilicon to silicate/silicon oxide chemical transformations. After exposure, the silicon-containing materials typically exhibited a ratio of silicon : oxygen of approximately 1 : 2. Similar behavior, with respect to organosilicon to inorganic-silicon chemical changes, was observed for copoly(imide-siloxane) flown on Long Duration Exposure Facility (LDEF).[25,33] The silicon and oxygen in these materials exhibited increases in binding energies and relative concentrations that were attributed to SiO_x formation as a result of the AO exposure. In addition, these materials exhibited lower weight losses than other siliconless organic polymers.

SUMMARY

EFS films were exposed to LEO at 120°C aboard the STS-46 materials exposure flight experiment, EOIM-III. The materials were exposed to 30.6 UV sun hours and $2.3 \pm 1 \times 10^{20}$ oxygen atoms/cm^2 under controlled temperatures. The observed changes in material properties were primarily due to AO exposure. The films remained clear after LEO exposure with no significant reduction in optical transparency. Changes in the surface chemistry of the exposed film consistent with conversion of the organosilicon to silicate/silicon oxide were evident from XPS analyses. Formation of this surface undoubtedly protected the underlying material from further erosion. Initial erosion due to AO was observed by STM. Presumably, this slight erosion is necessary to allow sufficient reaction of the AO with the silicon to form an *in situ* SiO_x protective coating.

These materials have potential applications on spacecraft in LEO in the form of coatings/paint formulations and carbon fiber reinforced composites. At the time of this flight experiment, no carbon fiber reinforced composites had been prepared. Recently, carbon fiber reinforced composites have been prepared and cured via electron radiation. As a matrix resin in fiber reinforced composites, these systems offer advantages over composites protected only by AO resistant coatings. They offer through-the-thickness protection because if the protective surface layer is imperfect or damaged, the underlying material will react with AO to reform the silicon oxide protective coating. In contrast, composites protected by only AO resistant coatings are subject to rapid erosion by AO if the protective coating is imperfect or sustains damage in orbit. This consideration is very important for longer duration missions in LEO where micrometeroids and debris are abundant and the chances of impact with a spacecraft are significant. These impacts would probably not cause catastrophic damage to the spacecraft, but would certainly damage painted or coated surfaces.

Two of the authors (J.V.C. and D.B.) would like to gratefully acknowledge financial support of this work under NASA Grant No. NAG-1-980.

REFERENCES

1. P. N. Peters, R. C. Linton, and E. R. Miller, *J. Geophys. Res. Lett.*, **10**, 569 (1983).
2. D. E. Bowles and D. R. Tenney, *SAMPE J.*, **23**(3), 49 (1987).
3. W. S. Slemp, B. Santos-Mason, G. F. Sykes, Jr., and W. G. Witte, Jr., *AO Effect Measurements for Shuttle Missions STS-8 and 41-G*, **1**, Sec. 5, 1 (1985).
4. A. Levine, Ed., LDEF-69 Months in Space, First Post Retrieval Symposium, NASA Conference Publication 3134, Part 2, 1991.
5. L. J. Leger, J. T. Visentine, and B. Santos-Mason, *SAMPE Q.*, **18**(2), 48 (1987).
6. A. E. Stiegman, D. E. Brinza, M. S. Anderson, T. K. Minton, G. E. Laue, and R. H. Liang, *Jet Propulsion Laboratory Publication 91-10*, May 1991.
7. B. A. Banks, M. J. Mistich, S. K. Rutledge, and H. K. Nahra, *Proc. 18th IEEE Photovoltaic Specialists Conf.*, 1985.
8. L. J. Leger, I. K. Spikes, J. F. Kuminecz, T. J. Ballentine, and J. T. Visentine, STS Flight 5, LEO Effects Experiment, AIAA-83-2631-CP, 1983.
9. K. A. Smith, *Evaluation of Oxygen Interactions with Materials (EOIM), STS-8 AO Effects*, AIAA-85-7021, 1985.
10. S. Packrisamy, D. Schwam, and M. Litt, *Polym. Prepr.*, **34**(2), 197 (1993).
11. J. T. Visentine, L. J. Leger, J. F. Kuminecz, and I. K. Spiker, AIAA-85-0415, AIAA 23rd Aerospace Conf., January 1985.
12. C. A. Arnold, J. D. Summers, Y. P. Chen, R. H. Bott, D. H. Chen, and J. E. McGrath, *Polymer*, **30**(6), 986 (1989).
13. C. A. Arnold, J. D. Summers, Y. P. Chen, T. H. Yoon, B. E. McGrath, D. Chen, and J. E. McGrath, in *Polyimides: Materials, Chemistry and Characterization*, C. Feger, Ed., Elsevier Science Publishers B. V., Amsterdam, 1989, pp. 69–89.
14. C. A. Arnold, D. H. Chen, Y. P. Chen, R. O. Waldbauer, Jr., M. E. Rogers, and J. E. McGrath, *High Perf. Polym.*, **2**(2), 83 (1990).
15. J. W. Connell, D. C. Working, T. L. St. Clair, and P. M. Hergenrother, in *Polyimides: Materials, Chemistry, and Characterization*, C. Feger, Ed., Technomic Pub. Co., Lancaster, PA, 1992, pp. 152–164.
16. J. W. Connell, J. G. Smith, Jr., and P. M. Hergenrother, *J. Fire Sci.*, **11**(2), 137 (1993).

