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## 36.1 INTRODUCTION

Composite usage has increased dramatically over the last three decades due to the advantages of light weight, specific strength and stiffness, dimensional stability, tailorability of properties such as coefficient of thermal expansion and high thermal conductivity. Environmental effects on these properties may compromise a structure and must be considered during the design process.

Because of the variety of uses, the composite environment cannot be exactly defined. This chapter details the major environmental concerns for the composite designer, problems encountered with these environments in the past, and some materials or protective systems effectively used. The use of trade names, however, does not constitute endorsement, either expressed or implied, by the authors.

## 36.2 HISTORICAL PERSPECTIVES

Use of composites in commercial aircraft increased under two NASA programs, the Flight Service Evaluation Program and the Aircraft Energy Efficiency Program, begun in the 1970s. These programs included evaluation of environmental effects on the composite parts of the Boeing 727, McDonnell Douglas DC-10 and Lockheed L-1011 commercial aircraft. Elevators, rudders, ailerons, horizontal

stabilizers, vertical fins and fairings were flight-tested with annual inspections. Satisfactory performance of the composite materials was noted over fourteen years, with some parts experiencing more than 39 000 hours of flight loads. Also evaluated were composite parts from military aircraft such as the C-130 center wing box, S-76 tail rotors and horizontal stabilizer, 206L fairing, doors, and vertical fin and the CH-53 cargo ramp skin. Boron/epoxy, graphite/epoxy, Kevlar/epoxy and Nomex honeycomb were used in these aircraft and helicopter components.

## 36.3 ENVIRONMENTS AND EFFECTS

### 36.3.1 BIOLOGICAL ATTACK

Biological attack on composites may consist of fungal growth or marine fouling. As reported in the literature, fungal growth does not appear to be as damaging as the wet conditions that promote growth. Fungicide has been mixed in with resins to retard this growth. Marine boring organisms do not appear to attack glass-reinforced composites. Even though marine organisms will grow on composite surfaces, mechanical properties do not appear to be affected, and the fouling can be removed by scraping (Fried, 1969).

Composites with graphite fibers have been used in medical applications for both internal and external purposes. Internal composite structures, such as artificial joints or plates for bone fracture support, must be biocompatible

or the material may degrade over time. External composite designs, such as artificial limbs or orthotic braces, may experience impact damage, flexural and torsional loading during use.

### 36.3.2 FATIGUE

Fatigue, either through mechanical loads or acoustic vibrations, can cause crack growth or local defect formation. Fatigue design depends not only on the load, but also on the use temperature range and amount of moisture present. Very cold temperatures (below  $-50^{\circ}\text{C}$  ( $-58^{\circ}\text{F}$ )) may increase the stiffness of some composite materials, thereby increasing the susceptibility to fatigue damage (Staunton, 1982).

Destructive effects of fatigue vary with the composite system tested. One example of fatigue resistance is the B-1 horizontal stabilizer torque box, an all-mechanically fastened hybrid composite structure (Staunton, 1982). Acoustic fatigue testing produced no degradation, nor did the service environment of moisture, mechanical fatigue, and temperature cycling from  $-12$  to  $+167^{\circ}\text{C}$  ( $10$  to  $260^{\circ}\text{F}$ ).

### 36.3.3 FLUIDS

#### Moisture

Moisture effects on composites have been studied for decades. Water acts as a plasticizer when absorbed by the matrix, softening the material and reducing some properties of the laminate. Moisture may also migrate along the fiber-matrix interface, affecting the adhesion. Moisture in composites reduces matrix-dominated properties, such as transverse strength, fracture toughness and impact resistance. Lowering of the glass transition temperature may also occur in epoxy and polyimide resins with an increase in absorbed moisture. Debonding can occur due to formation of discontinuous bubbles and cracking in the matrix. Mechanical properties can be reduced even

further if heat is present or if the composite is undercured or has a large amount of voids.

Moisture is absorbed into the composite until a saturation point is reached. This has been described as a non-Fickian process, meaning the rate of relaxation in the material due to water absorption is comparable to the diffusion rate of water. As the material properties change, such as a decrease in glass transition temperature, the diffusion process changes. Swelling stresses due to non-uniform water absorption have been investigated (Ashbee, 1989). Volume expansion due to water absorption can be a few percent at saturation. Moisture absorption is usually dependent on the matrix, but aramid fibers will also absorb water. The mechanical properties degrade in relation to the amount of moisture absorbed, with no further deterioration after saturation is reached. Strength reductions in polyester laminates have been found to be 10–15%, while epoxy resins are less vulnerable.

In a few cases, drying of the composite restored the original mechanical properties. Testing of a glass/polyester laminate allowed to dry after ocean exposure at 1700 m (5700 ft) below sea level for three years showed little change in compressive strength and modulus, flexural strength and modulus, or interlaminar shear strength (Fried, 1969).

