Low Earth Orbit Resistant Siloxane Copolymers

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SYNOPSIS

Two classes of siloxane copolymers were evaluated for their resistance to the low earth orbit (LEO) environment. Poly(imide–siloxane) (PISX) copolymers were used as the resin for PISX–carbon fiber composites. These composites were exposed to the LEO environment, for 50 h, as part of the "Effect of Oxygen Interaction with Materials" (EOIM-III) experiment aboard the space shuttle STS-46. XPS analysis showed primarily silicon oxides on the LEO-exposed surfaces and evidence of a thermally accelerated oxidation. The results of simulated LEO exposure of the PISX composites show that they are one to two orders of magnitude more resistant than are homopolyimide-based composites. Furthermore, we found, surprisingly, that these materials *erode slower* when far-UV radiation is combined with the atomic oxygen. XPS analysis of PISX exposed only to far-UV allowed a partial mechanism to be proposed for the effect of far-UV radiation on the PISX copolymers. Polyhedral oligosilsequioxane (POSS)–siloxane copolymers were evaluated in a simulated LEO environment and results indicate that the POSS–siloxane copolymers are even more resistant to the simulated LEO environment than are the PISX copolymers; POSS–siloxanes actually gained weight during the exposure and healed the microcracks present. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Materials with resistance to degradation by the aggressive conditions present in the low earth orbit (LEO) are necessary for extended use of lightweight, nonmetallic, structures in space.[1-3] It is well established that the degradation of carbon-based materials in the LEO environment is due to the presence of ground-state atomic oxygen, from photodissociation of molecular oxygen,[4] combined with solar UV radiation and the 8 km/s orbital velocity of vehicles in LEO.[5] A class of noncarbon-based materials with rates of erosion one to two orders of magnitude slower than organic polymers in LEO are the siloxane polymers which, when exposed to atomic oxygen (AO), convert to a protective silicalike coating.[6,7] In an attempt to utilize this desirable property, we selected poly(imide–siloxane) (PISX) copolymers and polyhedral oligosilsequioxane (POSS)–siloxane copolymers for evaluation as coatings and matrix materials for composites.

EXPERIMENTAL

The PISX and POSS–siloxane copolymers were synthesized using literature procedures and were characterized by NMR, ^{1}H and ^{29}Si, viscometry, and/or GPC and elemental analysis. The data for PISX agrees with that published for PISX copolymers.[8] For details on the synthesis and characterization of the POSS–siloxane copolymers, refer to our previous published work.[9]

Poly(dimethyl siloxane) (bispropylamine-terminated) (PDMS), used in the synthesis of PISX, was prepared according to a literature procedure. M_n (3000 g/mol) was determined from ^{1}H-NMR (Bruker AMX-300) and potentiometric titration (0.1M HCl, MCI GT-05 autotitrator). M_w was obtained from GPC analysis of a PDMS–diimine derivative (Hewlett-Packard 1090 LC, polystyrene standards). M_w/M_n = 1.6. PISX was phthalimide-endcapped and had an M_n = 13,000 g/mol; M_w/M_n = 1.7; [η] = 0.22; 5% PDMS in copolymer.

The prepreg tape for the PISX composites was fabricated by coating and drying Celion 6000 graphite fibers several times using a 10% solution of PISX
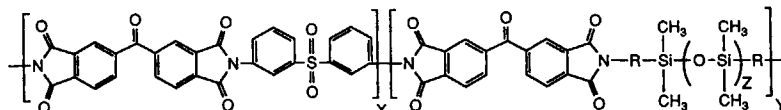
Figure 1   Poly(imide–siloxane) block copolymer.

in dimethylacetamide (DMAC). The percent resin was controlled by the number of times the fibers were coated. The prepreg tape was then hot-pressed to give the final composite (eight layers, unidirectional). The PISX thin films were exposed to a far-UV source: 180–250 nm, for 520 min (32.4 J/cm^2), under a vacuum (<1 × 10^{-4} Torr).

The POSS–siloxane copolymer, **1**—M_n = 46,700 g/mol, M_w = 203,000 g/mol, T_{dec} = 510°C—is a thermoplastic with T_g = 94°C. Samples were prepared for evaluation by hot pressing the powdered polymer into clear discs at ~ 110°C and 9 psi.