17. P. R. Young and W. S. Slemp, LDEF Materials Workshop '91, *NASA Conf. Pub. 3162,* Part 1, 1991, pp. 376–378.
18. J. Kulig, G. Jefferis, and M. Litt, *Polym. Mater. Sci. Eng. Proc.*, **61,** 219 (1989).
19. T. C. Walton and J. V. Crivello, *Soc. Adv. Mater. Proc. Eng. Ser.,* **39**(1), 497 (1994).
20. J. V. Crivello and J. L. Lee, *J. Polym. Sci., Polym. Chem. Ed.,* **28,** 479 (1990).
21. H. F. Lamoreaux, U.S. Pat. 3,197,432 (1965), 3,197,4332 (1965), and 3,220,972 (1965) (to General Electric).
22. B. D. Karstedt, U.S. Pat. 3,715,334 (1973), 3,775,452 (1973), and 3,814,730 (1974) (to General Electric).
23. J. V. Crivello and J. L. Lee, *J. Polym. Sci., Polym. Chem. Ed.,* **27,** 3951 (1989).
24. J. V. Crivello and D. Bi, *J. Polym. Sci., Polym. Chem. Ed.,* **32,** 683 (1994).
25. P. R. Young, W. S. Slemp, and C. R. Gautreaux, *Soc. Adv. Mater. Proc. Eng. Ser.,* **37**(1), 159 (1992).
26. P. R. Young, A. K. St. Clair, and W. S. Slemp, *Soc. Adv. Mater. Proc. Eng. Ser.,* **38**(1), 664 (1993).
27. P. R. Young, W. S. Slemp, and E. J. Siochi, *Soc. Adv. Mater. Proc. Eng. Ser.,* **39**(2), 2243 (1994).
28. J. W. Connell, P. R. Young, C. G. Kalil, A. C. Chang, and E. J. Siochi, *NASA-Conf. Proc. 3280,* 1994, 157–175.
29. N. J. Chou, C. H. Tang, J. Paraszcak, and E. Babich, *Appl. Phys. Lett.,* **46**(1), 31 (1985).
30. P. R. Young, W. S. Slemp, W. G. Witte, and J. Y. Shen, *Soc. Adv. Mater. Proc. Eng. Ser.,* **36**(1), 403 (1991).
31. M. J. Meshishnek, W. K. Stuckey, J. S. Evangelsides, L. A. Feldman, R. V. Peterson, G. S. Arnold, and D. R. Peplinsky, *NASA Technical Memorandum 100459,* **II,** Sec. 5-1 to 5-33 (1988).
32. W. S. Slemp, B. Santos–Mason, G. F. Sykes, and W. G. Witte, *ibid.,* **I,** Sec. 5-1 to 5-15 (1988).
33. C. R. Kalil and P. R. Young, *Int. Instrum. Symp. Proc.,* **39,** 445–455 (1993).

Received December 13, 1994
Accepted March 7, 1995