Fiberglass composites with either polyester or epoxy resins have been used extensively in marine structural applications because of their strength-to-weight characteristics and resistance to the marine environment. Glass reinforcement is preferred over carbon fibers due to carbon's electrical conductivity, which may result in severe dissimilar metals galvanic corrosion with sea water acting as an electrolyte.

MIL-HDBK-17B, besides providing guidelines for characterizing materials and designing a composite system, contains a wealth of mechanical property and environmental effects data. The effect of moisture absorption or water immersion on weight,

operational temperatures, and mechanical properties such as stress rupture characteristics is discussed.

### **Aircraft fluids**

The aircraft fluid environment consists of fuel, hydraulic fluid, lubricants, deicing compounds, and water. Polysulfone has been found to be sensitive to phosphate ester based hydraulic fluids. Some polymer resins, such as PEEK, may have lower glass transition temperatures after exposure to fluids with a high aromatic content. A study of stressed and unstressed composite materials (Dexter, 1987) evaluated short-beam shear strength and tensile strength after immersion in JP-4 fuel, hydraulic fluid, a fuel-water mixture and fuel/air cycling for 5 years. The composites tested were T300/5208 graphite/epoxy, T300/5209 graphite/epoxy and Kevlar 49/5209 in  $(\pm 45)_s$  configuration. The fuel-water immersion appeared to be the most damaging, reducing the tensile strength of the T300/5209 and the Kevlar/5209 by 11% and 25%, respectively. Fuel-water exposure also degraded short-beam shear strength by as much as 40%.

### **Automotive fluids**

The automotive fluid environment consists of gasoline, oil, battery acid, brake fluid, transmission fluid and coolant. A study by University of Michigan and General Motors (Springer, Sanders and Tung, 1981) details the effects of prolonged exposure of E-glass/polyester and E-glass/vinylester to automotive fluids. Composite samples were immersed in water, salt water, No. 2 diesel fuel, lubricating oil, antifreeze or gasoline. Property changes measured were weight, ultimate tensile strength, tensile modulus, short-beam shear strength and shear (flexural) modulus. Specific materials exposed were OCF-E-920-1 polyester/E-glass, OCF-E-980 polyester/E-glass, and vinyl ester/E-glass. In a moist high-temperature

(150°C (302°F)) environment, microcracking occurred. The amount of moisture absorbed, as measured by weight gain, is directly related to the change in mechanical properties. Salt water, antifreeze and gasoline had the most pronounced effect. Drying did restore some, but not all, of the strength and modulus.

Volkswagen of Germany tested composite systems for compatibility with gasoline, oil and coolant for engine use (Beckmann and Oetting, 1985). These materials were tested both as pure resin and in fiber reinforced laminate form. Among the materials tested were glass, carbon and aramid fibers, high-temperature epoxy, polyimide and polyester resin systems. Mechanical properties of the samples were measured after each 100 h of immersion up to 1000 h total. Adverse reactions of the carbon reinforced materials with metal parts, oil and combustion residues were noted.

### **Other fluids**

Liquids accidentally spilled on composite surfaces may also affect the mechanical properties. Methylene chloride, found in paint strippers, may cause severe damage to epoxy resins and a number of other polymers. Graphite/polyimide composites samples were immersed in various fluids for 10 min then tested for flexure strength and modulus (Lisagor, 1979). Slight increases in these properties were noted for samples immersed in hydraulic fluid, nitrogen tetroxide liquid, monomethyl hydrazine liquid and unsymmetrical dimethyl hydrazine. Samples exposed to hot hydrazine vapors were degraded beyond the ability for mechanical testing. Solvents, bases and weak acids at room temperature do not appear to affect graphite/epoxies and Kevlar/epoxies. Molten metal, such as aluminum or titanium, may react with carbon fibers.

### 36.3.4 WEATHERING

Warm, moist climates may affect the performance of composites. Decreases of 10–20% in tensile strength have been noted for fiberglass/polyester and fiberglass/epoxy (Graner, 1982) where the surface resin has been eroded away due to extended weathering. Resins which are more weather-resistant have been developed since this study. In a 10-year study of real-time weathering of graphite/epoxy, graphite/polysulfone, and Kevlar/epoxy (Dexter, 1987), the materials that absorbed the most moisture were most affected by UV radiation.