PISX–CARBON FIBER COMPOSITES

Thin-film coatings serve to retrofit current candidate composite materials for space. The effectiveness of this approach, however, is highly dependent on the completeness of coverage of the coating and does not address micrometeoroid or microcrack damage issues.[10,11] A more robust approach is to use an LEO-resistant *matrix* material for the composite. The "Atomic Oxygen Effects Experiment" on the space shuttle (space transportation system, mission-8) STS-8 demonstrated that coatings of PISX are resistant to the LEO environment.[12] It has been shown that the siloxane segments of siloxane segmented block copolymers, such as PISX, migrate to the surface, minimizing the surface energy and effectively dominating the surface chemistry.[13] This phenomenon combined with the surface oxidation of the siloxane to a silicalike material is responsible for the AO resistance.

For the purpose of preparing an LEO-resistant matrix composite, we synthesized the PISX block copolymer shown in Figure 1. We synthesized PISX with the composition shown in Figure 1 for the following reasons: (1) the SO$_2$ bridging units give good solubility and processability, and (2) the low percentage PDMS and low M_n give the best adhesion performance at high temperature while still maintaining the surface migration behavior.[14,15] Table I shows the fabrication conditions and the physical and mechanical properties of the PISX composites prepared.

Composite **1** is designed to be useful in space applications where a high resin content is required, i.e., for long-term survivability in LEO, but where the mechanical properties requirements are less demanding. Composite **2** has mechanical properties comparable to typical PMR-15/graphite composites (flexural strengths of ~ 235 Ksi) and would be useful in complimentary situations. These unoptimized fabrication conditions serve to demonstrate the feasibility of using PISX as the matrix for composites suitable for space applications.

"EFFECT OF OXYGEN INTERACTION WITH MATERIALS" (EOIM-III) EXPERIMENTS, STS-46 SHUTTLE FLIGHT

Samples of composite **2** were exposed to the actual LEO environment as part of the "Effect of Oxygen Interaction with Materials" (EOIM-III) experiment aboard the space shuttle STS-46 in March 1992.

Table I   Fabrication and Properties of PISX/Celion 6000 Composites

	Processing Method	Density (g/cc)	% Resin by Weight	Short-beam Shear Strength	Flexural Strength
Composite 1	200°–315°C 200 psi for 1–2 h	1.47	58	5 Ksi	105 Ksi
Composite 2	200–315°C 500 psi for 1–2 h	1.54	37	8 Ksi	194 Ksi

Table II XPS Surface Analysis of PISX Composites Flown on STS-46

Tray Temperature	PISX Composite Sample Surface	Atom % Compositions		
		% Si	% C	% O
60°C	Ram facing			
	Front	28.2	16.4	54.5
	Back[a]	10	60.8	23.4
	Change in atom %	+18.2	−44.4	+31.1
120°C	Ram facing			
	Front	27.3	13.7	58.1
	Back[a]	11.1	62.4	21.9
	Change in atom %	+16.2	−48.7	+36.2

[a] XPS of back surface agrees well with XPS of samples before space exposure.

The samples were exposed, in heated trays at 60 and 120°C, to the LEO environment. The heated trays allowed investigation of the effect of temperature, atomic oxygen, and UV radiation on the composite samples. The samples were exposed to LEO for ~50 h, the total AO fluence was 2.2×10^{20} O atom/cm^2, and the total time of exposure to the solar UV was 7.6 h.[16]

As expected, the investigation of the surface of PISX composite 2 using X-ray photoelectron spectroscopy (XPS) reveals that the siloxane-rich composite surface was oxidized to the silicalike material. Table II shows a large *increase* in the Si and O (atom %) levels and a *decrease* in the carbon levels from LEO exposure. Evidence of a thermally accelerated oxidation of the PISX composite is seen in the larger changes in atom % for the oxygen and carbon levels on the front (LEO-exposed) surface of the 120°C tray, as compared to the front surface on the 60°C

tray. Inspection of the front surfaces of the sample by SEM showed greater surface roughness for the 120°C tray samples as compared to the 60°C tray samples.

SIMULATED LEO EXPOSURE OF PISX COMPOSITES

A comparative exposure study was conducted at the University of Toronto's Institute for Aerospace Studies (UTIAS) space simulator. The results of the simulated LEO exposure of PISX composite 2 are shown in Table III.[†] The PISX composite was exposed to atomic oxygen with and without far-UV radiation. Comparison of the data shows that the PISX composites are *one to two orders of magnitude more resistant* to the simulated LEO environments than are the homopolyimide composites based on polyether-imide (PEI).[17]

A surprising result was observed when far-UV radiation was included in the exposure experiment. We found that these materials *erode slower* when far-UV radiation is combined with the atomic oxygen. This result is in contrast to the results for silicones,[18] FEP Teflon,[4] and those predicted for aramids,[19] where UV radiation accelerates the degradation process.