Erosion due to rain, snow or ice impact may be a problem for some aircraft parts, such as radomes or leading edge parts. Coatings, such as polyurethane, may be used to make composite parts more resistant to this erosion. A real-time weathering study was performed by Grumman on fiberglass parts from E-2A and A-6A aircraft (Staunton, 1982). Length of service varied from 12 to 19 years. Effects of weathering were dependent on the material used and whether a protective coating was intact. When a hygroscopic BF3–400 curing agent was used, the fiberglass/Epon 828 epoxy lost nearly half of its flexural strength. Fiberglass/Epon 828 epoxy with methylene dianiline/benzyl dimethyl amine (MNA/BDMA) curing agent performed well, retaining tensile and flexural strength. Tensile and flexural test samples taken from a fiberglass rotodome demonstrated the value of good coatings. Where the paint was intact, the material retained more than 90% of its original strength and 82–94% of modulus. Where the paint had been eroded away, the composite retained only 68% of its original strength.

### 36.3.5 SPACE

The Long Duration Exposure Facility (LDEF) has provided a wealth of information on the low-earth-orbit (LEO) space environment

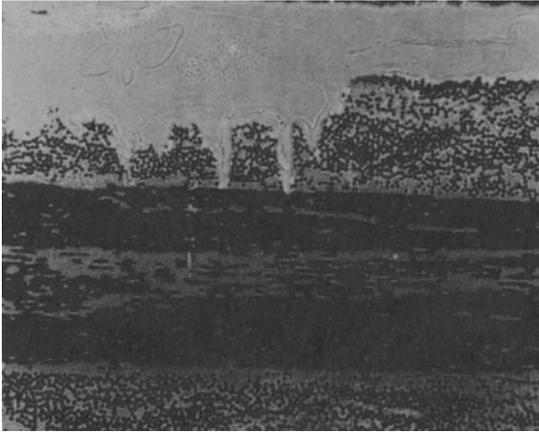
effects on composite materials. Over 35 different types of organic matrix composites were flown on LDEF during its 69-month mission in LEO. The post-flight testing and analysis of composites flown on LDEF has become the basis of understanding the long-term effects of the LEO environment on composites. Data from the Solar Array Materials Passive LDEF Experiment (SAMPLE), the Space Environment Effects on Spacecraft Materials Experiment, the University of Toronto Institute for Aerospace Studies (UTIAS) Experiment, and the Space Exposure of Composite Materials for Large Space Structures Experiment are presented here and in the section on design considerations. Further information may be found in the LDEF Post-Retrieval Symposium Proceedings (Levine 1991, 1992).

### Atomic oxygen

Atomic oxygen is formed through the dissociation of O<sub>2</sub> by UV radiation. It is the predominant molecular species at 100–1000 km orbital altitudes. Its destructiveness is caused by its strong chemical reactivity combined with its translational energy of 5 eV ( $8 \times 10^{-19}$  J) from the high velocity of the spacecraft. Studies on the effects of atomic oxygen have been performed both on samples exposed to the low earth orbit environment and in ground-based simulators.

The Mass Spectrometer Incoherent Scatter (MSIS) neutral atmosphere model is generally used for predicting the atomic oxygen fluence during a mission. Orbital altitude, inclination, other orbit parameters and solar activity are used as inputs. The amount of atomic oxygen received by a surface also depends on its orientation to the RAM or velocity vector.

RAM facing composites (facing into the velocity vector) flown on LDEF were subjected to an atomic oxygen fluence of approximately  $9 \times 10^{21}$  atoms/cm<sup>2</sup> which resulted in a thickness loss up to 0.013 cm (0.005 in) of material, the equivalent of



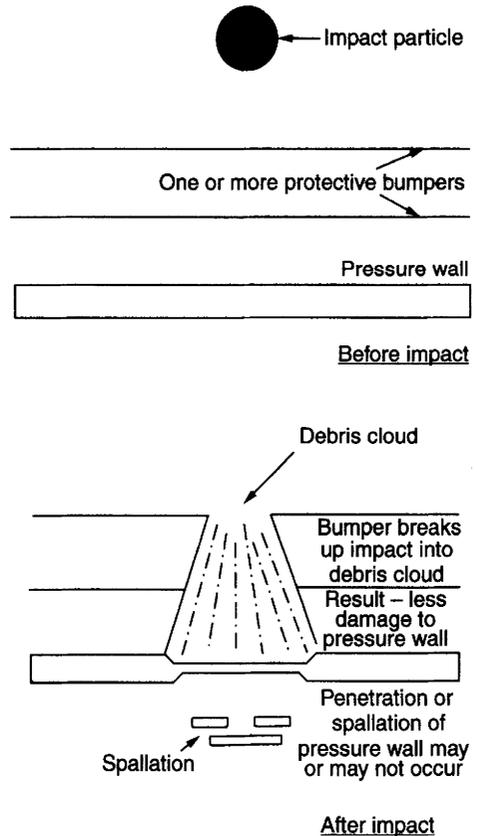
**Fig. 36.1** Cross-sectional photomicrograph of atomic oxygen exposed LDEF graphite-reinforced OMC showing approx. one ply (0.013 cm/0.005 in) of erosion.