Siloxanes are generally considered stable under photoaging or photo-oxidation conditions. Although they can protect underlying material from oxidation, they do not significantly absorb incident UV radiation, as long as they are alkyl-substituted siloxanes; hence, the underlying organic material, in this case aromatic polyimide, is unprotected from the UV ra-

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[†] W. D. Morrison and R. C. Tennyson of the University of Toronto Institute for Aerospace Studies performed the simulated LEO exposures; a description of their facilities appears in Ref. 6 and references therein.

Table III Simulated LEO Exposure of PISX Composites

Composite Sample	Exposure Conditions	Far-UV Intensity (mW/cm^2)	Total Fluence O atom/cm^2	Net Mass Change (mg/cm^2)
PISX/C	Atomic oxygen	0	1×10^{21}	−0.150
PISX/C	Atomic oxygen *and* far-UV	15 (7 earth suns)	1×10^{21}	−0.082
PEI/C[a]	Oxygen Plasma	0	3×10^{20}	−3

[a] Ref. 18.

Table IV XPS Surface Analysis of Far-UV-exposed PISX Coatings

	Atom % Composition				
PISX	C	O	N	S	Si
Unexposed	62.68	15.02	3.96	**2.34**	6.83
Exposed	72.98	12.75	1.79	**0.06**	6.18

diation.[20] One proposed explanation for the slower rate of mass loss from PISX-based composites, in the presence of far-UV, involves extensive cross-linking of the aromatic polyimide segment of the copolymer from the far-UV radiation, preventing formation of volatile oxidation products. Alternatively, photochemically generated radicals may combine with atomic oxygen as it impacts the surface, thus increasing the rate of formation of the protective silicate surface layer.

To attempt to further our understanding of the effect of UV radiation on PISX copolymers, the following experiment was performed[21]: A thin film (10–20 nm) of PISX was spin-cast onto a silver mirror. It was then exposed for 520 min, in vacuum, to the far-UV source. Table IV shows the XPS analysis. The XPS data show almost a complete loss of sulfur from the surface of the film. This is presumably through loss of SO_2, via the mechanism proposed in Figure 2. Since the sample becomes carbon-rich instead of, as expected, silicon-rich, there must be some carbonization of the aromatic structures on the surface. A variety of other radical reactions undoubtedly occur.

From the above experiments, the following conclusions may be drawn: (1) PISX is a suitable matrix for composites for space applications; (2) PISX composites are *one-to-two orders of magnitude more resistant* to the simulated LEO environments than are standard polyimide composites; and (3) PISX composites *erode slower* when far-UV radiation is combined with the atomic oxygen, in contrast to other materials where UV radiation accelerates the degradation process.

POLYHEDRAL OLIGOSILSESQUIOXANE (POSS)-SILOXANE COPOLYMERS

Another particularly attractive class of materials that we explored for use as LEO-resistant coatings and resins are polyhedraloligosilsesquioxane (POSS)-based copolymers. Polyhedral oligosilsesquioxanes ($RSiO_{1.5}$) contain a silicon–oxygen
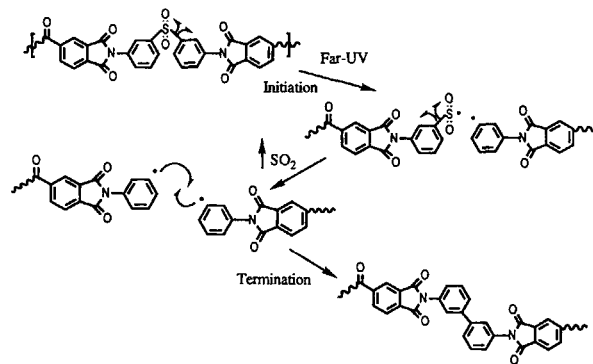

Figure 2 Mechanism for loss of sulfur. The generation of SO_2 in this far-UV-initiated process would supply the driving force for loss of sulfur from the PISX film.

ratio which is intermediate between that found in silicas (SiO_2) and siloxanes (R_2SiO) and very similar in composition to the surface of silicon-based materials after LEO exposure.

We synthesized a family of tractable, POSS–siloxane copolymers, one of which, **1**, is shown in Figure 3.[‡] Evaluation of the resistance of POSS–siloxane copolymer **1** to a simulated LEO environment was done at UTIAS. The samples were exposed to atomic oxygen with and without far-UV radiation.