approximately one ply of laminate (Fig. 36.1). For unidirectional reinforced specimens, the reduction in mechanical properties was proportional to the reduction in cross-sectional area. The SAMPLE experiment flown on the LDEF contained tensile specimens of graphite/epoxy systems and S-glass/epoxy. The composite systems flown were HMF 322/P1700 polysulfone in a ( $\pm 45$ )<sub>s</sub> weave, HMS/934 in both 0° and 90° unidirectional configurations, and P75S/934, also in both 0° and 90° unidirectional lay-ups. The S-glass/epoxy was flown with and without aluminized thermal control tape as a protective coating. These samples received direct atomic oxygen, as well as UV radiation, thermal cycling and micrometeoroid/debris impacts. Atomic oxygen reaction efficiency was calculated to be approximately  $1 \times 10^{-24}$  cm<sup>3</sup>/atom.

The thickness loss due to atomic oxygen erosion of the S-glass/epoxy samples in this experiment is estimated to be 9.14 μm (0.36 mil). The glass fibers are not susceptible to erosion, and thus protect the underlying matrix. The atomic oxygen reaction efficiency for these samples was calculated to be  $0.13 \times 10^{-24}$  cm<sup>3</sup>/atom.

**Meteoroid/debris impacts**

A spacecraft in any orbit is susceptible to micrometeoroid impact. These small particles, fragments of asteroids or comets, may impact at velocities up to 60 km/s (37 mi/s) but average 17 km/s (10.5 mi/s). Those spacecraft in near-earth orbit are also susceptible to impact from pieces of space junk or debris, also travelling at high speeds. Damage from impact may reduce the strength of composite structures or cause rupture in filament-wound tanks. Damage may consist of cratering, penetration, including penetration of thermal or protective coatings, and spallation Fig. 36.2 is of a classic Whipple-type meteoroid/debris shield before and after particle impact.

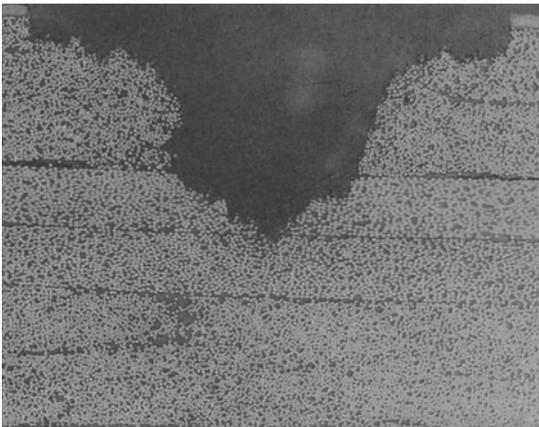


**Fig. 36.2** Hypervelocity impact of Whipple bumper design.

The potential hazard of a meteoroid or debris particle is dependent on its size, velocity, density and angle of impact. NASA SP-8042 may be used to predict the meteoroid environment encountered by a spacecraft in near-earth orbit, earth-to-moon space and near-lunar orbit. The space debris environment in earth orbit is continually changing as more debris is being added with every launch. At the time of publication, NASA TM-100471 is being used as the definition of the space debris environment.

Prediction of damage caused by meteoroid/space debris impact can be made either by using a variety of models, study of impact sites in flight hardware, or simulation in the laboratory. Hydrocodes such as CTH and HULL use finite elements or finite differences to predict penetration or spallation of a composite laminate. Inspection of composite samples from LDEF (Fig. 36.3) revealed 2–5 impacts of <0.1 cm diameter. (<40 mil) per sample. These impacts did not affect tensile strength as much as the atomic oxygen erosion (see previous discussion), but the potential effect of many impacts on a composite structure is obvious.

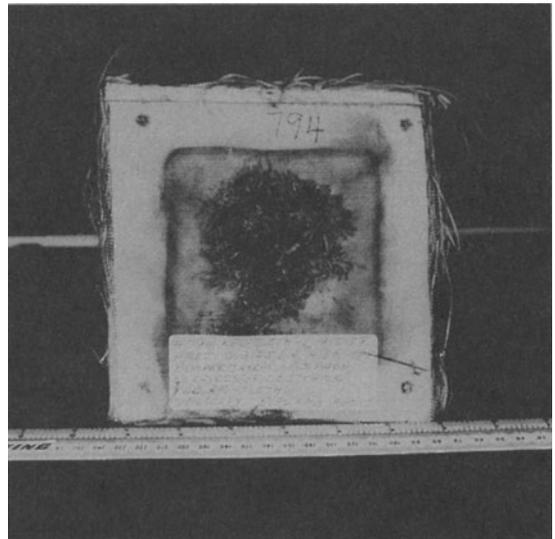
Ground simulations in the NASA/Marshall Space Flight Center Space Debris Impact



**Fig. 36.3** Cross-sectional photomicrograph of coated graphite-reinforced OMC showing impact damage and post-impact atomic oxygen erosion.

Facility have been performed on a number of composite materials. These materials were Kevlar 49/epoxy, non-impregnated Kevlar 49, Spectra 900/epoxy and IM6/3501-6 graphite/epoxy. The test configuration consisted of a classic Whipple design with the composite material used as a bumper protecting a 2219-T87 aluminum pressure wall sample.

The results of these tests (Schonberg, 1990) indicated that some composite systems, such as the Kevlar 49 cloth and Spectra 900/epoxy, performed better than equivalent weight aluminum systems as measured by damage to the pressure wall. However, the Kevlar 49/epoxy and IM6/3501-6 graphite/epoxy panels did not perform as well as an equivalent weight aluminum system at protecting the pressure wall plate from damage, but damage by spallation was far less for composite than metal bumper plates. The composite bumpers did experience large areas of delamination, though this was restricted to the outer layers with peeling in the direction of the surface laminate fibers. Some charring and melting did occur with the Kevlar 49 cloth (Fig. 36.4) and Spectra/epoxy test articles.



**Fig. 36.4** Simulated meteoroid/debris impact in Kevlar 49 cloth panel.

### Particulate radiation

Particulate or ionizing radiation in the space environment consists of trapped radiation in the Van Allen radiation belts, solar and galactic cosmic radiation and bremsstrahlung radiation. Protons, electrons, neutrons, alpha particles, X-rays, gamma rays and other charged particles bombard spacecraft in orbit. Bremsstrahlung radiation is ionizing radiation resulting from the deceleration of electrons. Various computer models exist for predicting the radiation dose during a mission at a particular orbit, but the high variability of solar activity and the resulting magnetic storms may give radiation calculations an uncertainty of an order of magnitude or more.

Protons, electrons and cosmic rays may affect composite materials by surface chemical changes. The radiation threshold for observing effects is between 10<sup>8</sup> and 10<sup>9</sup> rads for graphite/epoxy and graphite/polysulfone. In a cooperative effort between Boeing and Langley Research Center (Fogdall, Russell and Cannaday, 1980), these materials were irradiated with high-energy protons and electrons (approximately 1 MeV) then tested for flexural durability. The composite systems tested were T300/934, T300/5208, and C6000/P1700. Radiation doses of  $5 \times 10^9$  rads or more resulted in surface blistering of the T300/934, although this had a limited effect on mechanical properties. Flexural testing of irradiated samples showed no significant changes for low radiation doses.

A follow-on study performed at Boeing (Fogdall *et al.*, 1983) involved high radiation doses to T300/934, C3000/934, C3000/PMR-15 and C3000/P1700 composites. In this test, compressive breaking strength at a 45° fiber orientation and dynamic mechanical analysis (DMA) were used to measure the effect of 10<sup>10</sup> rads of electron radiation. As much as 15% degradation in breaking strength was noted. The DMA tests also showed a decrease in glass-transition temperature for irradiated samples.

### Thermal extremes

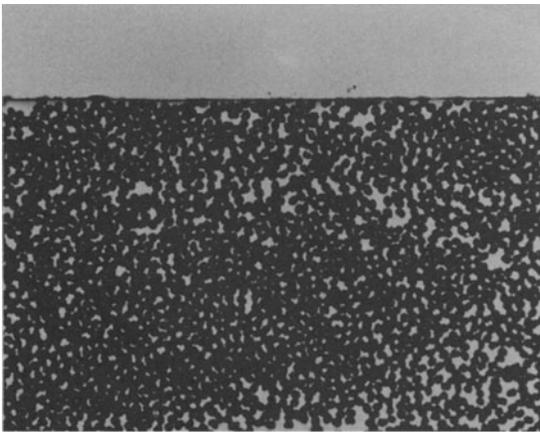
As a spacecraft orbits, it moves from sunlight to shadow. Solar radiation, both direct and reflected from the earth (albedo), and thermal radiation from the earth cause temperature extremes of -185 to +150°C (-300 to +300°F). Spacecraft heat sources, such as engines, electronic equipment and batteries, also contribute to the thermal environment. Active thermal control systems or protective coatings with optimized solar absorptance and infrared emittance can minimize thermal extremes. Solar absorptance is defined as the ratio of absorbed light to incident light, and infrared emittance is defined as the ratio of emitted heat to input heat. Low absorptance values reduce the maximum temperatures when exposed to direct or albedo radiation and low values of emittance reduce minimum temperatures when exposed to deep space. Stability of these properties is important for long-term exposures. Thermal cycling effects on composites will be discussed later in this chapter.