XPS analysis revealed that the surface of the copolymer samples became silicon- and oxygen-rich after exposure to atomic oxygen with and without far-UV radiation. Comparison of the results shown in Table V to those in Table III indicates that the POSS–siloxane copolymer has a greater resistance to the simulated LEO environment than does PISX. The POSS–siloxane copolymer actually gained weight during the exposures. Combining far-UV radiation with atomic oxygen does not appear to significantly change the results. This supports our

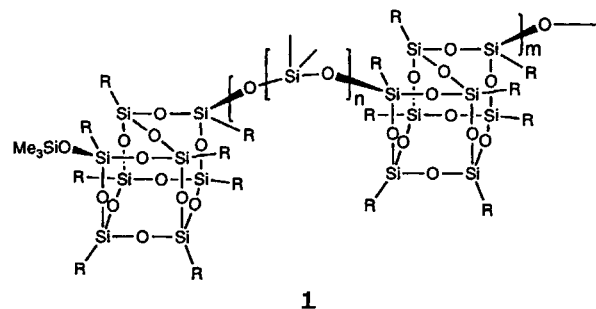‡ For other polyalkylsilsesquioxanes designed as coatings for space hardware, see Ref. 22.

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**Figure 3** POSS–siloxane copolymer **1**; R = cyclohexyl, $n = 5.4$ and $m = 34$.

Table V Simulated LEO Exposure of POSS–Siloxane Copolymers

Exposure Conditions	Far-UV Intensity (mW/cm^2)	Total Fluence O atom/cm^2	Net Mass Change (mg/cm^2)
Atomic oxygen	0	4.3×10^{21}	+0.01
Atomic oxygen and far-UV	15 (7 earth suns)	4.3×10^{21}	+0.02

contention, vida supra, that the effect of far-UV radiation on the PISX copolymer is due to the presence of organic (aromatic) polyimide segments and that the siloxane segment does not interact with the far-UV radiation.
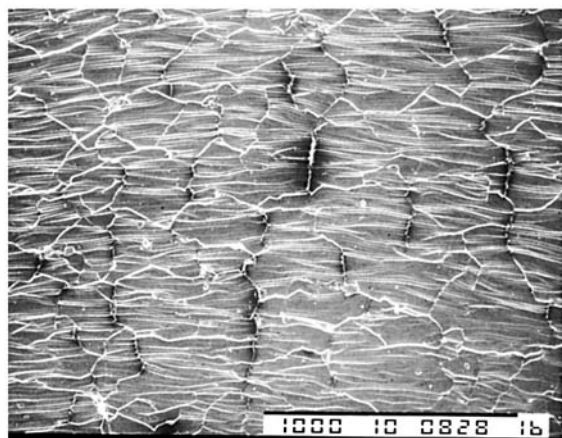
(a)
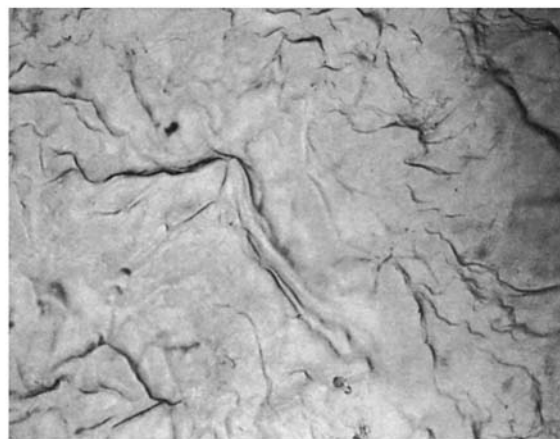
(b)

Figure 4   SEM of (a) unexposed and (b) exposed POSS–siloxane copolymer surfaces. The simulated LEO exposure has "healed" the microcracks present initially in the POSS–siloxane sample.

Comparison of the SEM of the exposed and unexposed POSS–siloxane copolymer samples, shown in Figure 4, reveals an interesting change in the surface morphology. The surface defects or microcracks in Figure 4(a), resulting from sample preparation, were completely "healed" by exposure to the atomic oxygen beam [Fig. 4(b)]. This is in contrast to the results from the Long Duration Exposure Facility (LDEF) experiment where all siloxane-coating samples showed extensive microcracking and oxidation of underlying organic polymeric material due to penetration of AO through the microcracked coating.[§] This annealing phenomenon seen in the POSS–siloxane copolymers may be from surface heating, both from the heat of reactions (ΔH) and from absorption of the kinetic energy (2–3 eV) of the atomic oxygen.[23] This also could be a significant advantage for these materials since microcracking exposes a coated surface to the LEO environment and to accelerated degradation and contributes to loss of long-term durability for composites used in space.[2,18] Future work will include optimization of the thermoplastic properties and exploration of these promising new POSS copolymeric materials for composites.

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