Spacecraft leaving and returning to earth must endure heating during ascent and re-entry through the atmosphere. Re-entry temperatures can reach 1482°C (2700°F). Reinforced carbon-carbon composites are currently utilized in the Space Shuttle nose-cap cover and wing leading edges. Another application under investigation is a composite nose cone for the Space Shuttle External Tank (Sigur and Gray, 1990). This design not only weighs less than an equivalent metallic design but also can maintain the internal environment within desired temperature limits without thermal insulation. Temperatures on the Space Shuttle External Tank nose cap may range from -150°C (-297°F) around the liquid oxygen vent louvers to 500°C (930°F) during ascent. Mechanical property tests, including tensile, compression, in-plane shear and interlaminar shear tests, have been performed on laminates, moisture saturated per ASTM-D618 to reproduce the high humidity at the launch site. These composite materials were also

tested for 'ply lift' or moisture-induced delamination at high temperatures. Several composite systems were studied, including graphite/bismaleimide and graphite/PMR-15, but Celion G-30/500-3K graphite/BASF 506 phenolic was chosen because of its durability during the ply lift testing.

### Ultraviolet radiation

Ultraviolet radiation is that band of light from 300 to about 4000 Å. Ultraviolet radiation may cause degradation through molecular weight change and cross-linking in the resin system. However, this damage is generally limited to darkening of the resin in the surface layer. Figure 36.5 is a photomicrograph of a LDEF composite laminate exposed only to UV. Coatings, such as thermal control tape, have been used to protect composite materials from degradation.



**Fig. 36.5** Cross-sectional photomicrograph of UV-exposed LDEF graphite-reinforced OMC showing minimal degradation.

### Vacuum and outgassing

Orbital atmospheric pressure varies according to altitude and solar activity. Average pressure is generally  $133 \times 10^{-7}$  N/m<sup>2</sup> ( $1 \times 10^{-7}$  torr) in low earth orbit, decreasing to  $133 \times 10^{-14}$  N/m<sup>2</sup> ( $1 \times 10^{-14}$  torr) at geosynchronous orbit.

Because moisture is removed from the composite in a vacuum, mechanical properties, such as compressive and interlaminar shear strengths, may be improved through exposure. However, the designer must consider possible dimensional changes due to moisture desorption. Dimensional stability is critical for space hardware such as optical benches and truss structures. Another design concern is the effect of outgassed moisture on sensitive optics or electronic equipment present on a spacecraft. Vapor barriers of metallic foils have been used to prevent line-of-sight deposition of moisture and other outgassing products.

The UTIAS experiment flown on LDEF (Tennyson, 1991) contained a variety of flat and tubular composite samples consisting of T300/5208, T300/SP-288 and T300/934 graphite/epoxy samples, boron/SP-290 epoxy and Kevlar/SP-328 epoxy. A data acquisition system recorded outputs from 16 strain thermal gages attached to the composite samples for 371 days. Outgassing was measured, ranging from 40 days for the T300/934 to 120 days for the Kevlar/SP-328. Coefficient of thermal expansion increased slightly for the 0° configuration (Table 36.1). This change should be considered when designing zero CTE laminates for space applications.

### 36.3.6 TEMPERATURE

Temperature effects on composite materials discussed in this section include cryogenic temperatures, elevated temperatures and thermal cycling between these extremes. Cryogenic temperatures do not appear to affect the mechanical properties of graphite/epoxies or graphite/polyimides significantly.

Elevated temperatures for a prolonged period of time can seriously affect the properties of a composite, with even greater effect if moisture is present. Susceptibility to matrix softening is not only dependent on the resin but also the lay-up. A study of graphite/polyimide properties used two different lay-ups, a

**Table 36.1** Summary of LDEF/UTIAS composite material thermal data (Tennyson, 1991)

Material type	Configuration	Strain gage number	Thermal gage number	Ambient <sup>a</sup> CTE (10 <sup>-6</sup> /°F)	Space <sup>b</sup> CTE (10 <sup>-6</sup> /°F)	Thermal vacuum facility <sup>c</sup> CTE (10 <sup>-6</sup> /°F)
Stainless Steel (calibration)	Tube	1	1	9.84	10.0	10.0
Graphite/Epoxy T300/934	Flat (0°) <sub>4</sub>	2 (0°)	2	1.32	3.33	2.50
		3 (90°)		14.7	13.9–15	16.1
Kevlar/Epoxy SP-328	Tube (90°) <sub>4</sub>	4 (90°)	3	33.9	30–35	35.3
		5 (0°)		0.10	0.71	0.63
Graphite/Epoxy T300/SP388	Tube (0°) <sub>4</sub>	6 (90°)	4	14.6	13.6–14.3	15.4
		7 (0°)		0.97–1.57	–1.14–3.33	3.75
Graphite/Epoxy T300/5208	Tube (90°) <sub>4</sub>	8 (90°)	5	15.6	12.5–15.3	16.1
Boron/Epoxy SP-290	Tube (±30°) <sub>2s</sub>	9 (±30°)	6	1.57	1.67–2.22	0.44–2.0
		10 (±60)		11.7	7.5–11.1	12.7

<sup>a</sup> At atmospheric pressure prior to launch.

<sup>b</sup> Measured in space environment on LDEF during first 371 days in orbit.

<sup>c</sup> Measured in laboratory thermal vacuum test facility (22 h at  $133 \times 10^{-5}$  N/m<sup>2</sup> ( $1 \times 10^{-5}$  torr), –40°F to 150°F) after 2114 days in orbit and 184 days at ambient conditions.

0° unidirectional lay-up and a (0, ±45, 90)<sub>2</sub> lay-up, tested at temperatures ranging from –157 to +315°C (–250 to +600°F) (Lisagor, 1979). Test results showed little change in interlaminar shear strength for the quasi-isotropic lay-up while the 0° unidirectional samples dropped to approximately 40% of original strength at elevated temperatures. Reduction of normal moisture content by vacuum drying reduced the loss to only 70% of room temperature strength.

High-temperature resins under development, such as AFR700B developed by the Air Force (Brown, 1991), have reached glass transition temperatures of 416°C (780°F). AFR700B retains 50% of its mechanical properties up to 370°C (700°F). PMR-15 is another high-temperature resin with excellent properties, but large or thick structures require debulking a few layers at a time due to the high volatile content. Other materials being developed for high-temperature applications include titanium matrix composites, ceramic matrix

composites, and advanced carbon/carbon composites.

Temperature effects are not limited to the matrix material. Extended operation at 350°C (660°F) and 450°C (840°F) can cause oxidation of low-modulus PAN-based fibers and high modulus PAN- or pitch-based fibers, respectively. Oxidation resistance can be improved with higher purity fibers.

Thermal cycling conditions are common for a number of applications, including aircraft and spacecraft. Thermal cycling may induce microcracking in some composites. A study of this microcracking behavior in graphite/PMR-15 composite materials was performed at Rohr Industries (Sullivan and Ghaffarian, 1988). Woven laminates of C3000/PMR-15 and unidirectional tape lay-up of C6000/PMR-15 were thermally cycled between –18 and +232°C (0 and 450°F) up to 2000 cycles. The C3000/PMR-15 developed microcracks, with the number of microcracks dependent on the number of thermal cycles. Decreases in compressive and shear

strengths were noted, although tensile strength, a fiber-dominated property, was not significantly affected. The unidirectional tape lay-up, C6000/PMR-15 did not crack during testing.

#### 36.4 PROTECTIVE COATINGS

When an environmentally resistant composite material cannot be utilized, protection of the material through the use of coatings is necessary. A variety of coatings have been developed for protecting composites from various environments. Standard marine paint, pigmented gel coatings and polyurethanes have been used to prevent ultraviolet damage and weathering erosion of marine composites. The following coating examples have been used in space but

may be applicable to other environments.

On the LDEF, S-901 glass/epoxy composites were exposed to the space environment. Three of these samples were flown with thermal control tape, consisting of 50.8  $\mu\text{m}$  (2 mil) aluminum with 50.8  $\mu\text{m}$  (2 mil) pressure-sensitive SR574 silicone adhesive. The glass/epoxy samples without tape suffered more mass loss than the protected samples, and solar absorptance of the unprotected samples increased 5.4%, probably due to ultraviolet radiation. Post-flight peel tests of the thermal control tape showed an increase in strength with some embrittlement of the adhesive. Figure 36.6, a SEM photograph, also shows the degree of micrometeoroid/debris protection provided by the tape.

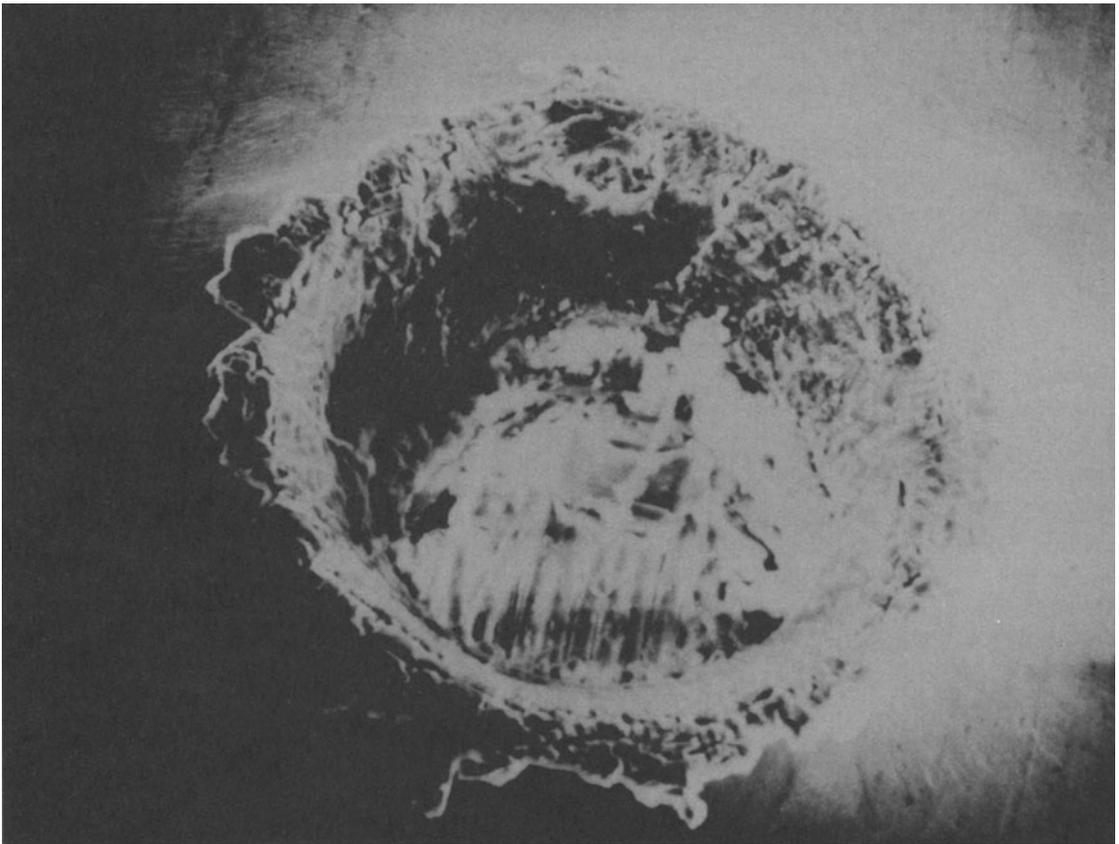


Fig. 36.6 Micrometeoroid/debris impact in thermal control tape. Substrate is S-glass/epoxy.

A 60 nm (600 Å) SiO<sub>2</sub>/100 nm (1000 Å) nickel vapor-deposited coating appears to have prevented resin loss in graphite/epoxy samples flown on LDEF (Young *et al.*, 1991). Inspection of selected composites (C6000/P1700, C3000/P1700, T300/934 (with two different fiber areal weights) and T300/5208) revealed dramatic visual effects, material loss and a deterioration in mechanical performance for unprotected composites. Chemical characterization suggests that there is no significant change in molecular structure of the surviving polymeric matrix resin in these composites. No change in glass transition temperature was apparent. The majority of the unprotected flight samples showed a decrease in tensile strength and modulus.

Coating/composite systems for large space truss structure applications have been tested in ground simulations of atomic oxygen, ultraviolet radiation, and thermal cycling (Dursch and Hendricks, 1987; Dursch and George, 1993). Coatings studied were chromic and phosphoric acid anodized aluminum foil, sputtered SiO<sub>2</sub>/sputtered Al/Al foil, bare Al foil, electroplated nickel with and without SiO<sub>x</sub> coatings and inorganic sol gel solutions. P75S/934 composite was used to form the truss tubes.

The aluminum foil used was 1145-H19 aluminum alloy with a thickness of 50.8 μm (2 mil). Thicker foils can be used, depending on weight constraints and flexibility of any coatings applied to the foil. The foil was bonded to the graphite/epoxy truss tube with an epoxy film adhesive and was co-cured. The chromic acid anodized foil provided good protection as well as optical properties. The phosphoric acid anodized foil also provided good protection while maintaining adhesion. Desired optical properties were obtained by varying thickness of silicon dioxide and sputtered aluminum on top of the aluminum foil. The optimized thicknesses were 1 μm (0.04 mil) SiO<sub>2</sub> and 300 nm (3000 Å) Al.

The electroplating process was chosen for study because of its low application costs,

good corrosion resistance and good uniformity. Irregular shapes, such as end fittings, may also be coated with this process. The composite surfaces were sanded prior to plating to improve adhesion. However, atomic oxygen attack resulted in loss of adhesion in the nickel coating without SiO<sub>x</sub> overcoat.

Numerous other coatings have been studied for space environment resistance. Braided and double-braided aluminum coverings, indium-tin eutectic coatings, various silicone-based paints and zinc oxide pigment in a potassium silicate and silicone elastomer binder have been tested (Piellisch, 1991). A proposed design for solar array backing on the NASA space station employs woven E-glass sandwiched between two layers of silicon dioxide-coated Kapton.

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